SITE-SPECIFIC QUALITY ASSURANCE PROJECT PLAN

For

Peoples Gas Light & Coke Company

Willow Street/Hawthorne Avenue Station Operable Unit
Chicago, Illinois

Managed By

Integrys Business Support

Administrative Settlement Agreement and Order on Consent No.

W-W-'08-C-917

Prepared for Use By

Burns & McDonnell Engineering Company, Inc.

September 21, 2009
Revision Number: 0

SITE-SPECIFIC QAPP DOCUMENT CONTROL

Number: _____

Initials: _____ Date: _____

Effective Date: September 21, 2009

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ATTACHMENT 1

STAT Analysis Corporation Quality Assurance Manual and Standard Operating Procedures

ATTACHMENT 2

PACE Analytical Quality Assurance Manual and Standard Operating Procedures

ATTACHMENT 3

TriMatrix Standard Operating Procedures

LIST OF ACRONYMS AND ABBREVIATIONS

BERA	Baseline Ecological Risk Assessment
BMcD	Burns & McDonnell Engineering Company, Inc.
BLRA	Baseline Risk Assessment
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
COC	Chain-of-Custody
DQO	Data Quality Objectives
DQI	Data Quality Indicator
FSM	Field Site Manager
FS	Feasibility Study
FSP	Field Sampling Plan
GC	Gas Chromatography
IBS	Integrys Business Systems, LLC
LTM	Long-Term Monitoring
MPC	Measurement Performance Criteria
MS	Matrix Spike
MSD	Matrix Spike Duplicate
NA	Not Applicable
NRT	Natural Resources Technology Inc.
Peoples Gas	Peoples Gas Light and Coke Company
PQL	Practical Quantitation Limit
PQO	Project Quality Objectives
PQL	Practical Quantitation Limit
QA	Quality Assurance
QAM	Quality Assurance Manual
QAPP	Quality Assurance Project Plan
QC	Quality Control
QCP	Quality Control Plan
QCSR	Quality Control Summary Report
QMP	Quality Management Plan
RAF	Risk Assessment Framework
RI	Remedial Investigation
SAA	Salina Airport Authority
SAFB	Salina Air Force Base
SAP	Sampling and Analysis Plan

LIST OF ACRONYMS AND ABBREVIATIONS (continued)

SI	Site Investigation
SOP	Standard Operating Procedure
SSWP	Site-Specific Work Plan
STAT	STAT Analysis Corporation
SVOC	Semivolatile Organic Compounds
TC	Table of Contents
TOC	Total Organic Carbon
UFP-QAPP	*Uniform Federal Policy for Quality Assurance Project Plans*
USEPA	United States Environmental Protection Agency
USGS	United States Geological Survey
VOC	Volatile Organic Compound

* * * * *

INTRODUCTION

This Site-Specific Quality Assurance Project Plan (QAPP) addresses the necessary procedures and tasks to be followed to complete the Remedial Investigation and Feasibility Study (RI/FS) for the Willow Street/Hawthorne Avenue Station Operable Unit (Willow/Hawthorne OU) of the North Branch Site located in Chicago, Illinois. This Site-Specific QAPP was prepared in accordance with the Administrative Order on Consent (AOC) and Statement of Work (SOW), CERCLA Docket No. V-W-'08-C-917, dated October 31, 2008 between the United States Environmental Protection Agency (USEPA) and The Peoples Gas Light and Coke Company (Peoples Gas).

This Site-Specific QAPP supplements the Multi-Site QAPP Rev 2 dated September 4, 2007 (Integrys 2007). Unless specifically noted otherwise, the Multi-Site QAPP will be followed while implementing the Site-Specific Work Plan (SSWP) at the Willow/Hawthorne OU. This Site-Specific QAPP presents modifications specific to the Willow/Hawthorne OU from the Multi-Site QAPP, provides a description of quality assurance (QA) and quality control (QC) procedures and establishes the policies, organization, objectives, functional activities and specific QA and QC activities for managing the project. At the request of USEPA, the site-specific revisions to the USEPA-approved Multi-Site QAPP (Integrys 2007) are presented in the Universal Federal Program (UFP) format. In addition, a "cross-walk" table has been prepared to transition from the Multi-Site QAPP (Integrys 2007) to the site-specific version.

This QAPP has been prepared in accordance with "EPA Requirements of Quality Assurance Project Plans (QA/R-5)" (EPA/240/B-01-003, March 2001), "EPA Guidance for Quality Assurance Project Plans (QA/G-5)" (EPA/600/R-02/009, December 2002), "EPA Guidance for the Data Quality Objectives Process" (EPA QA/G-4, August 2000), "USEPA Region 5 Instructions on the Preparation of a Superfund Division Quality Assurance Project Plan", based on EPA QA/R-5, Revision 0, June 2000, and guidance as included in the respective Administrative Order on Consent (AOC) and Statement of Work (SOW), CERCLA Docket No. V-W-'08-C-917.

SITE HISTORY AND DESCRIPTION

A discussion of the site history and description of the Willow/Hawthorne OU is provided in Section 2 of the SSWP. The Willow/Hawthorne OU encompasses approximately 7.4 acres and is located north of the intersection of North Kingsbury Street and Willow Street. The Willow/Hawthorne OU is divided by

North Kingsbury Street into western and eastern areas. The western portion of the OU is bounded by the North Branch of the Chicago River to the west, industrial commercial properties to the north and south, and North Kingsbury Street and the ComEd, Peoples Gas and Marcey parcels to the east. The eastern portion of the OU is bounded by North Kingsbury Street and the General Iron and AFS (formerly Finkl) parcels to the west, Wisconsin Street and industrial commercial properties to the north, Marcey Street and commercial properties to the east, and Willow Street and industrial commercial properties to the south.

The manufactured gas plant (MGP) process operations had historically been conducted on the General Iron, ComEd and Marcey parcels. The ComEd parcel is occupied by Commonwealth Edison and is used as an electrical substation. The Marcey parcel is developed commercially and has a limited amount of landscape area. The Peoples Gas parcel is gravel covered, and is used as a natural gas regulating station. The General Iron Parcel is currently used as a laydown area for unprepared steel, and the AFS parcel is vacant land.

INVESTIGATION AND RESPONSE ACTION HISTORY

A chronology of environmental investigations conducted at the Willow/Hawthorne OU is presented in Sections 2.3 and 3.6 of the SSWP. Several investigations involving soil and groundwater have been conducted on the OU between 1991 and 2006. Site investigations (SI) primarily focused on surface and subsurface soil and groundwater; however, an investigation of the River was conducted during 2006.

Extensive response actions were conducted on the General Iron parcel between December 2004 and April 2006. Response activities included the removal of soil impacted by tar. During response action activities on General Iron, soil excavations near the AFS parcel indicated MGP residuals may be present on the AFS parcel. As a result, tar impacted soil was removed from the AFS parcel as well.

Response actions were conducted on the western portion of the Marcey parcel from January through April 2003, and in July 2003. These activities included the removal of tar-impacted soil along with visually impacted pipe located on the southeastern portion of the parcel, the relocation of a high pressure gas main, and the removal of all surface soil. Subsurface soil removal was also completed in the south area and included backfilling with flowable grout.

Response actions on the Peoples Gas parcel included the removal of all surface soil in the north portion of the parcel, and the installation of a 40 millimeter high density polyethylene (HDPE) liner over a portion

of the former 5,000,000 ft^3 gas holder. A soil vapor extraction (SVE) system was installed and operated to reduce volatile concentrations of xylene in soil adjacent to the outside of the former 5,000,000 ft^3 gas holder. After excavation, areas were backfilled. The SVE system was in operation between March and October 2004. In addition, subsurface soil was excavated from limited areas.

No investigations or remediation have historically been conducted on the ComEd or most of the Marcey parcels.

Additional investigation activities are required to address soil and groundwater on the ComEd and Marcey East Parcels of the OU associated with the impacts potentially remaining in vicinity of the former gas holders, and sediment and surface water within the River. The investigation of the sediment and surface water within the River will include an evaluation of ambient conditions.

PURPOSE

This Site-Specific QAPP presents the organization, data quality objectives (DQOs), a set of anticipated activities, sample analysis, data handling and specific Quality Assurance/Quality Control (QA/QC) procedures associated with the Willow/Hawthorne OU SSWP. Specific protocols for sampling, sample handling and storage, chain-of-custody, and laboratory and field analyses that are common activities of the program not described in the Multi-Site QAPP are specified herein. The SSWP specifies the procedures to be used for identifying and evaluating the nature and extent of MGP residuals for use in a Baseline Risk Assessment (BLRA), Baseline Ecological Risk Assessment (BERA) and FS. It includes an evaluation of previously collected data and a rationale for selecting existing data that meets the DQOs. The BLRA and BERA will evaluate if the OU presents a risk to human health and/or the environment. The SSWP also sets forth the process to be used to develop and evaluate remedial alternatives. Section 6 of the SSWP details the additional investigation activities to be performed.

ORGANIZATION OF QAPP ELEMENTS

This Site-Specific QAPP has been prepared as part of the supplemental project planning documents for a RI/FS at the Willow/Hawthorne OU. This Site-Specific QAPP is Appendix C1 of the Willow/Hawthorne OU SSWP and is organized as follows:

Main Body of Site-Specific QAPP:

- Introduction

- UFP QAPP Format Worksheets and Supporting Documentation required to provide site-specific QA elements.
- References

Attachment 1 to Site-Specific QAPP: STAT Analysis Corporation Quality Assurance Manual and Standard Operating Procedures.

Attachment 2 to Site-Specific QAPP: Pace Analytical – Green Bay Quality Assurance Manual and Standard Operating Procedures.

This Site-Specific QAPP references information that is presented in other project documents that is not repeated here to avoid unnecessary duplication. These documents include:

- Willow/Hawthorne OU SSWP
- Multi-Site QAPP
- Multi-Site Field Sampling Plan (FSP).

GENERAL COMMENTS ON LABORATORY QAPP ELEMENTS

Following is a listing of USEPA comments that pertain to the Standard Operating Procedures (SOPs) for the STAT laboratory, referenced in this QAPP. USEPA made these comments on several previous SSWPs and they have been resolved. They are being presented herein for reference only as a reiteration of how they were previously resolved. Only relevant comments are listed, so the numbering is not consecutive, but rather it matches the numbers assigned in previous submittals. The following USEPA comments are in regular face font and the previous approved responses are in bold face font.

USEPA General Comment:

1) All project-specific Standard Operating Procedures should be updated and submitted for the review. The SOPs should be updated/reviewed by the laboratory at least every other year.

STAT Analysis Corporation reviews the analytical SOPs once a year. The SOPs are updated, as needed.

Organic Analytes

5) When the reference method did not include guidance or controlling limits, then the Contract Laboratory Program Statement of Work and Good Laboratory Practices was used for guidance. Comments and notations of method deviations for STAT Analysis SOP 4000 Analysis of Volatile Organic Compounds. This method references SW846 Method 8260B.

Comment acknowledged.

6) Paragraph 5.0: *Summary of Test Method:*

- Lists direct injection as a sample introduction technique;

  As discussed in Section 1.2 of SW846, Method 8260B, direct injection is an acceptable technique under limited circumstances for limited analytes.

- States Methanol extractions are analyzed by the heated soil method; EPA medium level samples are analyzed at ambient temperature using the water method;

  STAT uses the heated soil method so that all soils can be analyzed in the same analytical sequence/QC Batch. This is more straightforward and provides the best reproducibility for different collections of the same sample. We are aware that this method is not included in the SOW, and we have identified the procedure under method modification in the SOP.

- States that water soluble compounds have a 10X reporting limit; in Method 8260 the ketones, with the exception of Acetone and 2-Butanone, only have a 2X reporting limit. Do the elevated detection limits meet the site action limits?

  They do meet site action limits.

7) Paragraph 5.3 - states "Medium level dilutions are prepared from an aliquot of the preserved sample that is transferred into 5 mL reagent water and analyzed using the soil ARCON procedure." SW846 method 5035 states that the medium level

(methanol extract) samples are to be analyzed per SW846 method 5030, which is an unheated 5 mL purge.

STAT is aware that this method is not included in the SOW, and we have identified the procedure under method modification in the SOP.

10) Paragraph 10.4.1 -

- States ICAL levels 2, 3, 4 as being used as the CCV. The SOW and SW846 only use the mid-point level 3 for the CCV;

STAT varies the CCV levels so that a wider range of calibration curve can be verified between instrument calibrations. This was put in place to satisfy a requirement of NELAC accreditation.

11) Paragraph 10.4.2 - The instructions for the soil initial calibration do not include added solid material to the ICAL standards.

Method 8260B does not mention addition of solid material to the calibration standards. Some laboratories use certified clean sand, but that does not provide the matrix matching that may be intended. In any event, the calibration should be free of matrix effects. The Method blank, LCS and LCSD are prepared with certified clean sand, and the recoveries do not indicate any matrix effects. Sample matrix effects should be assessed with MS/MSDs and surrogate recoveries.

12) Paragraph 10.8 - The method described for preparing the Matrix Spike/Matrix Spike Duplicate could result in the loss of the five gases and some of the lighter VOA analytes.

Comment acknowledged. We have not encountered the problem in the laboratory.

13) When preparing the LCS standards, the SOP states to discard "the contents of the neck portion of the flask" before taking an aliquot. There might not be enough volume remaining in volumetric flask to completely fill a 40 mL VOA vial.

Comment acknowledged. We have not encountered the problem in the laboratory, as there has been enough volume to work with. Analysts are trained that enough volume must remain to fill the entire vial, with no headspace.

14) Paragraph 11.2 -

- "Stored under refrigeration at between 0.1°C and 6.0°" The SOW and SW846 state 4 °C ±2 °C

The SOW and SW 846 temperature range is 2 to 6ºC. NELAC allows 0.1 to 6ºC. If the temperature of the samples drops below 2 but remains above freezing, this would not impact analytes in the soil.

15) The SOP allows the "Use of single peak for mass ratio in BFB tune check". The minimum any of the reference methods allow is an average of three scans with a background subtraction. It is not always possible to find a single scan which meets the tuning criteria somewhere under the peak, but that does not mean that the ion ratios will accurately reflect the target compounds breakdown.

It is STAT's intent to be very specific on how BFB and DFTPP tune criteria are obtained from a tune acquisition. The option for using a single scan is only allowed for the apex of the peak; indeed this is how target spectra in the standards and samples are typically evaluated, and this technique is simple and straightforward. The CLP SOW is the only reference where the three scans (peak apex and the scans immediately preceding and following the apex) MUST be used to meet BFB or DFTPP tune criteria. We require STAT analysts to be unambiguous with regard to interpreting USEPA SW-846 8260B and 8270C/D terminology for acquiring an acceptable BFB or DFTPP spectrum.

16) Paragraph 13.2.9 - Calibration QC

- States "Calibration must be completed (all standard levels analyzed) within 36 hours or the entire calibration sequence must be repeated." Although the reviewer was unable to cite a specific reference requirement stating all must be under single instrument tune check, method 8260 states all standards must be within 12 hours of an instrument tune check. Good laboratory practice implies that the ICAL should be completed in the 12 hr time span of a single instrument tune check. As stated in the SOP, the ICAL would stretch over three BFB injections with three possible tune files.

Comment acknowledged. STAT normally completes ICALs within the 12-hour period; however, there may be instances when ICAL stretches over more than one tune check. Twelve hour tune checks are always required, even when running ICALS. It is unclear to us why this would not be consistent with GLP.

18) Paragraph 13.3.7.1 and 13.3.7.2 - How does the analyst know what is in the samples when evaluating if the CCV meets the QC requirement to continuing analyzing sample?

STAT's standard procedure is to stop analysis if CCV fails. Sections 13.3.7.1 and 13.3.7.2 are provided as reporting options in exceptional situations

19) Paragraph 13.3.7.3 – Please verify that this paragraph meets the People's Gas site Data Quality Objectives?

Peoples Gas may agree in writing to receive a laboratory report containing laboratory-qualified data that is due to CCV acceptance criteria exceedance. During the Peoples Gas third-party data validation process, this laboratory-qualified data will be accepted as meeting the DQOs with qualification, or rejected as not meeting the DQOs. Acceptance of laboratory-qualified data alone does not constitute acceptance of the data as meeting DQOs.

20) Paragraph 14.2.7 - does not agree with paragraphs 13.3.7.1, 13.3.7.2 and 13.3.7.3

As discussed above, this is intended as a reporting option for exceptional situations, not as a standard procedure.

21) The SOP implies that lab can report "wet-weight" results unless "dry weight results" are requested.

STAT provides those equations for calculating concentration without prejudice to moisture content. Reporting options are available for clients with differing needs.

24) Paragraph 18.6 - States "Note: the recovery of internal standards in these samples within the stated limits is not mandatory per the referenced method 8260B." Paragraph 7.4.7 of SW846 method 8260B Revision 2 December 1996 states "Internal standard response - If the EICP area for any of the internal standards in the calibration verification standard changes by a factor of two (-50% to + 100%) from that in the mid-point standard level of the most recent initial calibration sequence, the mass spectrometer must be inspected for malfunctions and corrections must be made, as appropriate. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is required."

Paragraph 7.4.7 of SW 846 refers to calibration verification standards. This is addressed in Section 13.3.5 of STAT SOP, which states that the internal standards of the CCVs must be between –50% and +100%. Comments and notations of method deviations for STAT Analysis SOP 4020, Analysis of Semivolatile Organic Compounds.

25) The STAT SOP references SW846 method 8270C, in February 2007, the USEPA issued Method 8270D as the approved SVOA method.

STAT is currently developing an SOP that is based on SW 846 Method 8270D. STAT also plans to participate in proficiency Testing program and will apply for Accreditation from NELAC as soon as possible. Currently, however, STAT is accredited by NELAC for SW 846 Method 8270C

26) Paragraph 5.0 Summary of Test Method

- Table 1 of SW846 methods 3510C and 3520C lists for 8270 analysis the initial pH extraction <2 secondary pH extraction >11

  Comment acknowledged. This information is included in Table 1 of STAT SOP 3500, Organic Extraction.

- Paragraph 5.2 states that MS tuning is an option in SW846 8270C, but paragraph 9.3 states "The GC/MS must be tuned to meet the recommended DFTPP criteria prior to the initial calibration and for each 12-hr period during which analyses are performed."

  STAT SOP does not state that MS tuning is an option. It states that tuning criteria specified in the CLP SOW is an option in Method SW 846 8270C.

33) Paragraph 16:

- If the standard deviation exceeds the average recovery for any compound, the method can produce false negatives for those compounds even though the system is in control.

Example provided in this section indicates that standard deviation can not exceed average recovery for any compound.

- The last sub-paragraph allows for the system to be optimized just for the recovery of either a single compound or a class of compounds to get "an acceptable results"

STAT is not optimizing the system. We acknowledge that because of large number of compounds, some may fail, and then, corrective action will be taken. This is how similar QC corrective actions are addressed SW-846.

35) Section 10 - REAGENTS AND STANDARDS

- The Acid Surrogates are added to the Secondary stock solution which is used to make the calibration solutions, but none of the acid fraction compounds are on the target analyte list.

- The surrogate spiking solution contains the acid surrogates.
  In SIM analysis, the presence of non-target analytes in the calibration solutions can lead to distorted ion ratios for the selected ions used for quantifying the compounds of interest.

PNA surrogate spike was originally a 1:10 dilution of the SVOC full scan surrogate spike solution. MDLs , DOCs, Initial Calibrations, ICVs, LCS, and MS/MSDs all contain Acid Surrogate Spike compounds. No discernable distorted ion ratios have been encountered in these analyses. The Acid surrogate spike has remained in these spikes

as the trend is to modify this PNA method for additional compounds, including acid compounds, for a Low Level SVOC analysis.

Mercury Analysis

47) STAT Analysis Corporation Standard Operating Procedure 4530 Mercury in Water, Solid or Semisolid Water (Manual Digestion /Automated Analysis Cold-Vapor Techniques) (EPA Methods 7470A and 7471A), Revision 3, effective date January 9, 2003, was reviewed for technical accuracy and agreement with published references. The STAT Analysis SOP/ addendum were issued as uncontrolled documents, with effective dates of January 9, 2003 and October 31, 2003. There was no evidence of a more recent review. Since the most recent update was over 5 years ago, the laboratory should consider reviewing the document in accordance with its Quality Assurance Plan and EPA SW846 Update lV to ensure no revisions are needed to reflect current practices in the laboratory. The format and level of detail in the SOP is excellent.

STAT conducts yearly review of its technical SOPs along with internal audits. The method is scheduled for audit in May and the SOP will be reviewed. The SOP will be updated, as needed.

General Comments:

49) Method reference for soil analyses is shown as EPA Method 7471A. On January 1, 2008, the USEPA issued the Availability of Final Update IV of SW846, which contains approval of Method 7471B, Mercury in Solid or Semisolid Waste (Manual Cold-Vapor Technique). The updated version, EPA Method 7471B, reflects more current technology and the understanding that most laboratory practices no longer include digestion in BOD bottles. However, it should also be noted that EPA Method 7471A is a promulgated method, while in accordance with the EPA's June 14, 2005, Methods Innovation Rule (MIR), Final Update IV methods are issued as guidance, rather than requirements. [1]

1 *The MIR removed from the RCRA hazardous waste regulations any requirement to use an analytical method found in SW846, unless that method is the only one capable of measuring a method-defined parameter (MDP). The MIR allowed EPA to issue final updates to SW846 as guidelines, provided the analytical methods contained in the update are not required by the RCRA hazardous waste regulations. On the EPA website http://www.epa.gov/osw/hazard/testmethods/faq/faqs metal.htm, under Triple Sample Aliquots for Mercury Analysis by Method 7471A , Answer, it states, " If you are not required to use the promulgated version of the method, 7471A, then we suggest that you use the latest Procedural Review:

STAT is currently reviewing Method 7471B. We plan to implement the method following EPA's promulgation.

Automated Sulfide

General Comments:

51) The SOP was written combining the titrimetic method SW846 9034 with the automated colorimetric method EPA 376.2. The methods should be separated into their own SOPs. The SOP met all other technical requirements for the methods.

STAT does not use results from the titrimetric method to report sulfide concentration. This result is used only for screening purposes to determine what dilution is required to make the calibrations standards. Therefore, the titrimetric method is used as a preliminary step in determining sulfide using the colorimetric method.

* * * * *

QAPP Worksheet #1
(UFP-QAPP Manual Section 2.1)
Title and Approval Page

Site Name/Project Name: North Branch Site, Willow Street/Hawthorne Avenue Station OU RI/FS

Site Location: Chicago, Illinois

Document Title: ***Site-Specific Work Plan, Willow Street/Hawthorne Avenue Station Operable Unit, Chicago, Illinois***

Lead Organization: Integrys Business Support, LLC

Preparer's Name and Organizational Affiliation: Amy Hanrahan, BMcD

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Preparation Date (Day/Month/Year): 21/09/2009

Lead Organization's Project Manager/Date:_____
Signature

Printed Name/Organization: Naren Prasad, IBS

Investigative Organization's Project Manager/Date:_____
Signature

Printed Name/Organization: Margaret Kelley, BMcD

Investigative Organization's Project QC Coordinator/Date:_____
Signature

Printed Name/Organization: Sharon Shelton, BMcD

Laboratory's Director/Date:_____
Signature

Printed Name/Organization: Donald Cortes, STAT

Laboratory's Project Manager/Date:_____
Signature

Printed Name/Organization: Pinaki Banerjee, STAT

Laboratory's Director/Date:_____
Signature

Printed Name/Organization: Nils Melberg, Pace-Green Bay

Laboratory's Project Manager/Date:_____
Signature

Printed Name/Organization: Brian Basten, Pace-Green Bay

Approval Signature/Date:_____
Signature

Printed Name/Organization: Tim Prendiville, USEPA Region V Project Coordinator

Approval Signature/Date:_____
Signature

Printed Name/Organization: Alida Roberman, USEPA Region V QA Coordinator

Document Control Numbering System: See QAPP Cover and Worksheet #3

QAPP Worksheet #2
(UFP-QAPP Manual Section 2.2.4)
QAPP Identifying Information

Site Name/Project Name: North Branch Site, Willow Street/Hawthorne Avenue Station OU RI/FS
Site Number/Code: Not Applicable
Operable Unit: Willow Street/Hawthorne Avenue Station
Contractor Name: Burns & McDonnell
Contract Number: Not Applicable
Contract Title: Not Applicable
Work Assignment Number: Not Applicable

1. **Identify regulatory program:** CERCLA – Superfund Alternative Sites Program

2. **Identify approval entity:** Not Applicable

3. **The QAPP is (select one):** Generic [Project Specific]

4. **List dates of scoping sessions that were held:** 3/19/09

5. **List dates and titles of QAPP documents written for previous site work, if applicable:**

Title	Approval Date
None	

6. **List organizational partners (stakeholders) and connection with lead organization:**

General Iron Parcel Owner: GI North Property, LLC
Contact: Ms. Marilyn Labkon, President

Finkl Parcel Owner: A. Finkl and Sons Company
Contact: Bruce Liimatainen, CEO

ComEd Parcel Owner:	Commonwealth Edison Company Contact: Mr. Frank M. Clark
Peoples Gas Parcel Owner:	The Peoples Gas Light and Coke Company Contact: Mr. Brian F. Bartoszek
Marcey East and West Parcel Owner:	Marcey Properties, LLC Contact: Mr. Kenneth L Skolnik, Esq.

7. List data users: BMcD, Integrys, NRT, Exponent, USEPA Region V, Illinois EPA

QAPP Worksheet #2
QAPP Identifying Information
(continued)

8. If any required QAPP elements and required information are not applicable to the project, then circle the omitted QAPP elements and required information on the attached table. Provide an explanation for their exclusion below:

Screening/Confirmatory Analysis Decision Tree is excluded since no screening samples will be collected.

Streamlining Data Review is excluded since no data review will be streamlined.

Documents referenced in table below are:

SSWP – *Site-Specific Work Plan, Willow Street/Hawthorne Avenue Station Operable Unit, Chicago, Illinois* (BMcD, 2009)

Multi-Site QAPP – *Multi-Site Quality Assurance Project Plan, Former Manufactured Gas Plant Sites, Volumes 1 and 2, Revision 2* (BMcD, September 2007)

Multi-Site FSP - Integrys, 2008. *Multi-Site Field Sampling and Analysis Plan Former Manufactured Gas Plant Sites, Revision 4* (Integrys, September 2008)

Required QAPP Element(s) and Corresponding QAPP Section(s)	Required Information	QAPP Worksheet # or Page #	Crosswalk to Related Documents
Project Management and Objectives			
2.1 Title and Approval Page	- Title and Approval Page	Worksheet #1	
2.2 Document Format and Table of Contents 2.2.1 Document Control Format 2.2.2 Document Control Numbering System 2.2.3 Table of Contents 2.2.3 QAPP Identifying Information	- Table of Contents - QAPP Identifying Information	Worksheet #2	

Required QAPP Element(s) and Corresponding QAPP Section(s)	Required Information	QAPP Worksheet # or Page #	Crosswalk to Related Documents
2.3 Distribution List and Project Personnel Sign-Off Sheet 2.3.1 Distribution List 2.3.2 Project Personnel Sign-Off Sheet	- Distribution List - Project Personnel Sign-Off Sheet	Worksheets #3 and #4	
2.4 Project Organization 2.4.1 Project Organizational Chart 2.4.2 Communication Pathways 2.4.3 Personnel Responsibilities and Qualifications 2.4.4 Special Training Requirements and Certification	- Project Organizational Chart - Communication Pathways - Personnel Responsibilities and Qualifications Table - Special Personnel Training Requirements Table	Worksheet #5	Multi-Site QAPP Section 1.2, pages 2-9 Multi-Site QAPP Section 1.25, pages 9-10
2.5 Project Planning/Problem Definition 2.5.1 Project Planning (Scoping) 2.5.2 Problem Definition, Site History, and Background	- Project Scoping Session Documentation (including Data Needs tables) - Project Scoping Session Participants Sheet - Problem Definition, Site History, and Background - Site Maps (historical and present)	Worksheet #9	Willow OU SSWP Section 5.1, pages 52-53 (project scoping) Multi-Site QAPP Section 1.3, pages 10-12 (problem definition/background) Willow OU SSWP Section 1.2, page 2 (problem definition; Section 2, pages 4-22 (site history and background) Willow OU SSWP Figures 1-11
2.6 Project Quality Objectives (PQOs) and Measurement Performance Criteria 2.6.1 Development of Project Quality Objectives Using the Systematic Planning Process 2.6.2 Measurement Performance Criteria	- Site-Specific PQOs - Measurement Performance Criteria Table		Multi-Site QAPP Section 1.5, pages 15-29 (quality objectives) Willow OU SSWP Section 4, pages 38-51; Section 5.4, page 54; and Figure 8
2.7 Secondary Data Evaluation	- Sources of Secondary Data and Information - Secondary Data Criteria and Limitations Table	Worksheet #13	Willow OU SSWP Section 2.3, pages 17-20

Required QAPP Element(s) and Corresponding QAPP Section(s)	Required Information	QAPP Worksheet # or Page #	Crosswalk to Related Documents
2.8 Project Overview and Schedule 2.8.1 Project Overview 2.8.2 Project Schedule	- Summary of Project Tasks - Reference Limits and Evaluation Table - Project Schedule/Timeline Table	Worksheet #15	Willow OU SSWP Section 5.1, pages 52-53 Willow OU SSWP Section 9, page 95 and Figure 12
Measurement/Data Acquisition			
3.1 Sampling Tasks 3.1.1 Sampling Process Design and Rationale 3.1.2 Sampling Procedures and Requirements 3.1.2.1 Sampling Collection Procedures 3.1.2.2 Sample Containers, Volume, and Preservation 3.1.2.3 Equipment/ Sample Containers Cleaning and Decontamination Procedures 3.1.2.4 Field Equipment Calibration, Maintenance, Testing, and Inspection Procedures 3.1.2.5 Supply Inspection and Acceptance Procedures 3.1.2.6 Field Documentation Procedures	- Sampling Design and Rationale - Sample Location Map - Sampling Locations and Methods/SOP Requirements Table - Analytical Methods/SOP Requirements Table - Field Quality Control Sample Summary Table - Sampling SOPs - Project Sampling SOP References Table - Field Equipment Calibration, Maintenance, Testing, and Inspection Table		Willow OU SSWP Sections 6.4 through 6.6, pages 60-82 Willow OU SSWP Figures 9 and 10 (sampling locations) and Table 1 (sampling parameters, number of samples, analytical methods, field QC sample summary, preservation and holding times) Multi-Site QAPP Section 2.2, pages 37-39 and Appendix D (field sampling SOPs) Multi-Site QAPP Section 2.2.3, page 40 (field equipment calibration, etc.) Multi-Site QAPP Section 2.2.4, pages 41-42 (supply inspection and acceptance) Multi-Site QAPP Section 2.9.1, pages 51-52 (field documentation); Multi-Site FSP Appendix B (field forms)

Required QAPP Element(s) and Corresponding QAPP Section(s)	Required Information	QAPP Worksheet # or Page #	Crosswalk to Related Documents
3.2 Analytical Tasks 3.2.1 Analytical SOPs 3.2.2 Analytical Instrument Calibration Procedures 3.2.3 Analytical Instrument and Equipment Maintenance, Testing, and Inspection Procedures 3.2.4 Analytical Supply Inspection and Acceptance Procedures	- Analytical SOPs - Analytical SOP References Table - Analytical Instrument Calibration Table - Analytical Instrument and Equipment Maintenance, Testing, and Inspection Table	Appendix A Worksheet #23 Worksheet #24 Worksheet #25	
Measurement/Data Acquisition (Continued)			
3.3 Sample Collection Documentation, Handling, Tracking, and Custody Procedures 3.3.1 Sample Collection Documentation 3.3.2 Sample Handling and Tracking System 3.3.3 Sample Custody	- Sample Collection Documentation, Handling, Tracking, and Custody SOPs - Sample Container Identification - Sample Handling Flow Diagram - Example Chain-of-Custody (COC) Form and Seal	Worksheet #26	Multi-Site QAPP Section 2.3, pages 42-47 and Appendix D SOPs SAS-03-01 and SAS-03-02 (contains example COC form and custody seal)
3.4 Quality Control Samples 3.4.1 Sampling QC Samples 3.4.2 Analytical QC Samples	- QC Samples Table - Screening/Confirmatory Analysis Decision Tree – Not applicable		Willow OU SSWP Table 1 and Multi-Site QAPP Section 2.5, pages 48-49 and Table 6
3.5 Data Management Tasks 3.5.1 Project Documentation and Records 3.5.2 Data Package Deliverables 3.5.3 Data Reporting Formats 3.5.4 Data Handling and Management 3.5.5 Data Tracking and Control	- Project Documents and Records Table - Analytical Services Table - Data Management SOPs	Worksheet #30	Multi-Site QAPP Section 2.3.2.3, page 47; Section 2.9, pages 51-55 and Appendix D – SOP SAS-01-02

Required QAPP Element(s) and Corresponding QAPP Section(s)	Required Information	QAPP Worksheet # or Page #	Crosswalk to Related Documents
Assessment/Oversight			
4.1 Assessments and Response Actions 4.1.1 Planned Assessments 4.1.2 Assessment Findings and Corrective Action Responses	- Assessments and Response Actions - Planned Project Assessments Table - Audit Checklists - Assessment Findings and Corrective Action Responses Table		Multi-Site QAPP Section 3.1, pages 56-60
4.2 QA Management Reports	- QA Management Reports Table		Multi-Site QAPP Section 3.2.1, pages 60-61
4.3 Final Project Report			Multi-Site QAPP Sections 3.2.2 and 3.2.3, pages 61-62
Data Review			
5.1 Overview			
5.2 Data Review Steps 5.2.1 Step I: Verification 5.2.2 Step II: Validation 5.2.2.1 Step IIa Validation Activities 5.2.2.2 Step IIb Validation Activities 5.2.3 Step III: Usability Assessment 5.2.3.1 Data Limitations and Actions from Usability Assessment 5.2.3.2 Activities	- Verification (Step I) Process Table - Validation (Steps IIa and IIb) Process Table - Validation (Steps IIa and IIb) Summary Table - Usability Assessment		Multi-Site QAPP Section 4, pages 63-68 and Tables 6 and 7
5.3 Streamlining Data Review 5.3.1 Data Review Steps To Be Streamlined 5.3.2 Criteria for Streamlining Data Review 5.3.3 Amounts and Types of Data Appropriate for Streamlining		Not applicable	Not applicable

QAPP Worksheet #3
(UFP-QAPP Manual Section 2.3.1)
Distribution List

The distribution list for controlled copies of the Site-Specific QAPP is maintained by and updated by BMcD as the QAPP preparation organization. Controlled copies of the Site-Specific QAPP are assigned to personnel within each project organization. Recipients of controlled copies are provided with all revisions to the Site-Specific QAPP and are responsible for removing all outdated materials from circulation within their organization. Personnel responsible for controlled copies of the document are responsible for distributing Site-Specific QAPP updates and revisions to personnel within their organization. Project team members will have access to controlled copies of the document through the project managers listed here. Personnel with access to the Site-Wide QAPP include, but are not limited to: Project Engineer, Project Study Leader, Project Chemist, QA Officer, QC Coordinator, Field Site Manager (FSM), field team members, and laboratory staff.

QAPP Recipients	Title	Organization	Telephone Number	E-mail Address	Document Control Number
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Margaret Kelley, PE	Consultant Project Coordinator	BMcD	630/724-3282	mkelley@burnsmcd.com	WHS OU-002
Tim Prendiville	Project Coordinator	USEPA	312/886-5122	prendiville.timothy@epa.gov	WHS OU-003
Doyle Wilson	Project Manager	Illinois EPA	217/782-7592	doyle.wilson@illinois.gov	WHS OU-004
Pinaki Banerjee	Laboratory Project Manager	STAT	312/733-0551	PBanerjee@STATAnalysis.com	WHS OU-005
Brian Busten	Laboratory Project Manager	Pace-Green Bay	920/469-2436	Brian.Busten@pacelabs.com	WHS OU-006

QAPP Worksheet #4
(UFP-QAPP Manual Section 2.3.2)
Project Personnel Sign-Off Sheet

Worksheet #4-1 IBS/Peoples Gas

Key project personnel from each organization should sign copies of this form to indicate that they have read the applicable Site-Specific QAPP sections and will perform the tasks as described. Each organization will forward signed sheets to BMcD for inclusion in the project file.

Project Personnel	Title	Telephone Number	Signature	Date QAPP Read Email Receipt
Naren Prasad	Project Manager	312-240-4569		

Worksheet #4-2 BMcD

Key project personnel from each organization should sign copies of this form to indicate that they have read the applicable Site-Specific QAPP sections and will perform the tasks as described. Each organization will forward signed sheets to BMcD for inclusion in the project file.

Project Personnel	Title	Telephone Number	Signature	Date QAPP Read Email Receipt
Margaret Kelley	Consultant Project Manager	630-724-3282		
Sharon Shelton	Consultant QC Coordinator	816-822-3168		
Amy Hanrahan	Consultant Study Lead	630-724-3255		
To Be Assigned	Field Team Members		When assigned, project team members will be required to sign that they have read applicable sections of the QAPP.	Project team members must read applicable sections of the QAPP prior to participating in the project.

Worksheet #4-3 STAT

Key project personnel from each organization should sign copies of this form to indicate that they have read the applicable Site-Specific QAPP sections and will perform the tasks as described. Each organization will forward signed sheets to BMcD for inclusion in the project file.

Project Personnel	Title	Telephone Number	Signature	Date QAPP Read Email Receipt
Pinaki Banerjee	Project Manager and QA/QC Director	312-733-0551		
Donald Cortes	Laboratory Director	312-733-0551		

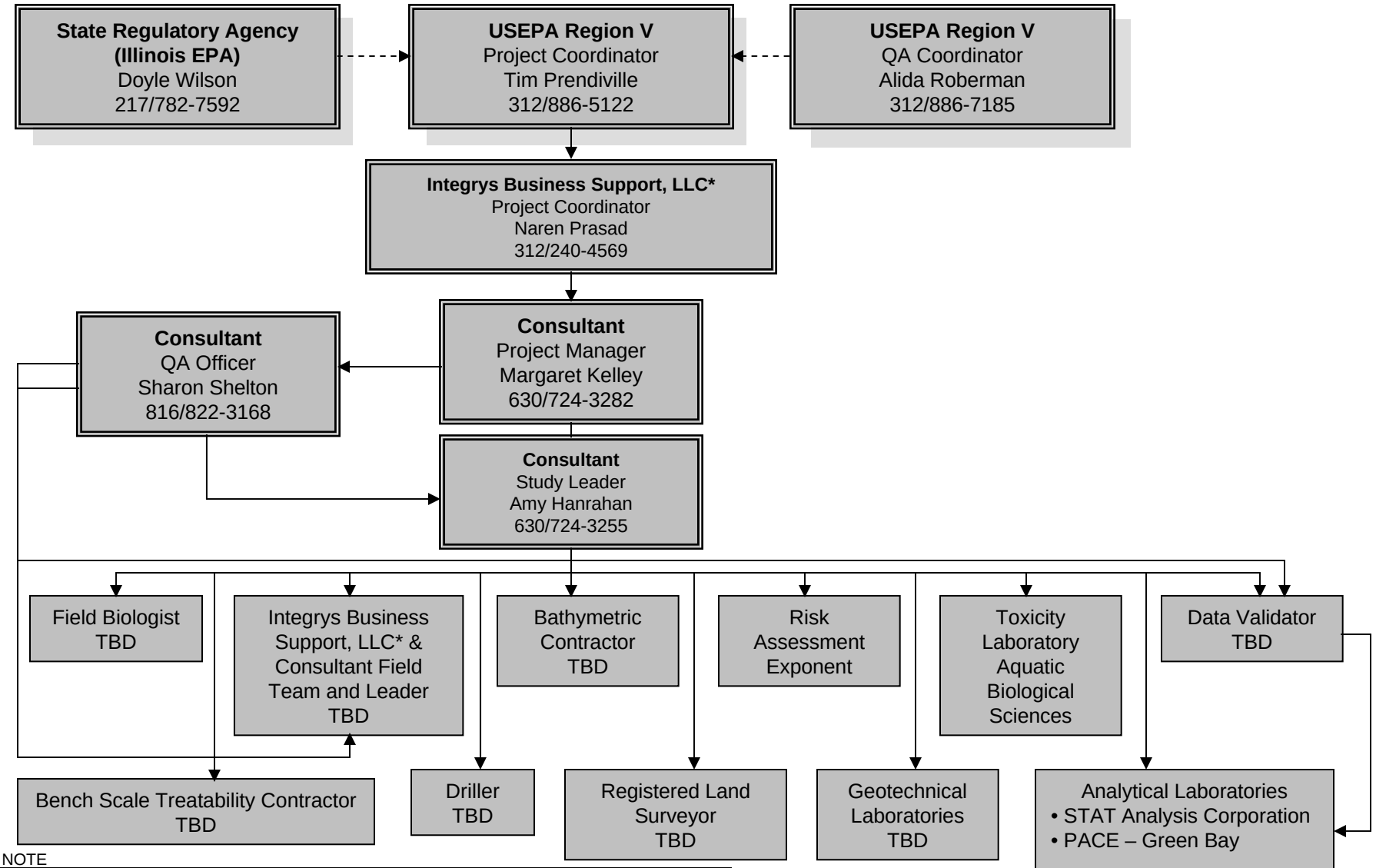
QAPP Worksheet #4
Project Personnel Sign-Off Sheet

Organization: Pace Team

Project Personnel	Title	Telephone Number	Signature	Date QAPP Read
Nils Melberg	General Manager-Green Bay Lab	(920) 469-2436		
Brian Basten	Client Service Manager/Integrys PM	(920) 469-2436		
Kate Grams	Quality Assurance Manager	(920) 469-2436		
Glen Coder	Section Head-Semivolatiles	(920) 469-2436		
Chad Rusch	Section Head-Inorganics	(920) 469-2436		
Jeff Bushner	Section Head-Volatiles	(920) 469-2436		
Mark Hampton	Sales Manager-Green Bay Lab	(262) 339-2579		

QAPP Worksheet #5
(UFP-QAPP Manual Section 2.4.1)
Project Organizational Chart

A project organizational chart is presented on Figure 1. The Multi-Site QAPP (Integrys 2007a) further defines the QC teams, roles, and responsibilities in Section 1-2, and pages 2 through 9.



NOTE

*Study work performed for Peoples Gas Light & Coke Company former MGP Sites is managed by Integrys Business Support, LLC.

FIGURE NO. 1	Burns & McDonnell 1431 Opus Place, Suite 400 Downers Grove, IL 60515	**Organization Chart for** **Willow Street/Hawthorne Avenue Station** **Operable Limit, North Branch Site** **INTEGRYS BUSINESS SUPPORT, LLC** USEPA REGION V CERCLA DOCKET NO. W-W-'08-C-917	DRAWN BY: JJ	DATE 07/01/09
REVISION NO. 0			CHECKED BY: KW	DATE 07/14/09
			APPROVED BY: MK	DATE 07/14/09

QAPP Worksheet #9
(UFP-QAPP Manual Section 2.5.1)
Project Scoping Session Participants Sheet

QAPP Worksheet #9-1 April 9, 2009 Project Status and Scoping Meeting

Project Name: Willow Street/Hawthorne Avenue Station Operable Unit (OU) **Projected Date(s) of Sampling:** 2009 **Project Manager:** Naren Prasad, Integrys Business Support (IBS)/Peoples Gas	**Site Name:** North Branch Site **Site Location:** Chicago, Illinois

Date of Session: April 9, 2009
Scoping Session Purpose: Project Status and Scoping

Name	Title	Affiliation	Phone #	E-mail Address	Project Role
Naren Prasad	Program Coordinator and Senior Environmental Engineer	IBS/Peoples Gas	(312) 240-4569	nmprasad@integrysgroup.com	Project management
Steve Matuszak	Director Environmental Affairs	IBS/Peoples Gas	(312) 240-4560	sjmatuszak@integrysgroup.com	Project management
Margaret Kelley	Consultant Program Coordinator and Project Manager	Burns & McDonnell	(630)724-3282	mkelley@burnsmcd.com	Project management
Brian Voss	Project Study Leader	Burns & McDonnell	(630) 724-3332	bvoss@burnsmcd.com	Technical management
Tim Prendiville	USEPA Project Manager	USEPA	(312) 886-5122	Prendiville.timothy@epamail.epa.gov	Project management
Robert Kay	USEPA Hydrogeologist	USGS/USEPA	(815) 756-9207	rtkay@usgs.gov	Technical advisor

Comments/Decisions: Findings from previous investigations and remediation activities were discussed. Data gaps were identified and proposed next steps for the land portion of the OU were discussed and agreed upon in concept.

QAPP Worksheet #13
(UFP-QAPP Manual Section 2.7)
Secondary Data Criteria and Limitations Table

This worksheet identifies all secondary data and information that will be used for the project and their originating sources. The use of the secondary data is specified as well as any limitations on their use.

Secondary Data	**Major Data Sources** (originating organization, report title and date)	**Data Generator(s)** (originating organization, data types, data generation / collection dates)	**How Data Will Be Used**	**Limitations on Data Use**
Soil and groundwater	*Barr, 2001. Site Investigation Summary Report – A Portion of Willow Street Station MGP Site, February.*	Barr Engineering Co.: BTEX, SVOCs and metals and cyanide soil data. VOCs, SVOCs, metals, cyanide, nitrate, ammonia and sulfide groundwater data. Collection Dates: November 2000	To determine the nature and extent of impacts on the Marcey West Parcel	Data is evaluated in an attached Table 1
Soil and groundwater	*Burns & McDonnell, 2005. Comprehensive Site Investigation Report – Former Willow Street Station Manufactured Gas Plant Site, 1640 North Kingsbury Portion, February. Supplemental Site Investigation Report/Remedial Objectives Report/Remedial Action Plan – Former Willow Street Station Manufactured Gas Plant Site, 1640 North Kingsbury Portion, November.*	Burns & McDonnell Engineering Inc.: VOCs, SVOCs, PCBs and metals soil data. VOC, SVOC, metals and cyanide groundwater data. Collection Dates: February-March 2002	To determine the nature and extent of impacts on the General Iron Parcel	Data is evaluated in an attached Table 1

Secondary Data	**Major Data Sources** (originating organization, report title and date)	**Data Generator(s)** (originating organization, data types, data generation / collection dates)	**How Data Will Be Used**	**Limitations on Data Use**
Soil	*Burns & McDonnell, 2002. Supplemental Site Investigation Summary Report – A Portion of Willow Street Station Manufactured Gas Plant Site, September.*	Burns & McDonnell Engineering Inc.: VOCs, SVOCs, PCBs and metals soil data. Collection Dates: June 2002	To further delineate the nature and extent of impacts on the Marcey West Parcel	Data is evaluated in an attached Table 1
Soil	*Burns & McDonnell, 2003. Comprehensive Site Investigation Report – Hawthorne Regulator Station Former Manufactured Gas Plant Site, June.*	Burns & McDonnell Engineering Inc.: VOCs, SVOCs, PCBs, metals and cyanide soil data. Collection Dates: June 2002	To determine the nature and extent of impacts on the Peoples Gas Parcel	Data is evaluated in an attached Table 1
Soil	*Burns & McDonnell, 2005. Supplemental Site Investigation Report/Remedial Objectives Report/Remedial Action Plan – Former Willow Street Station Manufactured Gas Plant Site, 1640 North Kingsbury Portion, November.*	Burns & McDonnell Engineering Inc.: VOCs, SVOCs, PCBs, metals and cyanide soil data. Collection Dates: November-December 2004	To further delineate the nature and extent of impacts on the General Iron Parcel adjacent to the ARA	Data is evaluated in an attached Table 1

Secondary Data	**Major Data Sources** (originating organization, report title and date)	**Data Generator(s)** (originating organization, data types, data generation / collection dates)	**How Data Will Be Used**	**Limitations on Data Use**
Soil	*Burns & McDonnell, 2006. DRAFT Site Investigation Report/Remedial Objectives Report/Remedial Action Plan/Remedial Action Completion Report – A. Finkl & Sons Property, June.*	Burns & McDonnell Engineering Inc.: VOCs, SVOCs, PCBs, metals and cyanide soil data. Collection Dates: August 2005	To determine the nature and extent of impacts on the Finkl Parcel	Data is evaluated in an attached Table 1
Soil	*Burns & McDonnell, 2006. DRAFT River Sediment Investigation Summary – Former Willow Street Station, December.*	Burns & McDonnell Engineering Inc.: Forensic soil data. Collection Dates: June-July 2006	To assess the nature and extent of impacts in the River adjacent to the General Iron Parcel	Data is evaluated in an attached Table 1

Table 1. Secondary Data Criteria Evaluation
Willow Street/Hawthorne Avenue Station OU

Source of Data	Media of Sample Data*	Quality of Field Procedures	Quality of QAPP used during SI	Field Documentation and Log Books	Photographs	Laboratory Reports and Documentation	Analytical Methods	Detection Limits	Laboratory QA/QC Documentation	Consistency	Age of Samples	Similar Field Conditions	Total Score **
Barr Engineering, 2000. Marcey West Parcel site investigation	S, GW	0	0	3	0	0	0	0	0	0	3	5	11
Burns & McDonnell, 2002. Supplemental Site Investigation Report for Marcey West	S, GW	5	3	5	5	5	5	3	5	5	5	5	51
Burns & McDonnell, 2003. Remedial Objectives Report/Remedial Action Plan for Marcey West	S, GW	5	3	5	0	5	5	3	5	5	5	5	46
Burns & McDonnell, 2003. Comprehensive Site Investigation Report for Peoples Gas Parcel	S	5	5	5	5	5	5	5	5	5	5	5	55
Burns & McDonnell, 2003. Remedial Objectives Report/Remedial Action Plan for Peoples Gas Parcel	S	5	0	5	0	5	5	5	5	5	5	5	45
Burns & McDonnell, 2003. Remedial Action Completion Report for Marcey West	S, GW	5	5	5	5	5	5	5	5	5	5	5	55
Burns & McDonnell, 2005a. Comprehensive Site Investigation Report for General Iron Parcel	S, GW	5	5	5	5	5	5	5	5	5	5	5	55
Burns & McDonnell, 2005b. Supplemental Site Investigation/Remedial Objectives Report/Remedial Action Plan for General Iron Parcel	S, GW	5	5	5	5	5	5	5	5	5	5	5	55
Burns & McDonnell, 2005. Remedial Action Completion Report for Peoples Gas Parcel	S	5	5	5	5	5	5	5	5	5	5	5	55
Burns & McDonnell, 2007. Remedial Action Completion Report for General Iron Parcel.	S, GW	5	5	5	5	5	5	5	5	5	5	5	55

Notes:

(1) Table compares previous data against Multi-Site QAPP, Rev 2,criteria and provides a numerical rating using a scale of 0 to 5.
5 = all criteria is met, 3 = most criteria is met, 1 = minimal criteria presented, 0 = no criteria met or information to evaluate is not available

(2) Reports include related sampling data books, if applicable.

(3) Barr - Barr Engineering Company. 8300 Norman Center Dr. Minneapolis, MN 55437-1026

(4) Burns & McDonnell - Burns & McDonnell Engineering Inc. 1431 Opus Place Suite 400. Downers Grove, IL 60515

(5) Groundwater samples previously collected are not useable since they are outdated and conditions have changed since they were collected.

(6) Many SI and SSI samples on the General Iron, AFS, West Marcey and Peoples Gas parcels were excavated so the evaluation only applies to soil samples remaining.

(7) * - Media includes: Soil (S), Groundwater (GW)

(8) ** - If total score is 45 or greater, the data meets the DQOs for characterization and use in the risk assessment

QAPP Worksheet #15
(UFP-QAPP Manual Section 2.8.1)
Reference Limits and Evaluation Table

STAT will perform analyses of water, soil and soil vapor. Tables 2, 3, and 4 present the reference limits and laboratory limits for water, soil and soil vapor. PACE Analytical will perform analyses of sediment. Table 5 presents the reference limits and laboratory limits for sediment analyses.

Table 2. Human Health Risk-Based Water Matrix

Analytical Methods, Practical Quantitation Limits (PQLs), Method Detection Limits (MDLs) and Reporting Limits (RLs)
Willow Street/Hawthorne Avenue Station OU
USEPA Region 5
CERCLA Docket No. W-W-'08-C-917

Project Compound List	CAS Number	Analytical Method Number[d]	Water Human Health Risk Based PQL				Analytical Method		STAT Analysis Corporation	
			EPA Reg IX PRGs[a] (µg/L)	NRWQC[c] Organism Only (µg/L)	NRWQC[c] Water and Organism (µg/L)	EPA Region 5 ESL[b] (Surface Water Only) (µg/L)	MDL µg/L	PQL µg/L	MDL µg/L	RL µg/L
Petroleum Volatile Organic Compounds										
Benzene	71-43-2	SW846-8260B	0.41	51	2.2	114	0.03	5	0.20	3
Ethylbenzene	100-41-4	SW846-8260B	1.5	2,100	530	14	0.03	5	0.30	5
Toluene	108-88-3	SW846-8260B	1,000	15,000	1,300	253	0.08	5	0.40	5
Xylenes	1330--20-7	SW846-8260B	200	--	--	27	NA	15	1.00	15
1,3,5-Trimethylbenzene	108-67-8	SW846-8260B	12	--	--	--	0.06	5	0.20	5
1,2,4-Trimethylbenzene	95-63-6	SW846-8260B	15	--	--	--	0.09	5	0.30	5
Semivolatile Organic Compounds										
Non-Carcinogenic PAHs										
Acenaphthene	83-32-9	SW846-8270C (SIM)	2,200	990	670	38	NA	10	0.05	0.2
Acenaphthylene	208-96-8	SW846-8270C (SIM)	--	--	--	4,840	NA	10	0.03	0.2
Anthracene	120-12-7	SW846-8270C (SIM)	11,000	40,000	8,300	0.035	NA	10	0.02	0.2
Benzo(g,h,i)perylene	191-24-2	SW846-8270C (SIM)	--	--	--	7.640	NA	10	0.02	0.1
Fluoranthene	206-44-0	SW846-8270C (SIM)	1,500	140	130	1.90	NA	10	0.02	0.2
Fluorene	86-73-7	SW846-8270C (SIM)	1,500	5,300	1,100	19	NA	10	0.03	0.1
2-Methylnaphthalene	91-57-6	SW846-8270C (SIM)	--	--	--	330	NA	10	0.03	0.1
Naphthalene	91-20-3	SW846-8270C (SIM)	0.14	--	--	13	NA	10	0.11	0.2
Phenanthrene	85-01-8	SW846-8270C (SIM)	--	--	--	4	NA	10	0.04	0.2
Pyrene	119-00-0	SW846-8270C (SIM)	1100	4,000	830	0.3	NA	10	0.02	0.13
Carcinogenic PAHs										
Benzo(a)anthracene	56-55-3	SW846-8270C (SIM)	0.029	0.018	0.0038	0.025	NA	10.0	0.02	0.13
Benzo(a)pyrene	50-32-8	SW846-8270C (SIM)	0.0029	0.018	0.0038	0.014	NA	10.0	0.02	0.2
Benzo(b)fluoranthene	205-99-2	SW846-8270C (SIM)	0.029	0.018	0.0038	9.07	NA	10.0	0.06	0.18
Benzo(k)fluoranthene	207-08-9	SW846-8270C (SIM)	0.29	0.018	0.0038	--	NA	10.0	0.08	0.17
Chrysene	218-01-9	SW846-8270C (SIM)	2.9	0.018	0.0038	--	NA	10.0	0.02	0.1
Dibenzo(a,h)anthracene	53-70-3	SW846-8270C (SIM)	0.0029	0.018	0.0038	5	NA	10.0	0.02	0.1
Indeno(1,2,3-cd)pyrene	193-39-5	SW846-8270C (SIM)	0.029	0.018	0.0038	4.31	NA	10.0	0.02	0.1
Phenols										
2,4-dimethylphenol	105-67-9	SW846-8270C	730	850	380	100	NA	10.0	1.3	5
2-methylphenol	95-48-7	SW846-8270C	1800	--	--	--	NA	10.0	1.3	5
4-methylphenol	106-44-5	SW846-8270C	180	--	--	--	NA	10.0	2.8	5
phenol	108-95-2	SW846-8270C	11000	1700000	21000	180	NA	10.0	0.8	5

Table 2. Human Health Risk-Based Water Matrix

Analytical Methods, Practical Quantitation Limits (PQLs), Method Detection Limits (MDLs) and Reporting Limits (RLs)
Willow Street/Hawthorne Avenue Station OU
USEPA Region 5
CERCLA Docket No. W-W-'08-C-917

Project Compound List	CAS Number	Analytical Method Number[d]	Water Human Health Risk Based PQL				Analytical Method		STAT Analysis Corporation	
			EPA Reg IX PRGs[a] (µg/L)	NRWQC[c] Organism Only (µg/L)	NRWQC[c] Water and Organism (µg/L)	EPA Region 5 ESL[b] (Surface Water Only) (µg/L)	MDL µg/L	PQL µg/L	MDL µg/L	RL µg/L
Inorganics										
Aluminum	7429-90-5	SW846-6020A	37000	--	--	--	NA	NA	0.016	0.04
Arsenic	7440-38-2	SW846-6020A	0.045	0.00014	0.000018	148	NA	NA	0.0016	0.004
Barium	7440-39-3	SW846-6020A	7,300	--	--	220	NA	NA	0.0011	0.004
Cadmium	7440-43-9	SW846-6020A	18	--	--	0.15	NA	NA	0.0005	0.002
Calcium	7440-70-2	SW846-6020A	TBD	TBD	TBD	--	NA	NA	0.184	0.2
Chromium (total)	16065-83-1	SW846-6020A	100	--	--	42	NA	NA	0.008	0.004
Cobalt	7440-48-4	SW846-6020A	11	TBD	TBD	--	NA	NA	0.0004	0.004
Copper	7440-50-8	SW846-6020A	1500	--	1.3	1.58	NA	NA	0.004	0.01
Cyanide (hydrogen)	57-12-5	SW846-9012A	6.2	0.14	0.14	5.2	NA	NA	0.0025	0.0050
Iron	7439-89-6	SW846-6020A	26,000	--	0.3	--	NA	NA	0.036	0.1
Lead	7439-92-1	SW846-6020A	15	--	--	1.17	NA	NA	0.0016	0.002
Magnesium	7439-95-4	SW846-6020A	TBD	TBD	TBD	--	NA	NA	0.046	0.1
Manganese	7439-96-5	SW846-6020A	880.000	0.1	0.05	--	NA	NA	0.0008	0.004
Mercury	7439-97-6	SW846-7470A	2	--	--	0.0013	NA	NA	0.00003	0.00025
Nickel	7440-02-0	SW846-6020A	730.000	4.6	0.61	28.9	NA	NA	0.0006	0.004
Potassium	7440-09-7	SW846-6020A	TBD	TBD	TBD	--	NA	NA	0.087	0.1
Sodium	7440-23-5	SW846-6020A	TBD	TBD	TBD	--	NA	NA	0.115	0.3
Vanadium	7440-62-2	SW846-6020A	180	--	--	12	NA	NA	0.001	0.004
Zinc	7440-66-6	SW846-6020A	1,100	26	7.4	65.7	NA	NA	0.006	0.02

[a]United States Environmental Protection Agency Region 9 Preliminary Remediation Goals (PRGs). October 2004. Revised April 2009.
[URL: http://www.epa.gov/region09/waste/sfund/prg/]. TOC PQLs to be evaluated prior to implementing Site-Specific Work Plans.
[PRGs correspond to residential exposure to tap water via ingestion based on target cancer risk = 1E-6 or noncancer hazard quotient = 0.1.
[URL: http://www.epa.gov/region09/waste/sfund/prg/]

[b] Region 5 Ecological Screening Levels

[c]NRWQC: National Recommended Water Quality Criteria - Correction." USEPA Office of Water. For human health consumption of water and organism and organism only. EPA 822-Z-99-001. April 1999. Updated 2006.

[d] "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods". Third Edition of SW-846, as updated by Updates I, II, IIA, IIB, III and IIIA. U.S.EPA

[e] TBD - To Be Determined, SW846-8082 MDL Range 0.054-0.90 ug/L and 57-70 ug/Kg

[f] If separate MDLs and CQRLs were cited for m & p- and o-Xylenes, the highest numbers are included in this table.

[B:] Test America available cyanide analysis by the OIA-1677 method.

[A.]: See individual laboratory SOPs for TOC analytical methods.

-- indicates a PQL has not been established

* Laboratory is in the process of updating or developing MDLs/RLs, to be determined prior to site investigation

Shaded cells indicate the laboratory is not intended to perform this analysis.

TBD - To Be Determined

NA - Not Applicable

Table 3. Human Health Risk-Based Soil Matrix

Analytical Methods, Practical Quantitation Limits (PQLs), Method Detection Limits (MDLs) and Reporting Limits (RLs)
Willow Street/Hawthorne Avenue Station OU
USEPA Region 5
CERCLA Docket Nos. W-W-'08-C-917

Project Compound List	CAS Number	Analytical Method Number[b]	Soil Human Health Risk Based PQL	Analytical Method		STAT Analysis Corporation	
			EPA Reg IX PRGs[a] (µg/kg, dry)	MDL µg/kg	PQL µg/kg	MDL µg/kg	RL µg/kg
Volatile Organic Compounds							
Benzene	71-43-2	SW846-8260B	1,100	NA	5	0.2	5
Ethylbenzene	100-41-4	SW846-8260B	5,700	NA	5	0.1	5
Toluene	108-88-3	SW846-8260B	5,000,000	NA	5	0.2	5
Xylenes	1330--20-7	SW846-8260B	600,000	NA	15	0.4	15
1,3,5-Trimethylbenzene	108-67-8	SW846-8260B	47,000	NA	5	0.2	5
1,2,4-Trimethylbenzene	95-63-6	SW846-8260B	67,000	NA	5	0.2	5
Semivolatile Organic Compounds							
Non-Carcinogenic PAHs							
Acenaphthene	83-32-9	SW846-8270C (SIM)	340,000	NA	660	2.6	25
Acenaphthylene	208-96-8	SW846-8270C (SIM)	--	NA	660	3.6	25
Anthracene	120-12-7	SW846-8270C (SIM)	17,000,000	NA	660	0.6	25
Benzo(g,h,i)perylene	191-24-2	SW846-8270C (SIM)	--	NA	660	0.8	25
Fluoranthene	206-44-0	SW846-8270C (SIM)	2,300,000	NA	660	1.5	25
Fluorene	86-73-7	SW846-8270C (SIM)	230,000	NA	660	1.2	25
2-Methylnaphthalene	91-57-6	SW846-8270C (SIM)	310,000	NA	660	4.0	25
Naphthalene	91-20-3	SW846-8270C (SIM)	39,000	NA	660	3.4	25
Phenanthrene	85-01-8	SW846-8270C (SIM)	--	NA	660	1.0	25
Pyrene	119-00-0	SW846-8270C (SIM)	1,700,000	NA	660	2.0	25
Carcinogenic PAHs							
Benzo(a)anthracene	56-55-3	SW846-8270C (SIM)	150	NA	660	0.6	25
Benzo(a)pyrene	50-32-8	SW846-8270C (SIM)	15	NA	660	0.7	25
Benzo(b)fluoranthene	205-99-2	SW846-8270C (SIM)	150	NA	660	1.1	25
Benzo(k)fluoranthene	207-08-9	SW846-8270C (SIM)	1,500	NA	660	0.8	25
Chrysene	218-01-9	SW846-8270C (SIM)	15,000	NA	660	0.6	25
Dibenzo(a,h)anthracene	53-70-3	SW846-8270C (SIM)	15	NA	660	0.9	25
Indeno(1,2,3-cd)pyrene	193-39-5	SW846-8270C (SIM)	150	NA	660	0.6	25
Phenols							
2,4-dimethylphenol	105-67-9	SW846-8270C	1,200,000	NA	660	26	170
2-methylphenol	95-48-7	SW846-8270C	3,100,000	NA	660	38	170
4-methylphenol	106-44-5	SW846-8270C	310,000	NA	660	40	170
phenol	108-95-2	SW846-8270C	18,000,000	NA	660	50	170

Table 3. Human Health Risk-Based Soil Matrix

Analytical Methods, Practical Quantitation Limits (PQLs), Method Detection Limits (MDLs) and Reporting Limits (RLs)
Willow Street/Hawthorne Avenue Station OU
USEPA Region 5
CERCLA Docket Nos. W-W-'08-C-917

Project Compound List	CAS Number	Analytical Method Number[b]	Soil Human Health Risk Based PQL	Analytical Method		STAT Analysis Corporation	
			EPA Reg IX PRGs[a] (µg/kg, dry)	MDL µg/kg	PQL µg/kg	MDL µg/kg	RL µg/kg
Inorganics							
Aluminum	7429-90-5	SW846-6020A	7,600	NA	NA	2.3	20.0
Antimony	7440-36-0	SW846-6020A	3.1	NA	NA	0.7	2.0
Arsenic	7440-38-2	SW846-6020A	0.39	NA	NA	0.3	1.0
Barium	7440-39-3	SW846-6020A	540	NA	NA	0.1	1.0
Beryllium	7440-41-7	SW846-6020A	TBD	NA	NA	0.1	0.5
Cadmium	7440-43-9	SW846-6020A	3.7	NA	NA	0.1	0.5
Calcium	7440-70-2	SW846-6020A	TBD	NA	NA	5.2	60.0
Chromium (total)	16065-83-1	SW846-6020A	210	NA	NA	0.2	1.0
Cobalt	7440-48-4	SW846-6020A	TBD	NA	NA	0.1	1.0
Copper	7440-50-8	SW846-6020A	310	NA	NA	0.2	2.50
Cyanide (hydrogen)	57-12-5	SW846-9012A	1.1	NA	NA	1.0	0.25
Iron	7439-89-6	SW846-6020A	2,300	NA	NA	6.0	30.0
Lead	7439-92-1	SW846-6020A	400	NA	NA	0.6	0.5
Magnesium	7439-95-4	SW846-6020A	TBD	NA	NA	13.6	30.0
Manganese	7439-96-5	SW846-6020A	180	NA	NA	0.1	1.0
Mercury	7439-97-6	SW846-7471B	2.3	NA	NA	0.0016	0.025
Nickel	7440-02-0	SW846-6020A	160	NA	NA	0.15	1.0
Potassium	7440-09-7	SW846-6020A	TBD	NA	NA	14.6	30.0
Sodium	7440-23-5	SW846-6020A	TBD	NA	NA	7.4	60.0
Selenium	7782-49-2	SW846-6020A	39	NA	NA	0.4	1.0
Thallium	7440-28-0	SW846-6020A	TBD	NA	NA	0.1	1.0
Vanadium	7440-62-2	SW846-6020A	7.8	NA	NA	0.2	1.0
Zinc	7440-66-6	SW846-6020A	2,300	NA	NA	0.3	5.0

[a]USEPA Region 9 Preliminary Remediation Goals (PRGs). Revised April 2009. [URL: http://www.epa.gov/region09/waste/sfund/prg/].
[PRGs correspond to residential exposure to soil via ingestion, dermal contact, and inhalation based on target cancer risk = 1E-6 or noncancer hazard quotient = 0.1.

[b] "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods". Third Edition of SW-846, as updated by Updates I, II, IIA, IIB, III and IIIA. USEPA
TBD - To Be Determined
[A]: See individual laboratory SOPs for TOC analytical methods.
[B] : Analyzed by SW846-6010B
[F] : Microwave digestion
* Laboratory is in the process of updating or developing MDLs/RLs, to be determined prior to site investigation
TBD - To Be Determined
NA - Not Applicable

1. Analytical methods refer to analytical procedure numbers used in the EPA publication, SW-846,"Test Methods for Evaluating Solid Waste", Third Edition.
2. Site specific PQLs and RLs are to be established in the Site-Specific Work Plans. PQLs and RLs presented herein, are for example only.

Table 4. Human Health Risk-Based Soil Vapor Matrix

Analytical Methods, Practical Quantitation Limits (PQLs), Method Detection Limits (MDLs) and Reporting Limits (RLs)
Willow Street/Hawthorne Avenue Station OU
USEPA Region 5
CERCLA Docket Nos. W-W-'08-C-917

Project Compound List	CAS Number	Analytical Method Number[d]	Soil Vapor Human Health Risk Based PQL[a] (µg/kg, dry)	Analytical Method MDL ppb	Analytical Method PQL ppb	STAT Analysis Corporation MDL ppb	STAT Analysis Corporation RL[b] ppb
Volatile Organic Compounds							
Benzene	71-43-2	TO-15	TBD1	0.34	--	0.022	0.2
Ethylbenzene	100-41-4	TO-15	TBD1	0.27	--	0.024	0.2
Toluene	108-88-3	TO-15	TBD1	0.99	--	0.024	0.2
Xylenes	1330--20-7	TO-15	TBD1	1.3	--	0.15	0.6
1,3,5-Trimethylbenzene	108-67-8	TO-15	TBD1	--	--	0.13	0.2
1,2,4-Trimethylbenzene	95-63-6	TO-15	TBD1	--	--	0.11	0.2
Semivolatile Organic Compounds							
Naphthalene[b]	91-20-3	TO-15	TBD1	---	---	0.086	0.2
Indicator Parameters						**%**	**%**
Oxygen	7782-44-7	3C	--	--	--	0.004	0.04
Carbon Dioxide	124-38-9	3C	--	--	--	0.027	0.3
Methane	74-82-8	3C	---	--	--	0.011	0.05

[a] TBD1 - To be determined. See Section 5.3 "Vapor Migration Screening" of the Multi-Site Risk Assessment Framework, Former Manufactured Gas Plant Sites (Exponent, September 5, 2007)

[b] Base RLs are given. These will vary based on sample volume (prep factor).

1. TO-15 Method is Determination of Volatile Organic Compounds (VOCs) In Air Collected In Specially-Prepared Canisters and Analyzed By Gas Chromatography/Mass Spectrometry (GC/MS), in *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air: Method TO-15* , 2nd ed., United States Environmental Protection Agency (USEPA), January 1999.

2. 3C Method is found in Code of Federal Regulations (CFR) Title 40 – Protection of Environment, Chapter I – Part 60 Standards of Performance for New Stationary Sources, Appendix A-2 Test Methods 2G through 3C, February 1988. Method 3C, Environmental Protection Agency – Determination of Carbon Dioxide, Methane, Nitrogen, and Oxygen from Stationary Sources.

QAPP Worksheet #15
Table 5 - PACE - Reference Limits and Evaluation

Matrix: Solid (Sediment Sampling)
Analytical Group: PVOC
Concentration Level: Low

Analyte	CAS Number	Project Screening Criteria/Action Limit	Project Quantitation Limit	Analytical Method[1] – SW-846 8260B		Achievable Laboratory Limits[2]	
				MDLs	Method QLs	MDLs (mg/kg)	QLs (mg/kg)
Benzene	71-43-2	0.057	0.057	MDL Study	Lab-Specific	0.0026785	0.02
Toluene	108-88-3	0.89	0.89	MDL Study	Lab-Specific	0.00352075	0.05
Ethylbenzene	100-41-4	3.6	3.6	MDL Study	Lab-Specific	0.005955	0.05
Xylene	1330-20-7	0.025	0.025	MDL Study	Lab-Specific	0.005187	0.15
MTBE	1634-04-4	NA	NA	MDL Study	Lab-Specific	0.0044042	0.05
1,2,4-Trimethylbenzene	95-63-6	NA	NA	MDL Study	Lab-Specific	0.00423595	0.05
1,3,5-Trimethylbenzene	108-67-8	NA	NA	MDL Study	Lab-Specific	0.0047545	0.05

[1] Analytical MDLs and QLs are those documented in validated methods.
[2] Achievable MDLs and QLs are limits that an individual laboratory can achieve when performing a specific analytical method.

The Achievable Laboratory Limits (MDLs and/or QLs) are laboratory-derived limits. The values are subject to change annually as part of laboratory evaluation/ performance updates.

QAPP Worksheet #15
Table 5 - PACE - Reference Limits and Evaluation

Matrix: Solid (Sediment Sampling)
Analytical Group: PAH
Concentration Level: Low

Analyte	CAS Number	Project Screening Criteria/Action Limit	Project Quantitation Limit	Analytical Method[1] – SW-846 8270 SIM		Achievable Laboratory Limits[2]	
				MDLs	Method QLs	MDLs (mg/kg)	QLs (mg/kg)
Acenaphthene	83-32-9	0.14	0.14	MDL Study	Lab-Specific	0.0009259	0.0166666
Acenaphthylene	208-96-8	0.129	0.129	MDL Study	Lab-Specific	0.00170233	0.0166666
Anthracene	12-12-7	0.17	0.17	MDL Study	Lab-Specific	0.0045705	0.0166666
Benzo(a)anthracene	56-55-3	0.24	0.24	MDL Study	Lab-Specific	0.00835	0.0166666
Benzo(b)fluoranthene	205-99-2	0.28	0.28	MDL Study	Lab-Specific	0.00565779	0.0166666
Benzo(k)fluoranthene	207-08-9	0.28	0.28	MDL Study	Lab-Specific	0.00619854	0.0166666
Benzo(a)pyrene	50-32-8	0.276	0.276	MDL Study	Lab-Specific	0.00933163	0.0166666
Benzo(g,h,i)perylene	191-24-2	0.313	0.313	MDL Study	Lab-Specific	0.00420735	0.0166666
Chrysene	218-01-9	0.241	0.241	MDL Study	Lab-Specific	0.00343567	0.0166666
Dibenzo(a,h)anthracene	53-70-3	0.321	0.321	MDL Study	Lab-Specific	0.00465756	0.0166666

[1] Analytical MDLs and QLs are those documented in validated methods.
[2] Achievable MDLs and QLs are limits that an individual laboratory can achieve when performing a specific analytical method.

The Achievable Laboratory Limits (MDLs and/or QLs) are laboratory-derived limits. The values are subject to change annually as part of laboratory evaluation/ performance updates.

QAPP Worksheet #15
Table 5 - PACE - Reference Limits and Evaluation

Matrix: Solid (Sediment Sampling)
Analytical Group: PAH-continued
Concentration Level: Low

Analyte	CAS Number	Project Screening Criteria/Action Limit	Project Quantitation Limit	Analytical Method[1] – SW-846 8270 SIM		Achievable Laboratory Limits[2]	
				MDLs	Method QLs	MDLs (mg/kg)	QLs (mg/kg)
Fluoranthene	206-44-0	0.202	0.202	MDL Study	Lab-Specific	0.0010996	0.0166666
Fluorene	86-73-7	0.154	0.154	MDL Study	Lab-Specific	0.0009121	0.0166666
Indeno(1,2,3-cd)pyrene	193-39-5	0.319	0.319	MDL Study	Lab-Specific	0.00419867	0.0166666
Naphthalene	91-20-3	0.11	0.11	MDL Study	Lab-Specific	0.0012327	0.0166666
Phenanthrene	85-01-8	0.17	0.17	MDL Study	Lab-Specific	0.00198677	0.0166666
Pyrene	129-00-0	0.199	0.199	MDL Study	Lab-Specific	0.0010154	0.0166666
2-Methylnaphthalene	91-57-6	NA	NA	MDL Study	Lab-Specific	0.00185523	0.0166666

[1] Analytical MDLs and QLs are those documented in validated methods.
[2] Achievable MDLs and QLs are limits that an individual laboratory can achieve when performing a specific analytical method.

The Achievable Laboratory Limits (MDLs and/or QLs) are laboratory-derived limits. The values are subject to change annually as part of laboratory evaluation/ performance updates.

QAPP Worksheet #15
Table 5 - PACE - Reference Limits and Evaluation

Matrix: Solid (Sediment Sampling)
Analytical Group: Alkylated PAH
Concentration Level: Low

Analyte	CAS Number	Project Screening Criteria/Action Limit	Project Quantitation Limit	Analytical Method[1] – SW-846 8270 SIM		Achievable Laboratory Limits[2]	
				MDLs	Method QLs	MDLs (mg/kg)	QLs (mg/kg)
C1-naphthalenes		0.127	0.127	MDL Study	Lab-Specific	0.0050	0.010
C2-napthalenes		0.146	0.146	MDL Study	Lab-Specific	0.0050	0.010
C3-napthalenes		0.166	0.166	MDL Study	Lab-Specific	0.0050	0.010
C4-napthalenes		0.188	0.188	MDL Study	Lab-Specific	0.0050	0.010
C1-fluorenes		0.174	0.174	MDL Study	Lab-Specific	0.0050	0.010
C2-fluorenes		0.196	0.196	MDL Study	Lab-Specific	0.0050	0.010
C3-fluorenes		0.22	0.22	MDL Study	Lab-Specific	0.0050	0.010
C1-phenanthrene/anthracenes		0.191	0.191	MDL Study	Lab-Specific	0.0050	0.010
C2-phenanthrene/anthracenes		0.213	0.213	MDL Study	Lab-Specific	0.0050	0.010
C3-phenanthrene/anthracenes		0.237	0.237	MDL Study	Lab-Specific	0.0050	0.010
C4-phenanthrene/anthracenes		0.261	0.261	MDL Study	Lab-Specific	0.0050	0.010

[1] Analytical MDLs and QLs are those documented in validated methods.
[2] Achievable MDLs and QLs are limits that an individual laboratory can achieve when performing a specific analytical method.

The Achievable Laboratory Limits (MDLs and/or QLs) are laboratory-derived limits. The values are subject to change annually as part of laboratory evaluation/ performance updates.

QAPP Worksheet #15
Table 5 - PACE - Reference Limits and Evaluation

Matrix: Solid (Sediment Sampling)
Analytical Group: Alkylated PAH-continued
Concentration Level: Low

Analyte	CAS Number	Project Screening Criteria/Action Limit	Project Quantitation Limit	Analytical Method[1] – SW-846 8270 SIM		Achievable Laboratory Limits[2]	
				MDLs	Method QLs	MDLs (mg/kg)	QLs (mg/kg)
C1-pyrene/fluoranthenes		0.22	0.22	MDL Study	Lab-Specific	0.0050	0.010
C1-benzo(a)anthracene/chrysenes		0.266	0.266	MDL Study	Lab-Specific	0.0050	0.010
C2-benzo(a)anthracene/chrysenes		0.288	0.288	MDL Study	Lab-Specific	0.0050	0.010
C3-benzo(a)anthracene/chrysenes		0.318	0.318	MDL Study	Lab-Specific	0.0050	0.010
C4-benzo(a)anthracene/chrysenes		0.347	0.347	MDL Study	Lab-Specific	0.0050	0.010

[1] Analytical MDLs and QLs are those documented in validated methods.
[2] Achievable MDLs and QLs are limits that an individual laboratory can achieve when performing a specific analytical method.

The Achievable Laboratory Limits (MDLs and/or QLs) are laboratory-derived limits. The values are subject to change annually as part of laboratory evaluation/ performance updates.

QAPP Worksheet #15
Table 5 - PACE - Reference Limits and Evaluation

Matrix: Solid (Sediment Sampling)
Analytical Group: Metals
Concentration Level: Low

Analyte	CAS Number	Project Screening Criteria/Action Limit	Project Quantitation Limit	Analytical Method[1] – SW-846 6020		Achievable Laboratory Limits[2]	
				MDLs	Method QLs	MDLs (mg/kg)	QLs (mg/kg)
Arsenic	7440-38-2	9.8	9.8	MDL Study	Lab-Specific	0.05	0.1
Barium	7440-39-3	NA	NA	MDL Study	Lab-Specific	0.0279	0.1
Beryllium	7440-41-7	NA	NA	MDL Study	Lab-Specific	0.0252	0.1
Cadmium	7440-43-9	0.99	0.99	MDL Study	Lab-Specific	0.0073	0.1
Chromium	7440-47-3	43	43	MDL Study	Lab-Specific	0.0308	0.1
Copper	7440-50-8	32	32	MDL Study	Lab-Specific	0.0281	0.1
Lead	7439-92-1	36	36	MDL Study	Lab-Specific	0.0231	0.1
Mercury	7439-97-6	0.18	0.18	MDL Study	Lab-Specific	0.00164	0.01
Nickel	7440-02-0	23	23	MDL Study	Lab-Specific	0.0256	0.1
Selenium	7782-49-2	NA	NA	MDL Study	Lab-Specific	0.0275	0.1
Silver	7440-22-4	1.6	1.6	MDL Study	Lab-Specific	0.0018	0.05
Zinc	7440-66-6	120	120	MDL Study	Lab-Specific	0.0452	2.0

[1] Analytical MDLs and QLs are those documented in validated methods.
[2] Achievable MDLs and QLs are limits that an individual laboratory can achieve when performing a specific analytical method.

The Achievable Laboratory Limits (MDLs and/or QLs) are laboratory-derived limits. The values are subject to change annually as part of laboratory evaluation/ performance updates.

QAPP Worksheet #15
Table 5 - PACE - Reference Limits and Evaluation

Matrix: Solid (Sediment Sampling)
Analytical Group: Total Cyanide
Concentration Level: Low

Analyte	CAS Number	Project Screening Criteria/Action Limit	Project Quantitation Limit	Analytical Method[1] – SW 846 9012		Achievable Laboratory Limits[2]	
				MDLs	Method QLs	MDLs (mg/kg)	QLs (mg/kg)
Total Cyanide	57-12-5	NA	NA	MDL Study	Lab-Specific	0.12	0.6

[1] Analytical MDLs and QLs are those documented in validated methods.
[2] Achievable MDLs and QLs are limits that an individual laboratory can achieve when performing a specific analytical method.

The Achievable Laboratory Limits (MDLs and/or QLs) are laboratory-derived limits. The values are subject to change annually as part of laboratory evaluation/ performance updates.

QAPP Worksheet #15
Table 5 - PACE - Reference Limits and Evaluation

Matrix: Solid (Sediment Sampling)
Analytical Group: Total organic Carbon-Lloyd Kahn
Concentration Level: Low

Analyte	CAS Number	Project Screening Criteria/Action Limit	Project Quantitation Limit	Analytical Method[1] – TOC by Lloyd Kahn		Achievable Laboratory Limits[2]	
				MDLs	Method QLs	MDLs (mg/kg)	QLs (mg/kg)
Total Organic Carbon-Lloyd Kahn	7440-44-0	NA	NA	0.01%	0.01%	0.003%	0.01%

[1] Analytical MDLs and QLs are those documented in validated methods.
[2] Achievable MDLs and QLs are limits that an individual laboratory can achieve when performing a specific analytical method.

The Achievable Laboratory Limits (MDLs and/or QLs) are laboratory-derived limits. The values are subject to change annually as part of laboratory evaluation/ performance updates.

QAPP Worksheet #15
Table 5 - PACE - Reference Limits and Evaluation

Matrix: Solid (Sediment Sampling)
Analytical Group: Black Carbon
Concentration Level: Low

Analyte	CAS Number	Project Screening Criteria/Action Limit	Project Quantitation Limit	Analytical Method[1] – Accardi-Day and Gschwend, 2003		Achievable Laboratory Limits[2]	
				MDLs	Method QLs	MDLs (mg/kg)	QLs (mg/kg)
Black Carbon		NA	NA	NA	NA	NA	0.01%

[1] Analytical MDLs and QLs are those documented in validated methods.
[2] Achievable MDLs and QLs are limits that an individual laboratory can achieve when performing a specific analytical method.

The Achievable Laboratory Limits (MDLs and/or QLs) are laboratory-derived limits. The values are subject to change annually as part of laboratory evaluation/ performance updates.

QAPP Worksheet #15
Table 5 - PACE - Reference Limits and Evaluation

Matrix: Solid (Sediment Sampling)
Analytical Group: Ammonia
Concentration Level: Low

Analyte	CAS Number	Project Screening Criteria/Action Limit	Project Quantitation Limit	Analytical Method[1] – EPA 350.1		Achievable Laboratory Limits[2]	
				MDLs	Method QLs	MDLs (mg/kg)	QLs (mg/kg)
Ammonia		NA	NA	MDL Study	Lab-Specific	15	30

[1] Analytical MDLs and QLs are those documented in validated methods.
[2] Achievable MDLs and QLs are limits that an individual laboratory can achieve when performing a specific analytical method.

The Achievable Laboratory Limits (MDLs and/or QLs) are laboratory-derived limits. The values are subject to change annually as part of laboratory evaluation/ performance updates.

QAPP Worksheet #15
Table 5 - PACE - Reference Limits and Evaluation

Matrix: Solid (Sediment Sampling)
Analytical Group: Total Sulfide
Concentration Level: Low

Analyte	CAS Number	Project Screening Criteria/Action Limit	Project Quantitation Limit	Analytical Method[1] – SW 846 9030B		Achievable Laboratory Limits[2]	
				MDLs	Method QLs	MDLs (mg/kg)	QLs (mg/kg)
Total Sulfide		NA	NA	MDL Study	Lab-Specific	11.6	50

[1] Analytical MDLs and QLs are those documented in validated methods.
[2] Achievable MDLs and QLs are limits that an individual laboratory can achieve when performing a specific analytical method.

The Achievable Laboratory Limits (MDLs and/or QLs) are laboratory-derived limits. The values are subject to change annually as part of laboratory evaluation/ performance updates.

QAPP Worksheet #15
Table 5 - PACE - Reference Limits and Evaluation

Matrix: Solid (Sediment Sampling)
Analytical Group: Fraction of Organic Carbon
Concentration Level: Low

Analyte	CAS Number	Project Screening Criteria/Action Limit	Project Quantitation Limit	Analytical Method[1] – ASTM-2974		Achievable Laboratory Limits[2]	
				MDLs	Method QLs	MDLs (mg/kg)	QLs (mg/kg)
Fraction of Organic Carbon		NA	NA	MDL Study	Lab-Specific	.058	.058

[1] Analytical MDLs and QLs are those documented in validated methods.
[2] Achievable MDLs and QLs are limits that an individual laboratory can achieve when performing a specific analytical method.

The Achievable Laboratory Limits (MDLs and/or QLs) are laboratory-derived limits. The values are subject to change annually as part of laboratory evaluation/ performance updates.

QAPP Worksheet #15
PACE - Reference Limits and Evaluation Table

Reference limits are not applicable for the following parameters:

- Field Parameters
- Forensic Fingerprinting
- Toxicity Testing
- Grain Size
- Atterburg Limits
- Moisture Content

QAPP Worksheet #23
(UFP-QAPP Manual Section 3.2.1)
Analytical SOP References Table

QAPP Worksheet #23-1 STAT Analytical SOP References Table

Reference Number	Title, Revision Date, and / or Number[a]	Definitive or Screening Data	Analytical Group	Instrument	Organization Performing Analysis	Modified for Project Work? (Y/N)
STAT 4020	Gas Chromatography/Mass Spectrometry (GC/MS) Analysis Based on SW-846 8270C. Prepared by STAT.	Definitive	SVOC	Gas Chromatograph/ Mass Spectrometer (GC/MS)	STAT Analysis Corporation	N
STAT 4000	Gas Chromatography/Mass Spectrometry (GC/MS) Analysis Based on SW-846 8260B. Prepared by STAT.	Definitive	VOC	Gas Chromatograph/ Mass Spectrometer (GC/MS)	STAT Analysis Corporation	N
STAT 4010	Gas Chromatography/Mass Spectrometry (GC/MS) Analysis Based on EPA Method TO-14A/TO-15	Definitive	VOC	Gas Chromatograph/ Mass Spectrometer (GC/MS)	STAT Analysis Corporation	Y
STAT 4500	Gas Chromatography/Mass Spectrometry (GC/MS) Analysis Based on SW-846 8270C-SIM. Prepared by STAT.	Definitive	PAH	Gas Chromatograph/ Mass Spectrometer (GC/MS)	STAT Analysis Corporation	N
STAT 4510	Inductively Coupled Plasma/ Mass Spectrometry (ICP/MS) Analysis Based on SW-846 6020. Prepared by STAT.	Definitive	Metals	Inductively Coupled Plasma /Mass Spectrometry (ICP/MS)	STAT Analysis Corporation	N
STAT 4530	Cold Vapor Technique. Analysis Based on SW-846 7471A. Prepared by STAT	Definitive	Mercury	Cold Vapor Technique	STAT Analysis Corporation	N

Reference Number	Title, Revision Date, and / or Number[a]	Definitive or Screening Data	Analytical Group	Instrument	Organization Performing Analysis	Modified for Project Work? (Y/N)
STAT 4710	Automated Cyanide Analysis by EPA 415.1	Definitive	Cyanide	LaCHAT Auto Analyzer	STAT Analysis Corporation	N
STAT 4630	Method based on EPA 415.1	Definitive	Organic Carbon in water	TOC Analyzer	STAT Analysis Corporation	N
STAT 4480	Method based on Standard Methods 5310	Definitive	Organic Carbon in soil	TOC Analyzer	STAT Analysis Corporation	N
STAT 4060	Method based on 40 CFR 60, Appendix A2	Definitive	Carbon Dioxide, Methane, Nitrogen, and Oxygen	Gas Chromatograph with Thermal Conductivity Detector	STAT Analysis Corporation	N
TriMatrix GR-05-128	Available Cyanide by USEPA Method OIA-1677	Definitive	Available Cyanide	Flow Injecting Analysis System with Amperometric Detector	TriMatrix Laboratories, Inc.	N

QAPP Worksheet #23
(UFP-QAPP Manual Section 3.2.1)
Analytical SOP References Table

QAPP Worksheet #23-2 Pace Analyatical SOP References Table

Reference Number	Title, Revision Date, and/or Number	Definitive or Screening Data	Analytical Group	Instrument	Organization Performing Analysis	Modified for Project Work? (Y/N)
SW-846 8021	Petroleum Volatile Organic Compounds (PVOCs) by Gas Chromatography	Definitive	PVOCs	GC	Pace	N
SW-846 8260B	Petroleum Volatile Organic Compounds (PVOCs) by Gas Chromatography-Mass Spectrometry	Definitive	PVOCs	GC-MS	Pace	N
SW-846 6000/7000	Inductively Coupled Plasma-Mass Spectrometry (Method 6020)	Definitive	Metals	ICP/MS	Pace	N
	Mercury in Solid or Semisolid Waste (Manual Cold-Vapor Technique) (Method 7471B)	Definitive	Metals	Cold-Vapor Atomic Absorption (AA)	Pace	N
SW-846 9012A	Total Cyanide (Automated Colorimetric, with Off-Line Distillation)	Definitive	Cyanide	Automated Spectrophotometer	Pace	N
Alpha Analytical SOP W-028	"Determination of Total Organic Carbon in Sediment"; Lloyd Kahn; USEPA Region II, 7/27/88	Definitive	TOC	PE 2400 Series II CHNS/O Analyzer	Alpha Analytical –Woods Hole Lab	N
SW-846 8270C	Semivolatile Organic Compounds (SVOCs) by Gas Chromatography-Mass Spectrophotomerty	Definitive	PAHs and Phenols	GC/MS	Pace	N

Reference Number	Title, Revision Date, and/or Number	Definitive or Screening Data	Analytical Group	Instrument	Organization Performing Analysis	Modified for Project Work? (Y/N)
SW-846 8270 SIM	Polynuclear Aromatic Hydrocarbons (PAHs) by Gas Chromatography-Mass Spectrophotometry with Selected Ion Montoring	Definitive	PAHs	GC/MS with SIM	Pace	N
SW-846 8270 SIM	Alkylated Polynuclear Aromatic Hydrocarbons (PAHs) by Gas Chromatography-Mass Spectrophotometry with Selected Ion Montoring	Definitive	Alkylated PAHs	GC/MS with SIM	Pace	N
Alpha Analytical SOP W-028-Addendum	Black Carbon by EPA - SW-846, "Method 9060 Total Organic Carbon", 1996; and Addendum: "Reinterpreting Literature Sorption Data Considering Both Absorption into Organic Carbon and Adsorption onto Black Carbon" published in Environmental Science and Technology, Vol. 37, No. 1, 2003	Definitive	Black Carbon	PE 2400 Series II CHNS/O Analyzer	Alpha Analytical – Woods Hole Lab	N
EPA Method 350.1	Ammonia Nitrogen by Semi-Automated Colorimetry	Definitive	Ammonia	Automated Spectrophotometer	Pace	N
EPA 9030B/9034	Acid-Soluble and Acid-Insoluble Sulfides: Distillation/Titrimetric Procedure for Acid-Soluble and Acid-Insoluble Sulfides	Definitive	Total Sulfide	Titrimetric	Pace	N

QAPP Worksheet #24
(UFP-QAPP Manual Section 3.2.2)
Analytical Instrument Calibration Table

QAPP Worksheet #24-1 STAT Analytical Instrument Calibration Table

Instrument	Calibration Procedure	Frequency of Calibration	Acceptance Criteria	Corrective Action (CA)	Person Responsible for CA	SOP Reference
ICP-MS	See SOP 4510	See SOP 4510	See SOP 4510	See SOP 4510	STAT	STAT-4510
GC-MS	See SOP 4000, 4020, and 4500.	See SOP 4000, 4020, and 4500.	See SOP 4000, 4020, and 4500.	See SOP 4000, 4020, and 4500.	STAT	STAT- 4000, 4020, and 4500.
Tekmar Autocan	See SOP 4010	See SOP 4010	See SOP 4010	See SOP 4010	STAT	See SOP 4010
Cold Vapor	See SOP 4530	See SOP 4530	See SOP 4530	See SOP 4530	STAT	STAT-4530
LaCHAT Auto Analyzer	See SOP 4710	See SOP 4710	See SOP 4710	See SOP 4710	STAT	SOP 4710
TOC Analyzer	See SOP 4630	See SOP 4630	See SOP 4630	See SOP 4630	STAT	SOP 4630
Flow Injecting Analysis System with Amperometric Detector	See TriMatrix SOP GR-05-028	See TriMatrix SOP GR-05-028	See TriMatrix SOP GR-05-028	See TriMatrix SOP GR-05-028	TriMatrix	TriMatrix SOP GR-05-028

QAPP Worksheet #24
(UFP-QAPP Manual Section 3.2.2)
Analytical Instrument Calibration Table

QAPP Worksheet #24-2 Pace Analytical Instrument Calibration Table

Instrument	Calibration Procedure	Frequency of Calibration	Acceptance Criteria	Corrective Action (CA)	Person Responsible for CA	SOP Reference
GC (PVOC)	Standard mixture with at least five concentrations to demonstrate linearity of detector response	Initial calibration: upon award of the contract, whenever major instrument maintenance or modification is performed or if the calibration verification technical acceptance criteria have not been met. Calibration verification: Once every 12 hours or every ten samples which ever is more frequent.	Initial calibration %RSD must be less than or equal to 15.0 percent. Calibration verification: %D less than 15%.	Initial calibration: inspect the system (e.g., change the column, bake out the detector, clean the injection port), correct problem, re-calibrate. Calibration verification: inspect system, recalibrate the instrument, reanalyze samples.	CRO Analyst	SW-846 8021
GC/MS (PVOC)	Standard mixture with at least five concentrations to demonstrate linearity of detector response	Initial calibration: upon award of the contract, whenever major instrument maintenance or modification is performed or if the calibration verification technical acceptance criteria have not been met. Calibration verification: Once every 12 hours or every ten samples which ever is more frequent.	Initial calibration %RSD must be less than or equal to 15.0 percent. Calibration verification: %RSD less than 30%.	Initial calibration: inspect the system (e.g., cut or change column, clean the injection port), correct problem, re-calibrate. Calibration verification: inspect system, recalibrate the instrument, reanalyze samples.	CRO Analyst	SW-846 8260C

Instrument	Calibration Procedure	Frequency of Calibration	Acceptance Criteria	Corrective Action (CA)	Person Responsible for CA	SOP Reference
ICP/MS (Metals)	Standard mixture with at least four concentrations and a blank to demonstrate linearity of detector response	Initial calibration is done per analytical run.	-Correlation Coefficient of ≥0.998 -Initial and Continuing Calibration Verifications must recover +/-10% -Initail and Continuing Calibration Blanks must be <Reporting Limit. -Repoting limit checks must recover withing +/-30% -ICSA/AB must recover w/in +/-20%	Verify failure, correct any issues and perform Initial Calibration with Calibration QC.	Section Supervisor or Lab Technician	S-GB-M-006-REV.00 (SW846 6020)
Cold-Vapor Atomic Absorption (AA) (Mercury)	Standard mixture with at least five concentrations and a blank to demonstrate linearity of detector response	Initial calibration is done per sample preparation event.	-Correlation Coefficient of ≥0.995 -Initial and Continuing Calibration Verifications must recover +/-10% -Initail and Continuing Calibration Blanks must be <Reporting Limit. -Repoting limit checks must recover withing +/-30%	Verify failure, correct any issues and perform Initial Calibration with Calibration QC.	Section Supervisor or Lab Technician	S-GB-M-004-REV.00 (SW846 7470/7471)
GC/MS and GC/MS with SIM (PAHs and Phenols)	Standard mixture with a minimum of five calibration points demonstrating instrument linearity and detector response	Initial calibration: before samples are analyzed or whenever major instrument maintenance is performed. If the calibration verification technical acceptance criteria is not been met after maintenance, a new initial calibration must also be analyzed. Calibration verification: Once every 12 hours	Initial Calibration: All compounds ≤ 20%, RF ≥ 0.050 Continuing Calibration: RF ≥ 0.050; and CCCs ≤ 20%	Initial calibration: inspect the system (e.g., cut or change column, clean the injection port), correct problem, re-calibrate. Calibration verification: inspect system, recalibrate the instrument, reanalyze samples.	Section Supervisor or Lab Technician	SW-846 8270C SW-846 8270 SIM

Instrument	Calibration Procedure	Frequency of Calibration	Acceptance Criteria	Corrective Action (CA)	Person Responsible for CA	SOP Reference
GC/MS with SIM (Alkylated PAH)	Standard mixture with at least five concentrations to demonstrate linearity of detector response	Initial calibration: whenever major instrument maintenance or modification is performed or if the calibration verification technical acceptance criteria have not been met. Calibration verification: Once every 12 hours	Initial calibration/ Calibration verification: %RSD calibration factor less than 15%, or if a linear regression is used the correlation coefficient must be less than 0.995 or a quadratic regression may be used with 6 calibration points and the COD must be greater than 0.990	Initial calibration: inspect the system (e.g., change the column, bake out the detector, clean the injection port), correct problem, re-calibrate. Calibration verification: inspect system, recalibrate the instrument, reanalyze samples.	Semi-Volatiles Supervisor Analyst responsible for running the system	S-MN-O-561-Rev.00
Automated Spectrophotometer-(Total Cyanide)	Standard mixture with at least five concentrations and a blank to demonstrate linearity of detector response	Initial calibration is done per analytical run.	-Correlation Coefficient of $\geq$0.995 -Initial and Continuing Calibration Verifications must recover +/-10% -Initail and Continuing Calibration Blanks must be <Reporting Limit. -Repoting limit checks must recover withing +/-30%	Verify failure, correct any issues and perform Initial Calibration with Calibration QC.	Section Supervisor or Lab Technician	S-GB-I-043-REV.01 (ASTM 2974/EPA 335.4)
Automated Spectrophotometer (Ammonia)	Standard mixture with at least five concentrations and a blank to demonstrate linearity of detector response	Initial calibration is done per analytical run.	-Correlation Coefficient of $\geq$0.995 -Initial and Continuing Calibration Verifications must recover +/-10% -Initail and Continuing Calibration Blanks must be <Reporting Limit. -Repoting limit checks must recover withing +/-30%	Verify failure, correct any issues and perform Initial Calibration with Calibration QC.	Section Supervisor or Lab Technician	S-GB-I-048-REV.01 (EPA 350.1)
PE 2400 Series II CHNS/O Analyzer (Black Carbon-TOC-Lloyd Kahn)	See Section 12.1 of lab SOP	Daily, prior to use.	See Section 12.1.2 of lab SOP	See Section 12.1.3 of lab SOP	Wet Chem Analyst	Alpha Analytical W-028

Instrument	Calibration Procedure	Frequency of Calibration	Acceptance Criteria	Corrective Action (CA)	Person Responsible for CA	SOP Reference
Titrimetric (Total Sulfide)	Iodine solution standardized with sodium thiosulfate solution.	Each day of analysis	N/A	N/A	N/A	SW-846 9030B/9034

QAPP Worksheet #25
(UFP-QAPP Manual Section 3.2.3)
Analytical Instrument and Equipment Maintenance, Testing, and Inspection Table

QAPP Worksheet #25-1 STAT Analytical Instrument and Equipment Maintenance, Testing, and Inspection Table

Instrument / Equipment	Maintenance Activity	Testing Activity	Inspection Activity	Frequency	Acceptance Criteria	Corrective Action	Responsible Person	SOP Reference
ICP-MS	See SOP 4510	See SOP 4510	See SOP 4510	See SOP 4510	See SOP 4510	See SOP 4510	See lab's QAM	See SOP 4510
GC-MS	See SOP 4000, 4020, and 4500.	See SOP 4000, 4020, and 4500.	See SOP 4000, 4020, and 4500.	See SOP 4000, 4020, and 4500.	See SOP 4000, 4020, and 4500.	See SOP 4000, 4020, and 4500.	See lab's QAM	See SOP 4000, 4020, and 4500.
Tekmar Autocan	See SOP 4010	See SOP 4010	See SOP 4010	See SOP 4010	See SOP 4010	See SOP 4010	See lab's QAM	See SOP 4010
Cold Vapor	See SOP 4530	See SOP 4530	See SOP 4530	See SOP 4530	See SOP 4530	See SOP 4530	See lab's QAM	See SOP 4530
LaCHAT Auto Analyzer	See SOP 4710	See SOP 4710	See SOP 4710	See SOP 4710	See SOP 4710	See SOP 4710	See lab's QAM	See SOP 4710
TOC Analyzer	See SOP 4630	See SOP 4630	See SOP 4630	See SOP 4630	See SOP 4630	See SOP 4630	See lab's QAM	See SOP 4630
Flow Injecting Analysis System with Amperometric Detector	See TriMatrix SOP GR-05-028	See TriMatrix SOP GR-05-028	See TriMatrix SOP GR-05-028	See TriMatrix SOP GR-05-028	See TriMatrix SOP GR-05-028	See TriMatrix SOP GR-05-028	See TriMatrix SOP GR-05-028	See TriMatrix SOP GR-05-028

Analytical Supply Inspection and Acceptance Procedures

The laboratories are responsible for maintaining procedures for inspection and acceptance of supplies, standards, and materials into their facility.

QAPP Worksheet #25
(UFP-QAPP Manual Section 3.2.3)
Analytical Instrument and Equipment Maintenance, Testing, and Inspection Table

QAPP Worksheet #25-2 Pace Analytical Instrument and Equipment Maintenance, Testing, and Inspection Table

Instrument/ Equipment	Maintenance Activity	Testing/Inspection Activity	Frequency	Acceptance Criteria	Corrective Action	Responsible Person	SOP Reference[1]
ICP/MS (Metals)	As per the laboratory's QA Manual and/or instrument manufacturer's recommendations and procedures	As per instrument manufacturer's recommendations and procedures; visual inspection; re-calibration	As per instrument manufacturer's recommendations; anytime anomaly suspected	Acceptable calibration (see Worksheet #24)	Inspect the system, correct problem, re-calibrate, and/or re-analyze samples	Inorganics Supervisor Laboratory Metals Technician	SW-846 6020A
Cold-Vapor AA (Mercury)	As per the laboratory's QA Manual and/or instrument manufacturer's recommendations and procedures	As per instrument manufacturer's recommendations and procedures; visual inspection; re-calibration	As per instrument manufacturer's recommendations; anytime anomaly suspected	Acceptable calibration (see Worksheet #24)	Inspect the system, correct problem, re-calibrate, and/or re-analyze samples	Inorganics Supervisor Laboratory Metals Technician	SW-846 7471B
GC (PVOC)	As per the laboratory's QA Manual and/or instrument manufacturer's recommendations and procedures	As per instrument manufacturer's recommendations and procedures; visual inspection; re-calibration	As per instrument manufacturer's recommendations; anytime anomaly suspected	Acceptable calibration (see Worksheet #24)	Inspect the system, correct problem, re-calibrate, and/or re-analyze samples	Volatiles Supervisor Analyst responsible for running the system	SW-846 8021
GC/MS (PVOC)	As per the laboratory's QA Manual, instrument manufacturer's recommendations and procedures	As per instrument manufacturer's recommendations and procedures; visual inspection; re-calibration	As per instrument manufacturer's recommendations; anytime anomaly suspected	Acceptable calibration (see Worksheet #24)	Inspect the system, correct problem, re-calibrate, and/or re-analyze samples	Volatiles Supervisor Analyst responsible for running the system	SW-846 8260B

Instrument/ Equipment	Maintenance Activity	Testing/Inspection Activity	Frequency	Acceptance Criteria	Corrective Action	Responsible Person	SOP Reference[1]
GC/MS and GC/MS with SIM (PAHs and phenols)	As per the laboratory's QA Manual and/or instrument manufacturer's recommendations and procedures	As per instrument manufacturer's recommendations and procedures; visual inspection; re-calibration	As per instrument manufacturer's recommendations; anytime anomaly suspected	Acceptable calibration (see Worksheet #24)	Inspect the system, correct problem, re-calibrate, and/or re-analyze samples	Semi-Volatiles Supervisor Analyst responsible for running the system	SW-846 8270C SW-846 8270 SIM
GC/MS with SIM (Alkylated PAHs)	As per the laboratory's QA Manual, instrument manufacturer's recommendations and procedures, and/or any applicable laboratory SOPs	As per the laboratory's QA Manual, instrument manufacturer's recommendations and procedures, and/or any applicable laboratory SOPs; visual inspection; re-calibration	As per instrument manufacturer's recommendations; anytime anomaly suspected	Acceptable calibration (see Worksheet #24)	Inspect the system, correct problem, re-calibrate, and/or re-analyze samples	Semi-Volatiles Supervisor Analyst responsible for running the system	S-MN-O-561-Rev.00
Automated Spectrophotometer (Total Cyanide)	As per the laboratory's QA Manual and/or instrument manufacturer's recommendations and procedures	As per instrument manufacturer's recommendations and procedures; visual inspection; re-calibration	As per instrument manufacturer's recommendations; anytime anomaly suspected	Acceptable calibration (see Worksheet #24)	Inspect the system, correct problem, re-calibrate, and/or re-analyze samples	Inorganics Supervisor Laboratory Metals Technician	SW-846 9012A
Automated Spectrophotometer (Ammonia)	As per the laboratory's QA Manual and/or instrument manufacturer's recommendations and procedures	As per instrument manufacturer's recommendations and procedures; visual inspection; re-calibration	As per instrument manufacturer's recommendations; anytime anomaly suspected	Acceptable calibration (see Worksheet #24)	Inspect the system, correct problem, re-calibrate, and/or re-analyze samples	Semi-Volatiles Supervisor Analyst responsible for running the system	EPA Method 350.1

Instrument/ Equipment	Maintenance Activity	Testing/Inspection Activity	Frequency	Acceptance Criteria	Corrective Action	Responsible Person	SOP Reference[1]
Titrimetric (Total Sulfide)	As per the laboratory's QA Manual and/or instrument manufacturer's recommendations and procedures	As per instrument manufacturer's recommendations and procedures; visual inspection; re-calibration	As per instrument manufacturer's recommendations; anytime anomaly suspected	Acceptable calibration (see Worksheet #24)	Inspect the system, correct problem, re-calibrate, and/or re-analyze samples	Subcontract Laboratory Metals Technician	SW-846 9030B/9034
PE 2400 Series II CHNS/O Analyzer (Black Carbon-TOC-Lloyd Kahn)	As per instrument manufacturer's user manual and lab QSM.	As per instrument manufacturer's user manual; calibration and/or re-calibration	Daily, prior to use	See Section 12.1.2 or Section 13.2.2 of lab SOP	See Section 12.1.3 of lab SOP	Wet Chem Analyst	Alpha Analytical W-028

[1] Specify the appropriate reference letter or number from the Analytical SOP References table (Worksheet #23).

QAPP Worksheet #26
(UFP-QAPP Manual Appendix A)
Sample Handling System

This worksheet identifies components of the project-specific sample handling system. Personnel who are primarily responsible for ensuring proper handling, custody, and storage of field samples from the time of collection, to laboratory delivery, to final sample disposal are presented on this worksheet. In addition, the number of days that field samples and their extracts/digestates will be archived prior to disposal is provided.

SAMPLE COLLECTION, PACKAGING, AND SHIPMENT
Sample Collection (Personnel/Organization): Field Sampling Team, BMcD
Sample Packaging (Personnel/Organization): Field Sampling Team, BMcD
Coordination of Shipment (Personnel/Organization): FSM, BMcD
Type of Shipment/Carrier: Overnight/FedEx, laboratory courier, or hand deliver
SAMPLE RECEIPT AND ANALYSIS
Sample Receipt (Personnel/Organization): Sample Custodian, STAT Analysis and Pace–Green Bay
Sample Custody and Storage (Personnel/Organization): Sample Custodian, STAT Analysis and Pace–Green Bay
Sample Preparation (Personnel/Organization): Team Leader (VOC/SVOC, Wet Chemistry, Metals), STAT Analysis and Pace–Green Bay
Sample Determinative Analysis (Personnel/Organization): Team Leader (VOC/SVOC, Wet Chemistry, Metals), STAT Analysis and Pace–Green Bay
SAMPLE ARCHIVING
Field Sample Storage (number of days from sample collection): Samples will typically be shipped within 24 hours of collection, particularly if samples have short holding times. Samples held after collection for batching purposes at the laboratory will be kept within the sample preservation range of 2-6 ^{o}C, where applicable.
Sample Extract/Digestate Storage (number of days from extraction/digestion): Sample extraction and digestion must be conducted according to the analytical methods and the requirements given in Table 1 of the SSWP, where applicable.
Biological Sample Storage (number of days from sample collection): Not Applicable
SAMPLE DISPOSAL
Personnel/Organization: Sample Custodian, STAT Analysis and Pace–Green Bay
Number of Days from Analysis: Soil and sediment: 6 months following receipt of final data package; surface water and groundwater 90 days following receipt of final data package.

QAPP Worksheet #30
(UFP-QAPP Manual Section 3.5.2.3)
Analytical Services Table

Matrix	Analytical Group	Concentration Level	Sample Locations/ ID Number	Analytical SOP	Data Package Turnaround Time	Laboratory / Organization (name and address, contact person and telephone number)	QA Split Sample Laboratory / Organization (name and address, contact person and telephone number)
Soil	VOCs	Low/Medium	See SSWP and Multi-Site QAPP, SOP SAS 03-01	4000	TBD (14 to 21 days)	STAT Analysis Corporation 2242 West Harrison Street, Suite 200 Chicago, Illinois 60612 Phone: (312) 733-0551 Contact: Pinaki Banerjee	Not Applicable
	SVOCs			4020 (8270C) or 4500 (8270 SIM)			
	Cyanide			4710			
	Metals			4510			
	Mercury			4530			
Water	PVOCs	Low/Medium	See SSWP and Multi-Site QAPP, SOP SAS 03-01	4000	TBD (14 to 21 days)	STAT Analysis Corporation 2242 West Harrison Street, Suite 200 Chicago, Illinois 60612 Phone: (312) 733-0551 Contact: Pinaki Banerjee	Not Applicable
	PAHs and Phenols			4020 (8270C) or 4500 (8270 SIM)			
	Total Cyanide			4710			
	Available Cyanide			TriMatrix GR-05-028			
	Metals			4510			
	Mercury			4530			
	Hardness			4510			

Matrix	Analytical Group	Concentration Level	Sample Locations/ ID Number	Analytical SOP	Data Package Turnaround Time	Laboratory / Organization (name and address, contact person and telephone number)	QA Split Sample Laboratory / Organization (name and address, contact person and telephone number)
Soil Gas	VOCs + Naphthalene	Low/Medium	See SSWP and Multi-Site QAPP, SOP SAS 03-01	4010	TBD (14 to 21 days)	STAT Analysis Corporation 2242 West Harrison Street, Suite 200 Chicago, Illinois 60612 Phone: (312) 733-0551 Contact: Pinaki Banerjee	Not Applicable
	Oxygen			4060			
	Carbon Dioxide			4060			
	Methane			4060			
Sediment	PVOCs	Low/Medium	See SSWP and Multi-Site QAPP, SOP SAS 03-01	S-GB-ALL-O-002-Rev.01	TBD (14 to 21 days)	Pace Analytical Services 1241 Bellevue Street, Suite 9 Green Bay, Wisconsin 54302 (920) 469-2436 Contact: Brian Basten	Not Applicable
	PAHs and Phenols			S-ALL-GB-O-001-Rev.00			
	Cyanide			S-GB-I-043-Rev.01			
	Metals			S-GB-M-006-Rev.00			
	Percent Solids			See Multi-Site QAPP			
	TOC			See Multi-Site QAPP			
	Black Carbon			See Multi-Site QAPP			
	Ammonia			See Multi-Site QAPP			
	Total Sulfide			See Multi-Site QAPP			

Attachment 1

STAT Analysis Corporation
Quality Assurance Manual and Standard Operating Procedures

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105	118	3005	SW845 3005A Acid Digestion of Waters for Total Recoverable or Dissolved Metals for Analysis by FLAA, ICP or ICP-MS
119	130	3110	SW846 3050B Acid Digestion of Sediments, Sludges, and Soils for Metals Analysis by FLAA, ICP, or ICP-MS
131	170	3500	Extractions of Samples for Organic Analyses (EPA Methods 3510C, 3520C, 3545, 3550B, 3580A, 8151A)
171	187	3610	Total and Amenable Cyanide: Distillation by EPA 9012A
188	227	4000	Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS) (EPA Methods 5030B/5035/8260B)
228	256	4010	Volatile Organic Compounds in Ambient Air by /Gas Chromatography/Mass Spectrometry (GC/MS) (EPA Method TO-14A/TO-15)
257	295	4020	Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS) (EPA Method 8270C)
296	312	4060	Determination of Carbon Dioxide, Methane, Nitrogen, and Oxygen in Air by GC with Thermal Conductivity Detection
313	324	4430	Alkalinity Analysis
325	337	4480	Gravimetric Determinations for Moisture, Solids, Ash, and Fraction Organic Carbon (FOC) (EPA Method 160.4, SW 3550B, & ASTM D2216, D2974)
338	378	4500	Polynuclear Aromatic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS) with Selective Ion Monitoring (SIM) (EPA Method 8270C SIM)
379	414	4510	Metals Analysis by Inductively Coupled Plasma – Mass Spectrometry 9EPA Method 6020 and EPA Method IO-3.5)
415	439	4530	Mercury in Water, Solid or Semisolid Water (Manual Digestion/Automated Analysis Cold-Vapor Technique) (EPA Methods 7470A & 7471A)
440	456	4630	Total Organic Carbon by EPA 415.1
457	484	4710	Automated Cyanide Analysis by EPA 9012A

Note: Extraction SOPs included to provide comprehensive overview of laboratory procedures.

Quality Assurance Manual

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QA 001

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Policy Statement

STAT Analysis Corporation

This Quality Manual summarizes the policies and operational procedures associated with STAT Analysis Corporation in Chicago, Illinois. Specific protocols for sample handling and storage, chain-of-custody, and laboratory analysis, data reduction, corrective action, and reporting are described. All policies and procedures have been structured in accordance with the National Environmental Laboratory Accreditation Conference (NELAC) standards adopted in June 2003 (current as of the date of this publication), American Industrial Hygiene Association (AIHA), National Voluntary Laboratory Accreditation Program (NVLAP) standards adopted in National Institute of Standards and Technology (NIST) Handbook 150, 2006 Edition and International Standards Organization/International Electrotechnical Commission (ISO/IEC) 17025 (2005) regulations, guidance, and technical standards. The laboratory management is committed to comply with these standards. NVLAP has issued specific requirements for referencing the NVLAP term, logo, and symbol (NIST Handbook 150, 2006). STAT uses the NVLAP term and symbol for purposes of announcing the accredited status and for use on reports that describe testing within the scope of accreditation. STAT complies with the conditions detailed in NIST Handbook 150, Annex A.

This manual has been prepared in accordance with the guidance documents listed in Appendix 3. Further details on these policies and procedures are contained in SOPs and related documents. This Quality Manual, SOPs, and related documentation describe the laboratory's management system policies related to quality. The purpose of this Quality Assurance Manual is to describe the quality management system in place at STAT Analysis Corporation.

STAT Analysis Corporation performs chemical analyses for inorganic and organic constituents, microbiological analyses, and asbestos analyses in various matrices. The objective of STAT Analysis Corporation's quality management system is to produce data that is scientifically valid and of known and documented quality in accordance with standards developed by NELAC, ISO/IEC 17025, AIHA, NIST/NVLAP and any applicable federal or state government entity's regulations or requirements. STAT Analysis Corporation conducts all business with integrity and in an ethical manner. The laboratory management is committed to good professional practice, to the quality of its environmental testing in servicing its customers, and to continually improve the effectiveness of the management system. All personnel involved with environmental testing activities within the laboratory must review this quality manual. It is the responsibility of each staff member, manager, director, and owner to perform their duties with the highest ethical standards and professional conduct to ensure compliance with this Quality Manual and related documentation.

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1. INTRODUCTION

It is the policy of STAT Analysis Corporation (STAT) to produce analytical results of the highest degree of repeatability, precision, and accuracy in a laboratory that employs state of the art analytical instrumentation operated by highly skilled, qualified, motivated, and responsible analysts. The laboratory management is committed to follow NELAC, AIHA, NIST/NVLAP, and ISO/IEC 17025 requirements. This Quality Manual is based on NELAC, ISO 17025, NIST/NVLAP and AIHA standards. All employees are to be trained and committed to following the requirements herein.

The primary purpose of this document is to establish and maintain uniform operational and quality control guidelines for operations that affect the quality of the data produced in this laboratory. The establishment of, and adherence to, uniform elements of an intra-laboratory quality control program are essential to the production of reliable analytical data. The QA/QC requirements for all relevant preparation and analytical methods, and any verified modifications of such, used in this laboratory are described in this manual or described in relevant Standard Operating Procedures (SOPs).

While the implementation of a quality assurance policy is a management function, each individual has a responsibility for the operational aspects of quality control. It is the individual responsibility of each analyst and his/her supervisor to monitor quality control indicators and to provide for corrective actions when necessary. Appropriate communication processes, such as training, seminars, and one-on-one instructions are used to train personnel regarding the effectiveness of the management system. Personnel are trained regarding relevance and importance of their activities and how they contribute to the achievement of the objectives of the management system. Personnel are trained on the importance of meeting customer requirements as well as statutory and regulatory requirements. Laboratory management ensures that the integrity of the management system is maintained when changes are planned and implemented.

This manual and the quality control protocols described herein are not to be viewed as all-inclusive. Rather, they serve as a basic foundation on which to build stronger quality assurance/quality control program. It is the policy of this laboratory to use the most stringent controls whether dictated by methodologies and SOPs, accrediting bodies, or Quality Assurance Project Plans (QAPP).

This revision (Rev.08) of the QAM was developed by modifying Rev.07 of the QAM. Summary of the changes made is presented in Appendix 1. An electronic file containing new text in italics and deleted text identified as strike-outs is archived on the network.

2. LABORATORY ORGANIZATION and MANAGEMENT STRUCTURE

Hi-Tek Environmental Inc., d/b/a, STAT Analysis Corporation (STAT), FEIN 36-4128978, was incorporated in December 1996. The laboratory is located at 2242 W. Harrison Street, Chicago, IL 60612. An electronic keypunch provides limited access to this building.

It is company policy that all employees must be free from commercial, financial and other pressures that might adversely interfere with the quality of their work. All employees must be aware that customer relations and service are an integral part of their job description. To prevent the possibility of staff being placed under pressure by customers or other sections of the laboratory, reporting relationships have been established to isolate staff from this pressure. The responsibilities of the employee in dealing with the customer will be specified in order to maintain independence of judgment and integrity.

The Organizational Chart for STAT is shown in Appendix 2.

2.1 Staff Qualifications and Responsibilities

This section will show that STAT have personnel, who, irrespective of other responsibilities, have the authority and the resources to fulfill their responsibilities, including the development, implementation, maintenance, and continuous improvement of the management system. They also have the resources to identify departures from the management system or other SOPs and to initiate corrective actions to minimize or prevent such departures.

2.1.1 President/CEO ensures that those who hold the positions of Laboratory Director, Technical Manager, and Quality Assurance Manager, meet the requirements of NELAC, ISO 17025, NIST/NVLAP, and AIHA.

2.1.2 Laboratory Director

Duties
The Laboratory Director has the overall responsibility for analytical and operational activities of the laboratory. The director will be responsible for supervision (and appointment of supervisors) of laboratory personnel and ensuring that sufficient numbers of qualified staff are employed to supervise and perform the work of the laboratory. The Director will be responsible for production and quality of data reported by the laboratory.

Qualifications
The Laboratory Director should have a minimum of 2 years experience managing a laboratory. He or she shall have earned a bachelor's degree, or higher, in chemistry.

2.1.3 Technical Manager

Duties
The Technical Manager, under the general direction of the laboratory director, is responsible for the appropriateness of the technical background of all tests performed by the laboratory. The Technical Manager has the responsibility to monitor performance standards in quality assurance and quality control and monitoring the validity of the analyses performed and the data generated in the

laboratory to assure quality data. This individual is part of the whole corrective action process and is responsible for the final approval of any corrective actions performed at the laboratory. He/she shall be available during at least 50 percent of the laboratory operating hours to address technical issues for laboratory staff and customers and acceptable onsite supervision must be demonstrated. The Technical Manager maintains the LIMS. The Technical Manager provides proper educational direction to laboratory staff. The Technical Manager's responsibilities meet those defined for the Technical Manager in NELAC Chapter 4.1.1.1, NIST Handbook 150 Section 4.1, and AIHA Laboratory Quality Assurance Program(LQAP) Section 2A.6.1.

The Technical Manager ensures that all laboratory personnel possess the necessary educational and technical background appropriate to the job they perform. By signing the Demonstration of Capability statement, the Technical Manager certifies that the laboratory analyst has met the requirements to perform the specific test method analysis.

In the event that the Technical Manager is absent for more than fifteen consecutive calendar days, the Technical Manager will appoint the Laboratory Director as a temporary replacement. In the event that the Technical Manager is absent for more that sixty-five consecutive calendar days, the acting Technical Manager or the Quality Assurance Manager will notify the Illinois Accrediting Authority in writing.

Qualifications
The Technical Manager should have a minimum of 4 years experience in an environmental laboratory. He or she shall have earned a bachelor's degree, or higher, in chemistry with a minimum of 24 college semester credit hours in chemistry.

2.1.4 EMPAT Technical Manager

Duties
The EMPAT Technical Manager, under the general direction of the laboratory director, is responsible for the appropriateness of the technical background of all tests performed by the microbiological laboratory. The EMPAT Technical Manager has the responsibility to monitor performance standards in quality assurance and quality control and monitoring the validity of the analyses performed and the data generated in the laboratory to assure quality data. The EMPAT Technical Manager is located on site and has the responsibility for the function and administration of the day-to-day operation of the microbiological laboratory. The EMPAT Technical Manager provides proper educational direction to microbiological laboratory staff. The EMPAT Technical Manager, or designee, functions as the approved signatory.

Qualifications
The EMPAT Technical Manager should have a minimum of 2 years experience in a microbiological environmental laboratory. He or she shall have earned a bachelor's degree, or higher, in microbiology, biology, or related life science, with a minimum of 20 college semester credit hours in microbiology.

2.1.5 Quality Assurance Manager/ Quality Assurance Coordinator

Duties
The Quality Assurance Manager (or Director) has the responsibility for the maintenance and coordination of the quality assurance and quality control (QA/QC) program for the laboratory. The QA Manager is responsible for the data review procedures for the laboratory. The QA Manager should have a general knowledge of the analytical test methods for which data reviews are performed. The QA Manager reviews and approves all analytical SOPs for test methods. The QA Manager is independent of the analyst. The QA Manager is responsible for conducting or arranging an annual internal audit of the entire laboratory operation and technical systems. The Quality Assurance Manager is responsible for the day-to-day monitoring of the laboratory quality systems.

The QA Manager reports directly to the President/CEO.

In the event that the QA Manager is absent for more than fifteen consecutive calendar days, the President/CEO will appoint either the Technical Manager or the Laboratory Director as a temporary replacement.

Qualifications
The Quality Assurance Manager must have a minimum of a bachelor's degree in natural or physical sciences and have documented training in QA/QC and statistical procedures. He/she also must have a general knowledge of the analytical test methods.

2.1.6 EMPAT Quality Assurance Manager

Duties

The EMPAT Laboratory Quality Assurance Manager has the responsibility for the maintenance and coordination of the quality assurance and quality control (QA/QC) program for the microbiological laboratory. The EMPAT Laboratory QA Manager is responsible for the data review procedures for the laboratory and re-analyzing five percent of all samples. The EMPAT Laboratory QA Manager will also provide genus/species identification when needed. The EMPAT Laboratory QA Manager is responsible for conducting an annual internal audit of the microbiological laboratory operation.

Qualifications
The EMPAT Laboratory QA Manager must have a minimum of a bachelor's degree in microbiology, biology, or related life science. The EMPAT Laboratory QA Manager must have a minimum of six months of relevant microbiological laboratory experience and familiarity with microbiological QA/QC.

2.1.7 Department and Project Managers

Duties
Department Managers are responsible for supervising analysts, analysts in training, and technicians. They are responsible for reviewing and verifying data produced by analysts in training and technicians. Project Managers are responsible for primary customer contact. They review and approve customer's reports for completeness and adherence to all project specific criteria.

Qualifications
Department Managers must have a minimum of a bachelor's degree in natural or physical sciences, enough course work to qualify for a minor in chemistry, and have at least one year of experience in the analyses pertaining to the applicable fields of testing.

Project Managers must have a minimum of a bachelor's degree in natural or physical sciences and have at least one year of experience in the analyses of environmental samples.

2.1.8 Analysts

Duties
The analyst is responsible, under the direction of the Department Manager, for the applicable analyses of the samples submitted to the laboratory. Analysts shall be responsible for complying with all quality assurance and quality control requirements pertaining to their technical functions.

Qualifications
The analyst shall have a bachelor's degree (or equivalent), or an associates degree with one year experience, or greater than two years experience with experience in

natural or physical sciences. Analysts will have one year of full-time employment in the environmental testing field, and have documented proof of technical proficiency via in-house training at STAT, including an Initial Demonstration of Capability (IDOC). Analysts shall have demonstrated ability to produce reliable results through accurate analysis of certified reference materials (CRMs), proficiency testing samples, or in-house quality control samples. Their performance must be documented. Instrumentation Analysts must have four hours of equipment manufacturer training or two-week apprenticeship under an experienced analyst.

2.1.9 Analyst in Training

Analyst in training must meet the requirements of Technician while in process of meeting the requirements of Analyst.

2.1.10 Technician

Duties
The technician is responsible for carrying out the designated activities related to the analysis of materials submitted to the laboratory and works under the direct supervision of the Department Manager or Analyst.

Qualifications
The Technician shall have a minimum of a high school diploma or equivalent. Technicians will have documented proof of technical proficiency via in-house training at STAT, including an IDOC. Instrumentation Technicians must have four hours of equipment manufacturer training or two-week apprenticeship under an experienced analyst.

2.2 Approved Signatories

All analysts that have passed training for a particular analysis can sign off on data either as analyst or secondary review (as appropriate). All customer correspondence is to be signed either by the Laboratory Director, Technical Manager, Department Managers, or Project Managers as appropriate. For asbestos and microbiology, analysts sign reports. Quotes can be generated and signed by the President/CEO, Laboratory Director or Project Manager (unless specific approval is given to another employee by the named individuals). All bid proposals are to be signed by the President/CEO, Laboratory Director, Project Managers or designee.

2.3 New Work Requirements

All new analyses must undergo a thorough review prior to release. The Laboratory Director, Technical Manager, Quality Assurance Manager, and Department Manager may undertake this review. This review may include:

- Staff and appropriate equipment are available as well as appropriate workspace to perform the task.
- Standard Operating Procedure must be in place.
- Initial Demonstration of Capability (IDOC) must be performed.
- Method Detection Limit Study (if applicable) must be performed.
- A Blind Quality Control Sample must be satisfactorily completed, if available.

The procedure to review new work and new test method analyses is outlined in SOP 220 Customer Service.

2.4 Departures from Policies and Procedures

All laboratory personnel are instructed to follow the policies and procedures as outlined in the Quality Assurance Manual and supporting laboratory documentation. On occasion, departures from these policies and procedures may be taken. Any such departures must be fully defined, documented, and approved by the Technical Manager or the President/CEO. If the departure is considered a permanent change, a new revision of the laboratory's quality documentation may be necessary.

Any modifications to reference test methods are listed in Section 5 of the test method SOPs. These modifications are approved by management as indicated by the signatures on the SOP cover page.

Minor modifications to test methods for particular samples are allowed if these modifications are fully documented. An example follows:

The test method SOP states that a 30-gram soil sample is extracted and analyzed for Semi-Volatile Organic compounds. The submitted sample weighs only 10 grams. The analyst notes in the logbook that the minimum amount of sample was not available for analysis. The customer agrees that the sample can be analyzed as submitted. The final reporting limit for this sample will be elevated due to limited sample size.

3. DOCUMENT CONTROL

All documents are logged into STAT Document Master List (attached as Appendix 3). Documents are assigned a unique document number, revision and effective date noted. Controlled documents (SOPs) are also listed with all individuals who have been issued these documents (including external customers). This document, QA 001 Quality Assurance Manual Revision 08, is a controlled document. The Document Master List includes software (e.g. excel spreadsheets and reporting templates, instrument operating software) and external source documents.

The procedure to maintain and control laboratory documents is outlined in SOP 005 Document Control.

4. GENERAL LABORATORY PRACTICES

A Document Control System is described in SOP 005. All aspects of laboratory operations are documented in Standard Operating Procedures (SOPs). Each page of these SOPs will contain 1) SOP Number, 2) Revision Number, 3) Effective Date, and 4) current page number of the total number of pages in the document. This is described in SOP 100, SOP on SOPs.

4.1 Introduction

Intrinsic to the production of quality analytical data is the quality of laboratory services available to the analyst. Without adequate quality control being exercised with regard to facilities, services, laboratory environment, instrumentation, and laboratory supplies, an analyst cannot be expected to produce reliable analytical data.

Access to the laboratory is restricted to STAT employees only, unless accompanied by a STAT employee. Recognizing the necessity of maintaining control over general laboratory operation, the subsequent sections outline provisions for maintaining the quality laboratory support services.

4.2 Laboratory Apparatus and Instruments

All support equipment is maintained in proper working order. All water baths, refrigerators, freezers, ovens, balances, pH meters, thermometers, mechanical pipettes, and the conductivity meter must be verified in accordance with SOP 1040 General Laboratory Practices (GLP) and/or the analytical SOP. Where possible, calibration and reference standards, traceable to national standards of measurement, are used in the laboratory to calibrate and/or verify the test equipment. These calibration and reference standards are only used for calibration and/or verification purposes. The laboratory uses an independent calibration service to perform an annual check of the balances and the calibration weights used to check the laboratory balances and an annual check of the mechanical pipettes. In addition, an independent calibration service is used to perform a calibration check of the NIST reference thermometer at least every three years.

Certificates for the calibration and reference standards, the thermometer calibration records, the annual calibration and service records for the balances, the annual calibration and service records for the mechanical pipettes, and the results of the independent calibration checks are kept in the QA Manager's files.

Correction factors are only used on laboratory thermometers; balances and mechanical pipettes must be within established acceptance tolerances listed in the SOP or the equipment is removed from service until repaired. Balances are marked with the calibration sticker received from the independent calibration service to indicate its calibration status. Thermometers are marked with the initials of the employee performing the annual calibration, date of calibration, and correction factor.

All quality control checks listed in this section must be recorded in the appropriate logbook. The acceptability of use is based upon the acceptance criteria listed in the SOP. Any equipment found to be defective or in need of maintenance is taken out of service. The procedure listed in Section 7.3, Equipment Maintenance Program, of the QA Manual is then followed.

Instructions for support equipment operations are found in STAT SOP 1040 General Laboratory Procedures.

4.2.1 Water baths

Check temperature with each use when the water bath is loaded to capacity.

Drain and clean water bath as required and refill with laboratory pure water.

4.2.2 Refrigerators and freezers

Check and document temperature daily.

Clean periodically and discard outdated materials

DO NOT store food in any laboratory refrigerator or freezer.

4.2.3 Ovens

When using the oven for analysis, record the temperature daily as per SOP.

4.2.4 Balances

Check with at least two Class 1 weights (traceable to NIST) over the expected range everyday that the balance is used and record in the balance logbook.

Clean and check level of the balance as needed.

Maintain annual maintenance service contract.

4.2.5 pH meters

Date all pH buffer solutions when opened. Buffers that have reached the manufacturer's expiration must be discarded and replaced.

Standardize meter daily, or before each use.

"Working" pH buffer solutions must be replaced weekly.

4.2.6 Thermometers

Unless otherwise specified by regulatory methodology, it is the policy of STAT to use only non-mercury containing thermometers in all laboratory operations.

Calibrate all laboratory thermometers annually with a reference NIST thermometer. Mark any necessary corrections on each thermometer and record in the Thermometer logbook. The reference NIST thermometer is calibrated annually by a vendor certified for calibrating NIST traceable thermometers.

4.2.7 Mechanical Pipettes

All mechanical pipettes are cleaned and checked quarterly. Annual calibration is documented in the pipette logbook.

4.2.8 Conductivity meter

Date all conductivity solutions when opened. Solutions that have reached the manufacturer's expiration must be discarded and replaced.

Standardize meter at least monthly or as needed.

"Working" conductivity solutions must be replaced weekly.

4.2.9 Incubators

When using the incubator, record the temperature daily as per SOP 1040.

4.2.10 Autoclaves

Record temperature, pressure, and time maintained during each autoclave use per SOP 1040.

4.3 Laboratory Supplies

4.3.1 Glassware

Glassware used in general laboratory operations must be of high quality borosilicate glass. Volumetric glassware must be of Class "A" quality, except where the method specifies plastic volumetric flasks.

Clean glassware in hot water with a suitable detergent, rinse in hot water to remove detergent residue, and finally rinse in laboratory pure water. Glassware used in special analyses may require more scrupulous cleaning (e.g., acid rinsing for metals or solvent rinsing for organics). Glassware must be dried or drained

thoroughly before use or storage. In operations of specific, low-level analyses, glassware should be isolated and maintained only for these specific operations.

If at any time a new washing compound or cleaning application is introduced, tests must be performed to ensure the glassware is free of interferences before routine analyses are begun. (STAT SOP QA 1020 Laboratory Glassware Cleaning)

4.3.2 Chemicals, Reagents, Solvents and Gases

The quality of chemicals, reagents, solvents, standards and gases used in the laboratory is determined by the sensitivity and specificity of the analytical techniques being used. Reagents of lesser purity than specified by a method will not be used.

Reagents, chemicals, solvents, and standard reference materials (excluding high-demand items) should be purchased in quantities to minimize extended shelf storage.

All reagents, chemicals, solvents, and standard reference materials are initialed and dated when received, when opened or prepared, and discard when outdated, or when evidence of discoloration or deterioration is detected (STAT SOP 1010 Analytical Standards and Reagents Receipt and Preparation).

4.3.3 Laboratory Reagent Water

The laboratory reagent water system is tap water that is processed through a carbon-filtering tank and two mixed-beds ion exchange tanks. This water is checked daily to ensure that it has at least 1 megohm-cm resistivity (= 1 umhos/cm conductivity) at 25°C and recorded in conductivity logbook (STAT SOP 4200 Conductivity and SOP 1040 General Laboratory Practices**)**. Reagent water blanks are performed with each water batch to monitor for potential contamination.

4.4 Laboratory Hazardous Wastes Handling and Disposal Procedures

It is the policy of STAT Analysis to collect, store, package, label, ship and dispose of hazardous wastes in a manner which ensures compliance with all Federal, State and local laws, regulations, and ordinances. These procedures are designed to minimize employee exposure to hazards associated with laboratory-generated hazardous wastes and to afford maximum environmental protection (STAT SOP 1130 Waste Disposal).

4.5 Selection and Purchasing of Services and Supplies

Goods and services are purchased from qualified companies and individuals. The purchased items may be chemicals, consumable items, equipment, calibration services,

repair services, sub-contract laboratory services, consultant services, and building and environmental services. The laboratory maintains a list of qualified and approved vendors, suppliers, sub-contractors, consultants, and contractors. Vendors are deemed qualified if they possess ISO 9000 registration or if they can provide traceability of their products to NIST or to another recognized national standard of measurement. Service suppliers are deemed qualified if they provide certificates of calibration traceable to NIST or to another nationally recognized accreditation body or if they possess ISO 9000 registration. Purchased supplies and reagents and consumable materials that affect the quality of tests and/or calibrations are not used until they have been inspected or otherwise verified as complying with standard specifications or requirements defined in test methods SOPs and/or calibrations concerned. Actions taken to check compliance are documented. A sub-contractor, usually a testing laboratory, provides test reports to STAT that is used to supplement the information sent to STAT's customers. A sub-contractor may perform test methods that are not currently being performed at STAT, or may serve as an adjunct to the testing methodology already in place at STAT. Sub-contractors are deemed qualified if they possess accreditation from the National Environmental Laboratory Accreditation Program (NELAP), American Industrial Hygiene Association (AIHA), Environmental Laboratory Accreditation Program (ELAP), National Voluntary Laboratory Accreditation Program (NVLAP), American Association for Laboratory Accreditation (A2LA), or from some other nationally recognized accreditation body. If there is no independent means to qualify a potential vendor or supplier, the following procedure is used: Obtain qualification statements, obtain a list of references or customers, and send inquiries to these parties to obtain written information concerning the quality of materials and services rendered. Contact the Better Business Bureau (BBB) to determine if any complaints have been filed. A request or a purchase order may be made to a vendor to supply a small lot of material to be qualified using STAT in-house test methodology. A request or a purchase order may be made to a supplier to perform a service that will be independently verified by an already approved supplier. If this qualifications procedure is deemed successful, the vendor or supplier may be added to the approved list. STAT will determine the best value for its expenditures if two equally qualified and approved vendors or suppliers offer the same materials or services.

5. VERIFICATION PROCEDURES

5.1 Introduction

It is the objective of STAT to provide our customers with data that is of known and documented quality consistent with the analytical methods and SOPs specified in Appendix 3. This is accomplished with the use of traceable calibrations and documentation of this traceability with external reference samples.

Where possible, calibration and reference standards, traceable to national standards of measurement, are used in the laboratory to calibrate and/or verify the test equipment.

These calibration and reference standards are only used for calibration and/or verification purposes.

5.2 Traceability of Calibrations

Each analytical process undergoes the following to document calibrations used in the laboratory:

5.2.1 Initial Demonstration of Capability: Each analyst/work cell to determine the range of instrument operation, if applicable, and to demonstrate precision and accuracy, analyzes a series of laboratory control standards. This study is signed by the analyst, Department Supervisor, the QA Director, and the Technical Manager. See the specific requirements in SOP 1230 Training and analytical SOPs.

5.2.2 Initial Calibration Determination: Based on the Initial Demonstration of Capability (IDOC), an initial calibration is performed. The ICAL determination must meet the criteria specified in the analytical SOP.

If the regulatory limit is stated or defined for a particular analysis or test parameter, the laboratory's policy is to perform the analysis using a calibration standard at or below the defined regulatory limit.

5.2.3 Initial Calibration Verification: The Initial Calibration Verification is immediately performed to determine the validity of the initial calibration. This standard is from a second source, if available. Concentrations and acceptance criteria are specified in the relevant analytical SOP.

5.2.4 Method Detection Limit Study: The laboratory performs an MDL study prior to instituting a new procedure/analysis and yearly thereafter. MDL study is not applicable for some tests, e.g., pH, odor, temperature, etc. These procedures are outlined in STAT SOP 1210 Method Detection Limits.

5.2.5 Quality Control Check Sample: External reference standards that are analyzed as an unknown by the analyst. This provides an independent check of the analytical process. These results may be placed in the analysts' training file. See section 5.3.2.2 for more details.

The laboratory maintains a reference slide and spore collection of each microbiological sample identified. Because microbiological analyses measures constantly changing living organisms, these organisms are inherently variable. Appendix 3 lists references used in this laboratory.

5.2.6 Continuing Calibration Verification: A calibration standard is prepared and analyzed when an initial calibration is not performed. At a minimum, a calibration check is analyzed at the beginning and at the end of each analytical

batch. Organic internal standard methods are an exception where the calibration check is analyzed only at the beginning of the analytical sequence. Refer to the analytical SOPs for frequency and acceptance criteria. If a calibration check fails the appropriate SOP stated criteria, and routine corrective action fails to produce a second calibration check within acceptance criteria, then the initial calibration and initial calibration verification is performed. All samples analyzed since the last calibration check was in control will be re-analyzed, except in those instances where the calibration check was exceeded high (high bias) and there are non-detect results for the corresponding analyte in the samples associated with the calibration check. Those non-detects may be reported.

5.2.7 Method Blank Determination: A method blank is performed once per preparation batch per matrix type. The method blank is a negative control. A method blank is acceptable if it does not contain an analyte of interest at a concentration greater than the highest of the following: the reporting limit, 10% of the regulatory limit for that analyte, or 10% of the measure concentration for that analyte in any environmental sample in the batch. Some approved test methods do not require method blanks (e.g., pH, temperature, conductivity, etc.)

5.2.8 Analytical Reagent Blank: Analytical reagents, without media, shall be prepared and analyzed, when applicable, with each batch of samples, using the same procedure that is used for field samples.

5.2.9 Field Blank: It is recommended that customers of the laboratory supply specimens of blank sampling media from the same source lot as was used for collecting the field samples. A field blank from this source lot can help determine possible contamination of an analyte during handling and shipping procedures.

5.2.10 Continuing Calibration Blank (Inorganic): Inorganic SOPs require continuing calibration blanks analyzed each time a calibration check is analyzed. The same criteria are used as specified for method blanks (5.2.7). All samples analyzed since the last continuing calibration blank that was in control will be re-analyzed, except in those instances where there are non-detected results for the corresponding analyte in the samples associated with the continuing calibration blank. Those non-detected results may be reported.

5.2.11 Interference Check Standards (ICS): ICSs used in ICP-MS analysis checks for metal complex interferents (e.g. Ar, C, Cl, etc) with a similar mass of low concentration analytes. The appropriate analytical SOP contains specific instructions for analysis of these standards.

5.2.12 System Tuning Verification (GC/MS and ICP/MS): The GC/MS is hardware tuned before performing the initial and continuing calibrations. These systems must meet the peak ratio criteria specified in the analytical SOPs. Volatile analyses use bromofluorobenzene (BFB) and Semi-volatile analyses use

decafluorotriphenylphosphine (DFTPP) to verify the hardware tune. The ICP-MS is similarly tuned with metals that span the mass range of interest prior to analysis. These criteria must be met before any of these analyses are performed. See the appropriate method SOP for specific criteria.

5.2.13 Internal Standard Area Monitoring (GC/MS and ICP/MS): Internal standards are monitored to determine the quality of the injection process. Criteria are in the appropriate analytical SOP with corrective action specified.

5.2.14 Laboratory Control Standard: Laboratory Control Standard (or Sample) (LCS) is performed at least once per preparation batch per matrix. The LCS and MS/MSD are positive controls that measure the percent recovery (5.5) of the analytes added prior to preparation/analysis. They provide the assurance that the analytical system is capable of measuring the analytes specified. If the LCS does not meet control limits specified in the SOP, analysis is halted and corrective action taken to bring the system under control, including re-preparation of all samples in the batch associated with the out-of-control LCS. LCS is not performed when spiking solutions are not available, e.g., color, odor, temperature, dissolved oxygen, or turbidity.

5.2.15 Surrogate or System Monitoring Compounds (Organic): Surrogate compounds are added to most organic chromatography methods. Surrogates indicate that sample preparation and analysis are within the appropriate method SOP criteria. Specific SOPs have procedures handling out-of-control situations, including sample re-extraction/re-analysis.

5.2.16 Matrix Spike/Matrix Spike Duplicate: Matrix Spike/Matrix Spike Duplicate analysis is similar to LCS analysis (5.2.14) except it is performed on customer samples. The MS/MSD shall be prepared once per preparation batch of 20 or less samples per matrix type. If more than 20 samples are prepared a second MS/MSD shall be prepared after the twentieth sample.. Samples specified for MS/MSD analysis by customers will be selected if so indicated. MS/MSDs indicate the effect of the sample matrix on the precision and accuracy of the results generated using the selected method. This information does not determine the validity of the entire batch. For cases where the sample cannot be divided (e.g., wipes, air samples, not enough sample provided by customer) and thus a MS/MSD pair cannot be prepared for the preparation batch, an LCS/LCSD pair is analyzed to measure precision.

5.2.17 The laboratory will maintain a reference slide collection of asbestos types with various asbestos concentrations from previous NIST Proficiency Analytical Testing rounds. Standard Reference Materials (SRMs) are purchased from NIST for calibrations.

5.2.18 Duplicate Analysis (for analyses not suitable for spiking): Samples that are not suitable for MS/MSD analysis will be analyzed in duplicate. A Laboratory Control Standard Duplicate (LCSD) will also be performed for tests not suitable for matrix spike analysis or duplicate analysis (e.g. wipes, air samples, etc.). Relative Percent Difference (5.4) is calculated and compared to control criteria listed in the approved method SOP.

Quality Control data such as the precision data (average percent RSD or RPD), and accuracy data (average total percent recovery of spiked samples and reference samples) are reviewed against statistical limits on a continuous basis to detect statistically significant trends.

5.3 Performance Testing Samples

5.3.1 Introduction

As part of the laboratory's Quality Assurance program, an independent means of assessing laboratory accuracy for its performance in the various test methodologies has been developed. The Performance Testing Program analyzes Performance Testing (PT) samples on a routine basis. These samples, are of an unknown concentration to the analyst who performs the test. The purpose of analyzing these samples is to determine whether the analyst/laboratory can produce analytical results within specified acceptance criteria.

For analysis of all PT samples, with the exception of the EMPAT fungal direct examination program, the laboratory's procedure is as follows:

- Upon receipt, the Performance Testing Samples are treated as any other sample submitted to the laboratory. They are logged into the system and assigned a unique laboratory number. A LIMS work order is generated and samples are distributed to the analysts. The samples are then prepared and analyzed in the same manner as any other submitted samples using the same procedures, equipment, and laboratory personnel. After the data review process, test results are recorded in the LIMS. A final report is generated and results are reported to the Technical Manager, Quality Assurance Manager and Laboratory Director. Depending upon the type of PT sample, the final report is then submitted to the PT provider or evaluated in-house. After evaluation, either by the PT provider or by the QA Manager, the report is filed in the QA Manager's office.
- For PT sample studies that are used for accreditation purposes, the evaluation report, copies of the PT study report forms, copies of all support documentation, and copies of any corrective action investigations and resolutions, are kept in the QA Manager's files. This allows easy reconstruction and review of this data by the accrediting authority during on-site audits. This data, along with any electronic records, is kept at a minimum of five years from the date of the evaluation report received from the PT provider. This time frame may be increased to comply with any additional regulatory program requirements.

- All analysts participate in the PT process. Successful analyses are used to obtain accreditation or to maintain the laboratory's current scope of accreditation. They may also be used to update employee-training records (continuing DOC), or to demonstrate to customers or other interested third parties that the laboratory is capable of producing quality data.
- For unacceptable results, or results that are in-control but are continually statistically biased high or low, corrective action must be taken to determine the cause of the problem. This is accomplished by the corrective action process (SOP QA 230 Corrective Action). For PT sample studies that are used for accreditation purposes, copies of any corrective action investigations and resolutions are available to accrediting authorities.
- For the EMPAT fungal direct examination program, the analyst views and identifies the unknown samples on-line. On a quarterly basis, the laboratory has access to 20 different digital images for identification of spores.
- The laboratory will notify its customers and interested third parties, in writing, of any change to the laboratory's scope of accreditation (addition or deletion of analytes or fields of testing).

The laboratory has established policies in reference to the analysis of PT samples. They are as follows:

- PT samples are treated and analyzed in the same manner as other sample submitted to the laboratory.
- The laboratory does not send any PT sample, or portion of a PT sample, for which it seeks to obtain accreditation or maintain its current accreditation to another laboratory for analysis.
- The laboratory does not knowingly accept PT samples or portions of PT samples from other laboratories for any analyses for which the sending laboratory seeks accreditation or is accredited.
- Laboratory personnel do not communicate with any other individuals from any other laboratories concerning PT samples.
- Laboratory personnel do not attempt to obtain the assigned value or analyte concentration of any PT sample from the PT provider.

5.3.2 NELAC Performance Samples

The PT program is divided into two sections.

5.3.2.1 External Evaluation of Performance Sample

The first section of the program is dedicated to the analysis of PT samples for compliance with accreditation programs such as NELAC. The PT samples for this section of the program are of an unknown concentration to all laboratory personnel (blind to the laboratory). At a minimum of two times per year (approximately every six months), PT samples for each field of testing (each analyte/method/matrix) are purchased from a Proficiency Testing Oversight Body/Proficiency Testing Provider Accreditor (PTOB/PTPA) approved PT

provider, when available. After analysis, a report is submitted to the PT provider for evaluation. The Technical Manager, Quality Assurance Manager and Laboratory Director are responsible for the accuracy and the format of the report submitted to the PT provider. In order to initially obtain and to currently maintain accreditation, the laboratory must be successful in the analysis of these samples in two of the three most recent rounds of testing. If there is a failure to successfully analyze a particular analyte or supplemental testing is warranted, the laboratory must wait at least 30 days before analyzing additional samples. To maintain accreditation, the laboratory will continue to analyze samples at the prescribed frequency (two PT studies for each PT field of testing per year) unless there is a change in the program or in the environmental regulations. It will maintain a history of at least two acceptable PT studies for each PT field of testing out of the most recent three studies. The laboratory authorizes the PT provider to release the results of the laboratory's performance (sample results and acceptable/not acceptable status) on any of the PT samples directly to any accrediting authority, NELAP, and the PTOB/PTPA.

5.3.2.2 In-House Evaluation of Performance Samples

The second section of the program is for in-house evaluation of analyst performance. The PT samples for this section of the program are of an unknown concentration to the analyst performing the test (blind to the analyst). The QA Manager purchases these samples that include the true analyte concentration and performance acceptance limits. The QA Manager does not divulge this information to any of the laboratory personnel. PT samples are purchased from a PTOB/PTPA approved PT provider or another provider that can provide samples that are traceable to NIST, when available. After analysis, a report is submitted to the QA Manager for evaluation. The successful analyses of these samples may be used as documentation for the analysts continuing Demonstration of Capability in the applicable test methods.

5.3.3 AIHA Performance Samples

For purposes of this program, an industrial hygiene laboratory is defined as a laboratory that analyzes samples or materials for the purpose of evaluating occupational exposure or contamination resulting from occupational activities. The laboratory participates in three programs for accreditation: 1) the AIHA Industrial Hygiene Laboratory Accreditation Program (IHLAP) for accreditation of industrial hygiene laboratories; 2) the AIHA Environmental Lead Laboratory Accreditation Program (ELLAP) for accreditation of laboratories performing lead analysis, and the AIHA; and, the AIHA Environmental Microbiology Laboratory Accreditation Program (EMLAP). For the ELLAP program, the laboratory analyzes PAT samples in the following Fields of Testing: airborne particulates, dust wipes, paint chips and soil. The purpose of the PAT program is to ensure that the laboratory meets established performance criteria for the analysis of industrial hygiene samples.

This laboratory chooses to participate in the four rounds of performance samples per year. AIHA PT programs are performance based and the programs do not specify the use of any particular analytical method when analyzing PT samples, except for asbestos by PCM. Proficiency testing samples shall be analyzed using the same analytical procedure used to test customer samples.

The laboratory shall be responsible for the timely and proper submission of all PT sample results to the AIHA. The laboratory shall submit data using the AIHA Data Entry Portal on the AIHA web site. The data must be entered into the system by the specified deadline. An unreported result is classified as an outlier unless the AIHA has pre-approved nonparticipation. The AIHA shall provide the PT reports to each participating laboratory forty-five days after the close of the PT round. Accredited laboratories shall maintain these records for use during the assessment process. The laboratory is responsible for notifying the AIHA of any changes in laboratory status that may affect the receipt of PT samples/information, such as a change in address or named recipient.

A result that is outside the statistical control limits determined for the Industrial Hygiene Performance Analytical Testing (IHPAT) or Environmental Lead Performance Analytical Testing (ELPAT) Environmental Microbiology Performance Analytical Testing (EMPAT) round is classified as an outlier.

5.3.3.1 IHPAT Round Performance Samples

Proficiency is determined Field of Testing by Field of Testing and round by round. A laboratory is rated proficient for a given round for the applicable Field of Testing (FoT) if there is not more than twenty-five (25) percent deficiency for a given Field of Testing for that round. A laboratory is rated as proficient for the FoT if it passes two out of three consecutive test rounds. The laboratory shall have participated in at least two (2) PT rounds to be considered for accreditation. When PT samples are analyzed by more than one analyst, averaging the results for reporting is not permitted. A single analyst's results are reported.

5.3.3.2 ELPAT Round Performance Samples

A laboratory is rated proficient for the applicable Field of Testing if there are not more than 25% cumulative outliers reported in the last four consecutive PT rounds in which the laboratory has participated at the time of accreditation or no outliers reported in the last two consecutive PT rounds. The laboratory shall have participated in at least two (2) PT rounds to be considered for accreditation.

5.3.3.3 EMPAT Round Performance Samples

In order to maintain accreditation, the laboratory must be 85 % successful in the analysis of microbiology samples in the three most recent rounds of testing. To maintain accreditation, the laboratory will continue to analyze samples at the prescribed frequency (three PT studies for each PT field of testing per year) unless there is a change in the program or in the environmental regulations. It

will maintain a history of at least 85 % acceptable PT studies for each PT field of testing out of the most recent three studies.

5.3.4 NVLAP Performance Samples

The PT program is divided into two sections.

The first section of the program is dedicated to the analysis of PT samples for compliance with accreditation programs such as NIST/NVLAP. The PT samples for this section of the program are of an unknown concentration to all laboratory personnel (blind to the laboratory). PT samples for each field of testing are provided by NVLAP, generally, at a frequency of two times per year (approximately every six months). After analysis, a report is submitted to the PT provider for evaluation. The analysts, Technical Manager, Quality Assurance Manager and Laboratory Director are responsible for the accuracy and the format of the report submitted to the PT provider. In order to initially obtain and to currently maintain accreditation, the laboratory must score less than 150 points on two out of the last three consecutive proficiency testing rounds. To maintain accreditation, the laboratory will continue to analyze samples at the prescribed frequency (two PT studies for each PT field of testing per year) unless there is a change in the program or in the environmental regulations. The laboratory authorizes the PT provider to the release the results of the laboratory's performance (sample results and acceptable/not acceptable status) on any of the PT samples directly to the NIST/NVLAP.

The second section of the program is for in-house evaluation of analyst performance. This is accomplished by a round-robin program. Asbestos samples are distributed to numerous laboratories and analysis is summarized and distributed to all participants. After analysis, a report is submitted to the QA Manager for evaluation. The successful analyses of these samples may be used as documentation for the analysts continuing Demonstration of Capability in the applicable test methods.

5.4 Precision

Precision is expressed as percent relative standard deviation and is calculated by the formula:

$$\% \text{ RSD} = \frac{S \times 100}{X}$$

Where: S = Standard Deviation
X = Mean

Precision can also be expressed as relative percent difference and is calculated by the formula:

$$\% \text{ RPD} = \frac{D \times 100}{X}$$

Where: D = Difference between measurements
X = Mean

Percent difference is calculated by the formula:

$$\%D = \frac{(X-Y) \times 100}{X}$$

Where: X = Initial Measurement
Y = Comparison Measurement

5.5 Accuracy

Accuracy is expressed as percent recovery and calculated by the formula:

$(Y - X)/Z \times 100 = \%$ Recovery

Where: X = concentration in unspiked sample.
Y = concentration in spiked sample.
Z = theoretical spike concentration

5.6 Analytical Performance Summary

Quality control data are reviewed on a continuous basis. During the review, percent RSD, percent RPD, upper warning and control limits of precision data and percent recovery of accuracy data are evaluated against established control limits. If a statistically significant trend is observed, then warning and control limits may be updated, and documented in Addendum to the SOP.

Annually, a summary report of the laboratory's analytical performance is prepared. Contained in this report are: the precision data (average percent RSD or RPD, upper warning and control limits), and accuracy data (average total percent recovery of spiked samples, reference samples, and performance audit samples). The Quality Assurance Manager prepares this summary and it is reviewed by the Technical and the Laboratory Director prior to distribution for use.

6. METHODOLOGY

Test method SOPs are based upon nationally recognized test method references such as the United States Environmental Protection Agency (USEPA), National Institute for Occupation Safety and Health (NIOSH), NIST/NVLAP, Standard Methods (American Public Health Association, American Water Works Association, Water Environment Federation) and American Society for Testing and Materials (ASTM). These test methods are used for sample analyses, and the related sample handling and storage activities are appropriate and consistent with the required quality and accuracy deemed

necessary for customers and their decision-making processes concerning environmental regulations and compliance. The laboratory uses the most stringent standard as stated in the reference test method or as specified in the applicable regulation.

Appendix 3 contains a table of the laboratory's scope of test methods and SOPs.

7. PHYSICAL FACILITIES AND EQUIPMENT

7.1 Facilities

STAT has over 12,000 square feet of state-of-the-art laboratory facilities. An electronic key-punch provides limited access to this building. The laboratory space and ventilation system was specifically refurbished to achieve the critical needs of an environmental laboratory. For example, laboratories for air toxics and volatiles analyses are positively pressurized and are supplied with fresh air that is carbon filtered. Environmental lead is digested and analyzed in a laboratory separate from bulk lead samples (paint chips, dust, etc) to prevent cross contamination. Separate laboratories are provided for microbiology, optical microscopy and electron microscopy. Three organic extraction laboratories occupy nearly 1400 square feet of space and allow for extraction of air, water and soil with room for further expansion.

There is no other testing facility being utilized other than the permanent lab premises. The rooms are dedicated to specific laboratory testing departments and administrative offices. The physical environment (temperature, humidity, lighting, and ventilation) is adequate to perform all testing methodologies. Temperature is monitored and controlled by individual thermostats in each room. Ventilation hoods are monitored as part of the laboratory safety program. Any problems encountered with the physical accommodations are immediately brought to the attention of the Technical Manager or the Laboratory Director. The building engineer is then notified to take immediate corrective action to remedy any problems.

As part of the Internal Audit Process (SOP 1220 Internal Quality Assurance Audit), the QA Manager is required to monitor the laboratory's facilities to ensure that the facilities are adequate and that personnel are in compliance with laboratory policies. Those areas audited include the following:

- Ventilation: hoods checked and tagged per the Chemical Hygiene Plan
- Room temperature: monitor the TCLP extraction area
- Voltage surge suppressors to protect computer network and critical instrumentation
- Separation of incompatible areas is maintained
- Personnel movement is limited to prevent cross-contamination
- Good housekeeping practiced - items reviewed: benches, floors, hood used properly, clutter, glassware cleaning space and storage, bottle/container storage
- Waste storage area is reviewed to ensure safe practices

- Air Monitoring for Spores in Microbiology Laboratory: Background contamination is to be checked periodically (once every Quarter). If growth of Aggressive spores is observed, all areas of the laboratory are cleaned. The air system is checked, and if necessary, filter is replaced. Cleaning will continue until no background contamination is detected.
- Air Monitoring for Asbestos: Background contamination is to be checked periodically (once every Quarter) by taking air samples from areas where asbestos is handled, such as sample receiving, bulk asbestos analysis Laboratory, and PCM and Transmission Electron Microscopy (TEM) Laboratory. Samples are analyzed by TEM. If presence of asbestos is confirmed, all areas of the laboratory are cleaned. Cleaning will continue until no background contamination is detected.
- Background Monitoring for Lead in Lead Laboratory: Background contamination is to be checked periodically (once every Quarter). If lead is observed, all areas of the laboratory are cleaned. Cleaning will continue until no background contamination is detected.

7.2 Equipment

The major equipment in use at STAT Analysis Laboratory is listed in Appendix 4. The equipment list is under the control of the Quality Assurance Manager. The list is updated as required whenever new equipment is purchased or current equipment is permanently removed from service.

7.3 Equipment Maintenance Program

Proper maintenance of laboratory instrumentation is a key to longevity of the instrumentation, as well as providing the analyst with equipment capable of producing reliable analyses. The analysts and on occasion, vendor specialists, share the responsibility for maintenance and repair of all STAT Analysis Laboratory equipment. The primary elements of the equipment maintenance program include:

- All major equipment receives a daily check for such things as: cooling fan operation, pump operation, indicator readings, mechanical checks, clean air filters, etc.
- Service schedules are established for performing routine preventative maintenance on all major equipment items.
- Records are maintained for major instrument repairs (See individual instrument maintenance logbooks).
- A conservative inventory of critical spare parts is maintained for high-use instrumentation.
- Vendor operation and maintenance manuals are maintained for laboratory instrumentation.

Any equipment that is found to be defective is taken out of service. The equipment is tagged by the person making the judgment and marked “Out of Service;” the person applies their initials and dates the tag. This action is noted in the maintenance logbook.

The department supervisor is notified of this action. If deemed necessary, a corrective action report is initiated to determine if the malfunctioning equipment has potentially generated data that is suspect. The equipment is not put back into service until repairs are made and the equipment is shown to be performing properly after calibration and/or verification procedures have been successfully completed and documented in the maintenance logbook.

8. SAMPLE RECEIPT and ACCEPTANCE

8.1 Introduction

Complete documentation of the sample collection and handling process is an extremely important aspect of a regulatory monitoring effort. Formal chain-of-custody procedures provide a written record of sample traceability, accountability and serve to validate sample integrity. All samples received by STAT Analysis are controlled by these procedures. For more information see STAT SOP 300 (Sample Receiving and Login Procedure).

Appendix 5 contains a table of acceptable sample containers with sample preservation requirements for analyses listed in section 6.

Sample collection is typically a function of our customer's activities. STAT does not provide sampling services. STAT's customers deliver samples to the laboratory for testing. However, STAT will attempt to ensure compliance with all applicable ISO/IEC 17025, NIST/NVLAP, AIHA, and NELAC requirements. STAT requests customers to submit field blanks with their samples, where applicable. A summary of STAT's written sample acceptance policy will be made available to sample collectors. Data from samples that do not meet the sample acceptance criteria will be unambiguously flagged to define the nature of the variance. Sampling procedures for collection of subsamples are described within each method's Standard Operating Procedure (SOP).

8.2 Sample Acceptance Policy

Please refer to Appendix 6 for a detailed description of STAT's Sample Acceptance Policy. It becomes the customer's responsibility to distribute the sample acceptance policy to all field collection personnel.

NOTE: STAT Analyses will not accept samples that require legal Chain-of-Custody.

8.3 Sample Acceptance Policy Differences

8.3.1 Additional Requirements for NELAC Samples :

8.3.1.1.1 Liquid Samples for volatiles analyses do not contain headspace.

8.4 Chain-of Custody Form

A Chain-of Custody (COC) should accompany every sample that is received for analysis by STAT Analysis. If the COC is not present, the customer will be notified and the exception noted on the Sample Log and Checklist/Receipt Form (Sample Receiving and Login Procedure). (Attachments 1-3 list examples of COC forms.)

8.5 Standard Operating Procedure – Sample Receipt/Custody

The sample custodian or a designated alternate receives samples. Below are general guidelines for sample receiving and login, for specific details refer to SOP 300 Sample Receiving and Login Procedure. STAT accepts samples between the hours of 8 AM to 8 PM, Monday through Friday. STAT has a secured sample drop box outside the building for samples that do not require preservation and can fit inside the box. For samples that arrive after hours, the sample custodian will receive the samples the next business day. At the time of receipt, the custodian or designee will perform the following actions:

8.5.1 While wearing proper protective equipment, (a minimum of gloves, a lab coat, and safety glasses) all shipping containers (coolers) are opened in an adequately ventilated area to assure worker safety.

8.5.2 All shipping containers (coolers) are examined to verify that the custody seal is intact (if present). The parts of the custody seal are maintained in the customer folder after opening.

8.5.3 If applicable, the temperature of the shipping cooler and/or temperature blank are measured to determine if proper temperature has been maintained. Proper temperature is defined as 0.1°C to 6°C (for NELAC-specific samples). Samples that have been received within six hours of collection and on ice will be noted as being received "On Ice" as complete cooling to 4°C will not have been completed by that time.

8.5.4 The condition of the sample container (leaking, broken, mislabeled or unclearly labeled) is checked. Exceptions are noted on the Sample Receipt Checklist Form and the customer is notified of the impact that the exception will have on the quality of data generated.

8.5.5 The COC is examined for accuracy and completeness. For all samples, especially environmental or industrial hygiene samples, it is vital that all COC procedures are followed properly. This is necessary to preserve the security of samples as evidence. Samples are considered secure for evidentiary purposes if they are in your possession, within view, or in a secured area. The laboratory is considered secure because access is limited. The COC record is used to document the change in possession from sampling, delivery, and receipt by the laboratory.

8.5.6 Samples received and sample container labels are compared against those listed on COC. Sample hold times are verified for sample acceptance. The customer is notified if holding times have been exceeded.

8.5.7 Sample pH is verified for those samples that require specific chemical preservation. The sample pH result is recorded on the Sample Receipt Checklist Form and in LIMS. VOA water samples are not checked for pH at time of receipt but are checked after analysis. VOA samples are checked for headspace at time of receipt. Samples for cyanide analysis are checked for free chlorine at time of receipt. The sample free chlorine result is recorded on the Sample Receipt Checklist Form and in LIMS. The sample custodian treats samples that require additional preservation for pH adjustment or require the removal of free chlorine. The identification of chemical preservative is recorded on the Sample Receipt Checklist Form. The customer is notified if samples have not been properly preserved.

8.5.8 Samples requiring refrigeration are stored in the appropriate sample refrigerators. Samples not requiring refrigeration are placed in the appropriate department storage areas.

8.5.9 The Chain of Custody is then signed, dated and timed. The Chain of Custody, Custody Seals, Waybill and Sample Receipt Checklist Form are placed in a Job Folder that is labeled with STAT Work Order Number and Customer Name. All information/analytical reports pertaining to the specific job are stored in this folder. This includes quotes, faxes, correspondences, analytical reports, sub-contracted analytical reports, etc.

8.5.10 Any problems associated with samples on the COC are immediately noted on a Sample Log and Checklist form. The assigned STAT Project Manager is notified of the problem(s). The Project Manager is responsible for communicating with the customer on how to resolve issues associated with the samples.

8.5.11 The LIMS is used to generate the sample log and assign sample numbers that are a link to the sample field identification code or name. The sample log generates a unique work order for a specific project or group of samples. All sample containers are labeled with a unique laboratory sample number. This numbering system is also used to uniquely identify separate containers of the same sample submitted within the work group. The unique laboratory sample number is used throughout all of the laboratory records to identify the sample and any subsequent subsamples, extracts, or digestates of the original sample. The entry of sample information into the LIMS is password controlled. Thus, the name of the person entering the information is recorded. The following information is entered into the sample log (as applicable):

1. Customer Name

2. Customer Project Number
3. Customer Project Name
4. Customer Sample Number
5. Date and Time Sampled
6. Date Received
7. Turn Around Time
8. Date Due
9. Analytical Parameters performed in house
10. Subcontracted Analytical Parameters (if needed)
11. Subcontract Laboratory
12. Storage Refrigerator Number

8.5.12 The LIMS can generate work lists that contain Sample ID, Client ID, Date Received, Date Collected, Date Due, Test Code Test Name, Holding Time, Prep Date, Hold Time, Date, Storage Area, as well as indication that the hold time and/or due date is about to expire.

8.6 Policy for Disposal of Laboratory Samples

Samples and their extracts will normally be disposed of within (STAT SOP 1130 Waste Disposal) 90 days from receipt of samples or in accordance with individual SOPs. The exception to this will be when a sample hold request is implemented.

A disposal report will be generated and provided to designated staff as appropriate for samples characterized as non-hazardous (routine environmental). Sample disposal of the routine environmental samples should be completed by the appropriate analyst within 2 weeks from disposal report distribution. The routine environmental samples will be disposed of in the following manner:

Soil samples are placed in 55-gallon drums and disposed of as special waste with an approved special waste hauler.

Water samples are disposed of by pouring the water into 30-gallon plastic drum or, if deemed to be non-hazardous, are poured down the laboratory drain. Preserved samples may be neutralized prior to placing into the 30-gallon plastic drum. These drums are disposed with an approved special waste hauler.

Hazardous samples will be disposed as hazardous waste. All microbiological samples will be autoclaved prior to disposal. All waste is disposed according to SOP 1130 Waste Disposal.

9. SAMPLE RECORDS, DATA REVIEW AND DATA HANDLING

Sample accountability through the analytical process can be divided into five major elements: (1) initial sample logging, (2) sample preparation, (3) data acquisition, (4) data review, and (5) documentation/storage. The location of the sample and data records is discussed in SOP 1000 Control and Use of Laboratory Notebooks and in SOP 240 Archiving. Sample records must be able to reproduce the resultant analytical data. It is management's responsibility to ensure that all analytical and operational activities of the laboratory are properly and sufficiently documented. This is accomplished through the periodic audit and review processes as outlined in SOP 1220 Internal Quality Assurance Audit and SOP 006 Management Review of the Quality System. All data, whether manually generated or electronically generated, and final reports are available to the accrediting authority (NELAC, AIHA, etc.).

The following sections outline current sample and data documentation and review procedures.

9.1 Sample Logging

Samples received at STAT with accompanying identification and COC are logged into the Laboratory Information Management System. The sample custodian, or designate, signs the laboratory receipt section of the COC. Each sample, and each sub-sample appropriately preserved, is assigned a unique sample ID.

9.2 Analytical Data Review and Handling

All raw analytical and instrument control data generated in the laboratory are either entered into bound data books or kept as strip charts, or in instruments computer hardcopy, tape, CD-ROM, or disk. The analyst reviews the data initially and all data entries checked 100% and then the data under goes a second review by a technical peer or supervisor. Errors, or potential errors, are investigated and corrected as necessary. The analytical section manager, Project Manager, Technical Manager, or Laboratory Director, for consistency of data and for assuring customer's needs are met, performs final review. Refer to STAT SOP 1250 Data Review.

Information contained in these data logbooks includes the following: Work Order Number, Sample number, parameter, date of preparation or analysis, analyst, and all pertinent instrument identification with analytical conditions. For non-computerized instruments all calibration data, all readout data, calculations, final concentration, and quality control data should be recorded in the logbook.

9.3 Computerized Analytical Data System

9.3.1 All sample results are entered into the STAT Analysis Laboratory Information management System (LIMS). Sample preparation, as appropriate, will also be entered in LIMS.

9.3.2 For NELAC and Lead AIHA samples, all appropriate Quality Control data associated with these results are entered into the LIMS, including, but not limited to, Initial Calibration, Initial Calibration Verification, Continuing Calibration Verification, Continuing Calibration Blank, Method Blanks, Laboratory Control Standards, Matrix Spike/Matrix Spike Duplicate, Internal Standard Recoveries, and Surrogate Recoveries.

9.3.3 For all other samples, the quality control information is entered into a separate database or spreadsheet. The information is stored under a unique batch identification number. This information may include: Initial Calibration, Initial Calibration Verification, Continuing Calibration Verification, Continuing Calibration Blank, Method Blanks, Laboratory Control Standards, and Matrix Spike/Matrix Spike Duplicate recoveries as applicable.

9.3.4 Analytical Data Processing. All final analytical results are calculated after entry into the analytical results database.

9.3.5 Analytical Backlogs can be generated through the LIMS system. Sample Status will be updated to complete after results are calculated. Samples that are complete will no longer appear on an analytical backlog report. The work order will only be available for Final Report after all sample results have been calculated and subjected to the Quality Control Validation Process.

9.4 Reporting

Final results of all analyses are provided in a standard computerized report format and forwarded to the requester (customer) with cover memorandum. Remarks should be used with reported data to alert the user to some specific conditions that affects the data (e.g., holding times missed, samples diluted to remove interferences, etc.).

Exceptions to this report format must be noted and have approval of the Technical Manager or Laboratory Director.

Amendments or corrections to the issued test report are only made in the form of a revised document that includes the statement “This report is revised to reflect changes made after the initial report was issued” in the cover letter or in the case narrative.

Customers are notified immediately, in writing, of any event that cast doubt on the correctness or validity of the laboratory's calibrations, or test results given in any test report or amendment to a report. Such events might include: identification of defective measuring, identification of defective test equipment, or audit findings.

Test results are certified to meet all requirements of NELAC, NVLAP, and AIHA standards, or reasons are stated if they do not meet these standards.

In addition to the items mentioned, below, in 9.4.1 (7), the analytical report will make the following statements:

1. The report shall not be reproduced except in its entirety, unless written approval has been obtained from the laboratory.
2. The results of this report relate only to the samples tested.
3. The laboratory certifies that the test results meet all requirements of IEPA code, Title 35, Subtitle: A, NELAP/Part 186 or NIST Handbook 150 (2006 Edition) or the AIHA LQAP Policy Document, current revision.
4. Accredited and non-accredited analyses will be distinguished.

9.4.1 Reporting Requirements

The Analytical Report will only be issued in its entirety. The Report will include:

1. The statement "Analytical Report";
2. Date, name and address of laboratory, phone number and name of contact person (with signature) and laboratory accreditation number. The person signing the report is accepting responsibility for the content of the report;
3. A unique Work Order Number and the total number of pages in the report, with all pages sequentially numbered;
4. Name and address of customer and project identification;
5. Description and unambiguous identification of the sample(s) including the customer identification code, date of sample receipt, date and time of sample collection;
6. Clear identification (including lab name and accreditation number) of any sample results that were generated by a subcontracted laboratory;
7. Case Narrative outlining any sample acceptance outliers and /or sample results with any failures or deviations from approved SOPs including the use and definitions of data qualifiers; as well as reporting uncertainties as required.
8. Identification of approved test method with date of sample preparation, sample preparation method, and/or analysis;
9. Identification of reporting units, such as mg/L, mg/Kg, mg/Kg–dry, ppbv, µg/filter µg/wipe, mg, µg, wt. %, or $\mu g/m^3$;
10. Measurements, examinations and derived results, supported by tables, graphs, sketches and photographs as appropriate, and any failures identified;

11. A statement to the effect that sample results relate only to the analytes of interest tested or to the sample as received by the laboratory;
12. Reference to sampling procedures if performed by the laboratory;

9.4.2 Reporting Differences

9.4.2.1 NELAC Differences
9.4.2.2 9.4.2.1.1 Clear identification of numerical results with values outside the quantitation limits.

10. CORRECTIVE AND PREVENTIVE ACTIONS

Out-of-control situations arise out of the analytical process. Corrective and Preventive actions are mechanisms for identifying and correcting out-of-control situations. Quality control data are evaluated, and if data are found to be outside control limits, corrective actions are taken to correct the problem and to prevent incorrect data from being reported.

10.1 Corrective Action

Routine corrective action will be taken at any time during the analytical process as outlined in the quality control sections of each SOP. These types of out-of-control situations include such things as: instrument calibration outliers, blank contamination, poor laboratory control standard recovery, poor surrogate recovery, poor matrix spike/ matrix spike duplicate recovery or RPD, etc. These situations require immediate corrective action. These required actions are specified in each analytical SOP. These actions are documented by the analysts on the prep and work sheets to assure traceability of analysis performed.

Some out-of-control situations require a more formal corrective action process. They may be the result of internal or external audits, out-of-control proficiency testing analysis, continuing control chart outliers, or even the inability to produce analytical results on time. These situations require a more stringent process. This process may involve technicians, analysts, and laboratory management. The Quality Assurance Manager monitors this process (STAT SOP QA 230 Corrective Action). Essential steps in this process include documentation of the following:

- Identification of the problem.
- Assigning a tracking number to the Corrective Action.
- Assigning personnel to investigate the problem.
- Uncovering the cause of the problem.
- Correcting the problem.
- Monitoring the corrective action.
- Documentation of the corrective action.

Corrective Actions are resolved in a time frame relative to the severity of the defined problem. Some corrective actions may need to be immediately implemented in order for production to continue. Other corrective actions may require a certain amount of time in order to complete a full investigation. An appropriate time frame for completion of the corrective action is discussed with the affected parties. All corrective action investigations are to be completed within a two-week time frame unless unusual circumstances are documented that would extend this deadline. Corrective Actions investigations involve assigning an individual to investigate and determine the cause of the problem.

10.2 Preventive Action

Preventive actions are pro-active processes to identify opportunities for improvement rather than a reaction to the identification of problems. Preventive actions will be taken upon identification of needed improvements and potential sources of nonconformity. Action plans will be developed, implemented, and monitored to reduce the likelihood of the occurrence of such nonconformities and to improve on existing procedures. As part of the preventive action, operational procedures will be reviewed. Data review may also be conducted that include trend and risk analyses and proficiency-testing results.

Steps in the preventive action process may include:

- Identification of the source of nonconformity or needed improvements.
- Assigning personnel to investigate
- Reviewing operational procedures.
- Implementing needed improvements or procedure to avoid potential nonconformity.
- Monitoring the preventive action.
- Documentation of the preventive action.

11. QUALITY EXCEPTION REPORT

Some out-of-control situations are not correctable (e.g., silver matrix recovery when certain levels of chloride are present or VOA system monitoring compound recoveries on samples containing activated carbon). The Quality Exception report is executed and included in the case narrative of the analytical final report (STAT SOP QA 230 Corrective Action).

12. COMPLAINT

Customer complaints are logged and resolved by project managers as outlined in STAT SOP 220 Customer Service. STAT seeks feedback from its customers so that improvements can be made to the management system, testing and calibration activities, and customer service.

13. CONFIDENTIALITY

All customers, including government entities, are entitled to all aspects of their project to be considered confidential. To protect national security concerns and proprietary rights, STAT Analysis will ensure customer confidentiality. No aspects of customer project can be released to others without the expressed written consent of the customer. All data, electronic media, and reports are considered confidential

A Notice of Confidentiality is affixed to outgoing e-mails and facsimiles transmittals. Examples of these can be viewed in Attachments 4 and 5, respectively.

14. INTERNAL AUDITS

The Laboratory will undergo an annual internal audit, or more frequently if warranted. The Quality Assurance Manager will take the lead in this activity. If the Quality Assurance Manager is responsible for analytical activity, another member of the management team will audit that area. These activities are outlined in STAT SOP 1220 Internal Quality Assurance Audit.

15. MANAGEMENT REVIEW of the QUALITY SYSTEM

STAT strives continually to improve the effectiveness of its management system through the use of the quality policy, quality objectives, audit results, data analysis, corrective and preventive actions, and management review. This document, and the entire Quality Systems, is reviewed yearly. This process and procedures for development and submittal of quality assurance reports to management are outlined in STAT SOP 006 Management Review of Quality Systems. In addition to the annual report, quarterly quality assurance reports are developed and submitted to management. Finding from management reviews include recommended actions for improvement and the actions are carried out within a reasonable time frame and documented.

Changes made to appendices of this document will not constitute a revision to this Quality Assurance Manual.

16. TRAINING

STAT ensures that all employees will have proper training for their job. A training file is maintained for each employee (STAT SOP 1230 Training (for NELAC/AIHA)). It is the responsibility of STAT Management to ensure all employees are educated on ethical and legal responsibilities, as well as, the punishment and penalties for improper, unethical, or illegal actions. Every employee is expected to read, understand, and sign a code of ethics statement.

The need for training beyond initial training on analytical SOPs will be assessed on a case-by-case basis. The department manager and laboratory director will determine if

additional training is needed. The introduction of a new technique is an example of the need for additional training. The effectiveness of the training actions is evaluated by the trainer.

17. DATA INTEGRITY

STAT's management is committed to support and implement specific requirements of the data integrity procedure. STAT's procedures ensure that management and personnel are free from any undue internal and external commercial, financial, and other pressures and influences that may adversely affect the quality of their work. STAT promotes a culture of receptive environment where all employees can privately discuss ethical issues or report items of ethical concern. Such discussions are kept confidential, if need to be. The data integrity system includes four elements discussed below.

- Data Integrity Training: STAT has a training program in place for new employee orientation and on an annual basis for all employees to prevent breaches of ethical behavior. Written training material includes Appendix 7. Topics include:

  - Discussion regarding all data integrity procedures, data integrity training documentation, data integrity monitoring, and procedure documentation.
  - Employees are trained on STAT's responsibility to produce data that is scientifically valid, defensible, and of known and documented quality in accordance with all applicable federal, State, and local laws and regulations consistent with accepted professional and analytical practices in a manner that justifies the public trust. The employees are required to understand the critical need for honesty and full disclosure in all analytical reporting.
  - Employees are provided specific examples of unethical behavior including improper data manipulations, adjustment of instrument time clocks, and inappropriate changes in concentrations of standards.
  - Personnel are trained to inform STAT of any accidental or intentional reporting of non-authentic data by the employee or other employees. Employees are trained not to comply with instructions, requests, or direction by any manager or representative of management to perform any improper laboratory practices. Employees are trained to immediately report such event to all appropriate members of management including department manager, the Laboratory Director, the QA Manager and President/CEO, excluding such individuals who participated in such perceived improper instruction, request, or directive.
  - Employees are required to understand that any infractions to the data integrity procedures will result in a detailed investigation. Any allegation of misconduct will be promptly investigated in an unbiased and confidential manner by an investigative team designated by the President. Investigation could lead to very serious consequences for the employee including immediate termination. The investigation, including any

supporting documentation, actions and resolution, will be recorded and archived by the QA Director.
- Analysts are trained on proper documentation in Case Narratives where analytical data may be useful, but are partially deficient.

- Signed data integrity documentation for all employees: The initial data integrity training and the annual refresher training have a space for employee signature to verify that the employee has participated in the training and understands his or her obligations related to data integrity issues (see Appendix 7: Ethics Policy and Data Integrity Agreement.).

- In-depth periodic monitoring of data integrity: STAT is committed to document all activities associated with generating valid data. All tasks from sample receipt to issue of analytical reports are tracked and reviewed. Some examples of data monitoring activities include:
  - Documentation and secondary review of sample log-in
  - Documentation and review of all sample preparation activities in specific logbooks
  - Primary and secondary review of all analytical data
  - Primary and secondary review of all manual integration
  - Further review of all of the above steps by project manager and/or Quality Manager
  - Calibration of measuring devices, such as thermometers, balances, weights, and pipettes.

- Data Integrity Procedure documentation: All aspects of the data integrity procedures are documented. These include documenting all data monitoring activities. All customer communications are recorded. As discussed above, data integrity training material are developed and documented. Actions arising from data integrity issues, whether technical or ethical in nature, are documented.

18. SUB-CONTRACTING

Any sub-contracting of accredited analytical work must be to another NELAC or AIHA accredited laboratory with the appropriate fields of testing, approved test methods and analytes. STAT retains on file a copy of the certificate issued pertaining to the sub-contracting laboratory. The customer will be notified in writing of the intention to sub-contract analytical work. The analytical report contains the name and accreditation number of the sub-contracted laboratory. STAT maintains a record of all laboratories to which we subcontract analytical work. See STAT SOP 220 Customer Service for additional information.

19. LABORATORY SAFETY

19.1 Introduction

All STAT employees must accept the responsibility for acting in accordance with safety rules and practices and for reporting any observed safety hazard. This section highlights some general guidelines and rules that specifically apply to the analytical laboratory. Therefore, in addition to adhering to guidelines, each person is trained in, and expected to read, understand, and follow STAT SAP 003 Chemical Hygiene Plan.

19.2 General

Lab coats and safety glasses should be worn at all times in the laboratory. The only exception to this is when personnel are working at computer terminals or microscopes. Lab coats are left in the laboratory. Latex or nitrile gloves are worn when chemical or samples are handled.

Open sandals and shorts will not be worn in the laboratories.

When working in any of the laboratories, it is recommended that all jewelry be removed and that personnel wash their hands frequently. Always wash hands thoroughly when leaving the laboratory.

When working with flammable materials, nylon or other totally synthetic clothing should be avoided to minimize the possibility of static sparks.

All containers should be labeled as to contents, with particular care to note corrosive or hazardous materials.

There will be no eating, drinking, or smoking in any of the laboratories.

Glassware that is chipped but still usable must be polished before re-use; otherwise, it must be discarded.

Never use any lab glassware as a container for food or drink.

An inventory of all chemicals used in the laboratory will be maintained.

Return all chemicals to their proper storage areas after use.

Never pipette by mouth.

The Safety Officer will conduct a quarterly safety inspection of the laboratory.

Perchloric acid or perchlorate salts are not stored or used in the laboratory. If at any time these chemicals are required in a method, special precautions will be necessary and should be coordinated with the Inorganic or Organic Manager and Laboratory Director.

All work areas should be cleaned at the end of each workday. Spills should be cleaned up immediately.

Samples should be in laboratories only during preparation and analysis; other wise keep them in the storage area.

All stock standards of a toxic nature should be prepared in a hood and stored in designated areas. Only experienced personnel should handle these standards.

Work of a hazardous nature will not be performed in a laboratory after normal business hours when only one person is present.

New personnel must be familiarized with safety practices, location of safety equipment, and made aware of possible hazards in the areas in which they will be working.

When conducting routine maintenance of electrical equipment observe all shock hazard warnings displayed on instrumentation.

Use safety guards where appropriate when using electrical equipment or ventilation/fume hood systems.

Observe all warnings regarding cylinders and sample storage areas.

When using pressurized systems, take care to tighten restraints before pressurizing system and depressurize the system before loosening restraints.

19.3 Sample Receiving and Login

When possible, determine the source of the samples and any special hazards that might be associated with them.

Some samples, when sealed in containers will build up pressure. Samples that indicate pressure should be brought to the attention of the Safety Officer or Laboratory Management.

20. DEFINITIONS

Acceptance Criteria: specified limits placed on characteristics of an item, process, or service defined in requirement documents. (ASQC)
Acceptance Limits: Established mathematical data quality limits for analytical method performance. (AIHA LQAP)

Accreditation: the process by which an agency or organization evaluates and recognizes a laboratory as meeting certain predetermined qualifications or standards, thereby accrediting the laboratory. In the context of the National Environmental Laboratory Accreditation Program (NELAP), this process is a voluntary one. (NELAC)
A formal recognition that a facility meets AIHA Policy Requirements to carry out specific tasks or specific types of tests. (AIHA LQAP)
Accredited Laboratory: A testing laboratory that has been evaluated and granted accreditation covering a specific measurement or task, usually for a specific property or analyte, and for a specified period of time. (AIHA LQAP)
Accrediting Authority: the Territorial, State, or federal agency having responsibility and accountability for environmental laboratory accreditation and which grants accreditation (NELAC)[1.5.2.3]
Accrediting Authority Review Board (AARB): five voting members from Federal and State Accrediting Authorities and one non-voting member from USEPA, appointed by the NELAP Director, in consultation with the NELAC Board of Directors, for the purposes stated in 1.6.3.e. (NELAC) [1.6.3]
Accuracy: the degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components which are due to sampling and analytical operations; a data quality indicator. (QAMS) (AIHA LAQAP)
AIHA: American Industrial Hygiene Association (AIHA LQAP)
Aliquot (subsample): A representative portion of a sample. It may be taken from any location or from a field sample. (AIHA LQAP)
Analysis: The qualitative or quantitative determination of a property or analyte in a substance or material. (AIHA LQAP)
Analyst: the designated individual who performs the "hands-on" analytical methods and associated techniques and who is the one responsible for applying required laboratory practices and other pertinent quality controls to meet the required level of quality. (NELAC)
Analytical Run: An analytical run consists of all samples processed continuously using an item of instrumentation or equipment. Such samples are analyzed applying the same set of standard calibration data. (AIHA LQAP)
Analytical Sensitivity: The lowest concentration that can be detected by the method, based upon the amount or portion of sample analyzed (e.g., for methods involving a count = 1 raw count per amount or portion of sample analyzed, calculated and expressed in the final reporting units) (AIHA LQAP).
Applicant Laboratory or **Applicant:** the laboratory or organization applying for NELAP accreditation. (NELAC)
Approved Signatory: Person who is recognized by a laboratory as competent and authorized by the laboratory management to sign test reports. (AIHA LQAP)
Asbestos: A commercial term applied to the asbestiform varieties of six different minerals. The asbestos types are chrysotile, amosite, crocidolite, and asbestiform anthophyllite, asbestiform tremolite, and asbestiform actinolite. The properties of asbestos that caused it to be widely used commercially are: 1) its ability to be separated into long, thin, flexible fibers; 2) high tensile strength; 3) low thermal and electrical conductivity; 4) high chemical and mechanical durability; and 5) high heat resistance.

Assessment: the evaluation process used to measure or establish the performance, effectiveness, and conformance of an organization and/or its systems to defined criteria (to the standards and requirements of NELAC). (NELAC)
Assessment Criteria: the measures established by NELAC and applied in establishing the extent to which an applicant is in conformance with NELAC requirements. (NELAC)
Assessment Team: the group of people authorized to perform the on-site inspection and proficiency testing data evaluation required to establish whether an applicant meets the criteria for NELAP accreditation. (NELAC)
Assessor: One who performs on-site assessments of accrediting authorities and laboratories' capability and capacity for meeting NELAC requirements by examining the records and other physical evidence for each one of the tests for which accreditation has been requested. (NELAC)
A person who conducts technical systems audits. Used interchangeable with site visitor, and auditor. (AIHA LQAP)
Assessor Body: the organization that actually executes the accreditation process, i.e., receives and reviews accreditation applications, reviews QA documents, reviews proficiency testing results, performs on-site assessments, etc., whether EPA, the State, or contracted private party. (NELAC)
ASTM: American Society for Testing and Materials
Audit: a systematic evaluation to determine the conformance to quantitative and qualitative specifications of some operational function or activity. (EPA-QAD)
Batch: environmental samples that are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents. A **preparation batch** is composed of one to 20 environmental samples of the same NELAC-defined matrix, meeting the above-mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be 24 hours. An **analytical batch** is composed of prepared environmental samples (extracts, digestates or concentrates) that are analyzed together as a group. An analytical batch can include prepared samples originating from various environmental matrices and can exceed 20 samples. (NELAC Quality Systems Committee)
A group of samples that are processed in one operation: considered to be a uniform, discrete unit (AIHA LQAP)
Bias: A systematic error manifested as a consistent positive or negative deviation from the known true value. (AIHA LQAP)
Blank: a sample that has not been exposed to the analyzed sample stream in order to monitor contamination during sampling, transport, storage or analysis. The blank is subjected to the usual analytical and measurement process to establish a zero baseline or background value and is sometimes used to adjust or correct routine analytical results. Blanks include:
Equipment Blank: a sample of analyte-free media that has been used to rinse common sampling equipment to check effectiveness of decontamination procedures. (NELAC)
Field Blank: blank prepared in the field by filling a clean container with pure de-ionized water and appropriate preservative, if any, for the specific sampling activity being undertaken. (EPA OSWER)
Instrument Blank: a clean sample (e.g., distilled water) processed through the instrumental steps of the measurement process; used to determine instrument contamination. (EPA-QAD)
Method Blank: a sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed simultaneously with and under the same

conditions as samples through all steps of the analytical procedures, and in which no target analytes or interferences are present at concentrations that impact the analytical results for sample analyses. (NELAC)
Reagent Blank: (method reagent blank): a sample consisting of reagent(s), without the target analyte or sample matrix, introduced into the analytical procedure at the appropriate point and carried through all subsequent steps to determine the contribution of the reagents and of the involved analytical steps. (QAMS)
Blind Sample: a sub-sample for analysis with a composition known to the submitter. The analyst/laboratory may know the identity of the sample but not its composition. It is used to test the analyst or laboratory's proficiency in the execution of the measurement process. (NELAC)
A sample submitted for analysis with a composition and identity known to the submitter, but unknown to the analyst, and used to evaluate proficiency in the execution of the measurement process. (AIHA LQAP)
Calibration: to determine, by measurement or comparison with a standard, the correct value of each scale reading on a meter, instrument, or other device. The levels of the applied calibration standard should bracket the range of planned or expected sample measurements. (NELAC)
A set of operations used: (1) to determine the value of a reference standard or reference material to a stated uncertainty; or (2) to determine the accuracy of the reading of a test device to a stated uncertainty. (AIHA LQAP)
Calibration Curve: the graphical relationship between the known values, such as concentrations, of a series of calibration standards and their instrument response. (NELAC)
A graphical relationship between the known values for a series of calibration standards and instrument responses. The levels of the calibration standards should bracket the range of measurements. (AIHA)
Calibration Method: a defined technical procedure for performing a calibration. (NELAC)
Calibration Standard: a substance or reference material used to calibrate an instrument. (QAMS)
Certification: Procedure by which a third party gives written assurance that the competence of a person, organization, or other entity to perform a function or service conforms to specified requirements. (AIHA LQAP)
Certified Reference Material (CRM): a reference material, one or more of whose property values are certified by a technically valid procedure, accompanied by or traceable to a certificate or other documentation which is issued by a certifying body. (ISO Guide 30 - 2.2)
A reference material that has one or more of its property values established by a technically valid procedure, and is accompanied by or traceable to a certificate or other documentation issued by a certifying body. (AIHA LQAP)
Chain-of-Custody: Definitive evidence (a record) of the persons who had possession or custody of the sample(s) for all periods of time, as it moved from the point of collection to the final analytical result. (AIHA LQAP)
Chain-of-Custody Form: record that documents the possession of the samples from the time of collection to receipt in the laboratory. This record generally includes: the number and types of containers, the mode
Check Sample: An uncontaminated sample matrix spiked with a known amount of analyte, usually from the same source as the calibration standard. It is generally used to establish the

stability of the analytical system, but also may be used to assess the performance of all or a portion 2 of the measurement system. (AIHA LQAP)

Clean Air Act: the enabling legislation in 42 U.S.C. 7401 *et seq.*, Public Law 91-604, 84 Stat. 1676 Pub. L. 95-95, 91 Stat., 685 and Pub. L. 95-190, 91 Stat., 1399, as amended, empowering EPA to promulgate air quality standards, monitor and to enforce them. (NELAC)

Client: See Customer.

Comparability: Refers to the ability to compare data from different sources with a degree of confidence.

Completeness: Refers to the amount of data that is successfully collected with respect to that amount intended in the study design.

Comprehensive Environmental Response, Compensation and Liability Act (CERCLA/Superfund): the enabling legislation in 42 U.S.C. 9601-9675 et seq., as amended by the Superfund Amendments and Reauthorization Act of 1986 (SARA), 42 U.S.C. 9601et seq., to eliminate the health and environmental threats posed by hazardous waste sites. (NELAC)

Confidential Business Information (CBI): information that an organization designates as having the potential of providing a competitor with inappropriate insight into its management, operation or products. NELAC and its representatives agree to safeguard identified CBI and to maintain all information identified as such in full confidentiality.

Confirmation: verification of the identity of a component through the use of an approach with a different scientific principle from the original method. These may include, but are not limited to:
Second column confirmation
Alternate wavelength
Derivatization
Mass spectral interpretation
Alternative detectors or
Additional cleanup procedures. (NELAC)

Conformance: an affirmative indication or judgment that a product or service has met the requirements of the relevant specifications, contract, or regulation; also the state of meeting the requirements. (ANSI/ASQC E4-1994)

Contributor: a participant in NELAC who is not a Voting Member. Contributors include representatives of laboratories, manufacturers, industry, business, consumers, academia, laboratory associations, laboratory accreditation associations, counties, municipalities, and other political subdivisions, other federal and state officials not engaged in environmental activities, and other persons who are interested in the objectives and activities of NELAC. (NELAC)[Art III, Const]

Control Chart: A graph of some measurement plotted over time or sequence of sampling, together with control limit(s) and, usually, a central line and warning limit(s). (AIHA LQAP)

Corrective Action: the action taken to eliminate the causes of an existing nonconformity, defect or other undesirable situation in order to prevent recurrence. (ISO 8402)
All activities taken, whether unsuccessful or not, to eliminate the cause(s) of an existing nonconformity or deficiency in order to prevent recurrence. (AIHA LQAP)

Customer: Any person or organization that engages the services of a laboratory. Used interchangeably with “client” in this and other quality system documents.

Data Audit: a qualitative and quantitative evaluation of the documentation and procedures associated with environmental measurements to verify that the resulting data are of acceptable quality (i.e., that they meet specified acceptance criteria). (NELAC)
Data Reduction: the process of transforming raw data by arithmetic or statistical calculations, standard curves, concentration factors, etc., and collation into a more useable form. (EPA-QAD)
Deficiency: an unauthorized deviation from acceptable procedures or practices, or a defect in an item. (ASQC)
A failure to comply with a requirement of the AIHA Accreditation Program(s) or a laboratory's own stated quality system requirements. (AIHA LQAP)
Delegate: any environmental official of the States or the Federal government not sitting in the House of Representatives, who is eligible to vote in the House of Delegates. (NELAC)
Demonstration of Capability: a procedure to establish the ability of the analyst to generate acceptable accuracy. (NELAC)
Denial: to refuse to accredit in total or in part a laboratory applying for initial accreditation or resubmission of initial application. (NELAC)[4.4.1]
Detection Limit: the lowest concentration or amount of the target analyte that can be identified, measured, and reported with confidence that the analyte concentration is not a false positive value. See Method Detection Limit. (NELAC)
Determination: An analysis with a qualitative result. (AIHA LQAP)
Deviation: A departure from written procedures, test methods, contracts or any other standard operating procedure that is part of the laboratory Quality Assurance System. (AIHA LQAP)
Document Control: the act of ensuring that documents (and revisions thereto) are proposed, reviewed for accuracy, approved for release by authorized personnel, distributed properly and controlled to ensure use of the correct version at the location where the prescribed activity is performed. (ASQC)
Duplicate Samples: Two samples taken from and representative of the same population and carried through all steps of the sampling and analytical procedures in an identical manner. Duplicate samples are used to assess variance of the total method including sampling and analysis. (AIHA LQAP)
Environmental Laboratory Advisory Board (ELAB): a Federal Advisory Committee, with members appointed by EPA and composed of a balance of non-state, non-federal representatives, from the environmental laboratory community, and chaired by an ELAB member. (NELAC)[1.6.2]
Environmental Lead Laboratory Accreditation Program (ELLAP): This AIHA program complies with the requirements of the EPA National Lead Laboratory Accreditation Program (NLLAP) Laboratory Quality System Requirements (LQSR) and also conforms to the ISO/IEC 17025 Standard and ISO/IEC Guide 58 requirements. (AIHA LQAP)
Environmental Lead Proficiency Analytical Testing (ELPAT): Required quarterly quality assurance lead samples of various matrices analyzed by all accredited and participating laboratories of the ELLAP. Results are evaluated by AIHA and are used to determine laboratory proficiency. (AIHA LQAP)
Environmental Monitoring Management Council (EMMC): an EPA Committee consisting of EPA managers and scientists, organized into a Policy Council, a Steering Group, *ad hoc* Panels, and work groups addressing specific objectives, established to address EPA-wide monitoring issues. (NELAC)

Equipment: All physical items (including software and instruments) in the facility used in the performance of analytical testing. (AIHA LQAP)

Equipment Log: A chronological record of preventive and emergency maintenance performed on any equipment. The logs include a record of calls, service technician summaries, records of calibration by the manufacturer, routine user maintenance, and other information as required by these policies. (AIHA LQAP)

Federal Insecticide, Fungicide and Rodenticide Act (FIFRA): the enabling legislation under 7 U.S.C. 135 *et seq.*, as amended, that empowers the EPA to register insecticides, fungicides, and rodenticides. (NELAC)

Federal Water Pollution Control Act (Clean Water Act, CWA): the enabling legislation under 33 U.S.C. 1251 *et seq.*, Public Law 92-50086 Stat. 816, that empowers EPA to set discharge limitations, write discharge permits, monitor, and bring enforcement action for non-compliance. (NELAC)

Field Blank: An analyte-free matrix carried to the sampling site, exposed to the sampling conditions (e.g., bottle caps removed), returned to the laboratory, treated as a sample, and carried through all steps of the analysis. For example, a clean culture media plate, sorbent tube, or a clean filter could be used as a field blank. The field blank, which should be treated just like the sample, evaluates possible effects attributable to shipping and field handling procedures. (AIHA LQAP)

Field of Accreditation: (previously Field of Testing) NELAC's approach to accrediting laboratories by matrix, technology/method and analyte/analyte group. Laboratories requesting accreditation for a matrix-technology/method-analyte/analyte group combination or for an updated/improved method are required to submit only that portion of the accreditation process not previously addressed (see NELAC, section 1.8 ff). (NELAC)

Field of Proficiency Testing: NELAC's approach to offering proficiency testing by matrix, technology, and analyte/analyte group.

FoT: Field of Testing

Finding: an assessment conclusion that identifies a condition having a significant effect on an item or activity. An assessment finding is normally a deficiency and is normally accompanied by specific examples of the observed condition. (NELAC)

Governmental Laboratory: as used in these standards, a laboratory owned by a Federal, state, or tribal government; includes government-owned contractor-operated laboratories. (NELAC)

Holding Times (Maximum Allowable Holding Times): the maximum times that samples may be held prior to analysis and still be considered valid or not compromised. (40 CFR Part 136)

Inspection: an activity such as measuring, examining, testing, or gauging one or more characteristics of an entity and comparing the results with specified requirements in order to establish whether conformance is achieved for each characteristic. (ANSI/ASQC E4-1994)

Interim Accreditation: temporary accreditation status for a laboratory that has met all accreditation criteria except for a pending on-site assessment which has been delayed for reasons beyond the control of the laboratory. (NELAC)

Inter-laboratory Comparisons: Evaluation of tests on the same or similar items by two or more laboratories. (AIHA LQAP)

Internal Quality Control: Routine activities and checks, such as periodic calibrations, duplicate analyses and matrix spikes that are included in routine internal procedures to control the accuracy and precision of measurements.

Internal Standard: a known amount of standard added to a test portion of a sample as a reference for evaluating and controlling the precision and bias of the applied analytical method. (NELAC)

Laboratory: a body that calibrates and/or tests. (ISO 25) An entity that tests, either at a fixed site, mobile facility or field operations facility. (AIHA LQAP)

Laboratory Assessment: An onsite evaluation of a laboratory for the purpose of conducting a technical systems audit to assess compliance with AIHA accreditation requirements and technical competence to perform the testing for which the Lab is seeking accreditation. (AIHA LQAP)

Laboratory Control Sample (however named, such as laboratory fortified blank, spiked blank, or QC check sample): A sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes. It is generally used to establish intra-laboratory or analyst specific precision and bias or to assess the performance of all or a portion of the measurement system. (NELAC)

Laboratory Control Sample (LCS)/Method Spike Sample: A matrix-based reference material with an established concentration obtained from a source independent of the instrument calibration and traceable to NIST or other similar reference materials. The LCS is carried through the entire procedure from sample preparation through analysis as if it were a field sample. The purpose of the LCS is to evaluate bias of the method. (AIHA LQAP)

Laboratory Control Sample Duplicate (LCSD)/Method Spike Sample Duplicate: A duplicate of the LCS. (AIHA LQAP)

Laboratory Duplicate: aliquots of a sample taken from the same container under laboratory conditions and processed and analyzed independently. (NELAC)

Laboratory Quality Assurance Program(s) (LQAP): General term referring to any AIHA program or programs established to maintain the highest possible standards of performance for analysts and/or laboratories analyzing samples and evaluating exposures to hazardous agents. (AIHA LQAP)

Legal Chain-of-Custody Protocols: procedures employed to record the possession of samples from the time of sampling until analysis and are performed at the special request of the customer. These protocols include the use of a Chain of Custody Form that documents the collection, transport, and receipt of compliance samples by the laboratory. **In addition, these protocols document all handling of the samples within the laboratory**. (NELAC)

Manager (however named): the individual designated as being responsible for the overall operation, all personnel, and the physical plant of the environmental laboratory. A supervisor may report to the manager. In some cases, the supervisor and the manager may be the same individual. (NELAC)

Matrix: the substrate of a test sample.

Field of Accreditation Matrix: these matrix definitions shall be used when accrediting a laboratory (see Field of Accreditation).

Drinking Water: any aqueous sample that has been designated a potable or potential potable water source.

Non-Potable Water: any aqueous sample excluded from the definition of Drinking Water matrix; includes surface water, groundwater, effluents, water treatment chemicals, and TCLP or other extracts.

Solid and Chemical Materials: includes soils, sediments, sludges, products and by-products of an industrial process that results in a matrix not previously defined.

Biological Tissue: any sample of a biological origin such as fish tissue, shellfish, or plant material. Such samples shall be grouped according to origin.

Air and Emissions: whole gas or vapor samples including those contained in flexible or rigid wall containers and the extracted concentrated analytes of interest from a gas or vapor that are collected with a sorbent tube, impinger solution, filter, or other device. (NELAC).

Quality System Matrix: These matrix definitions are an expansion of the field of accreditation matrices and shall be used for purposes of batch and quality control requirements. These matrix distinctions shall be used:

Aqueous: any aqueous sample excluded from the definition of Drinking Water matrix or Saline/Estuarine source; includes surface water, groundwater, effluents, and TCLP or other extracts.

Drinking Water: any aqueous sample that has been designated a potable or potential potable water source.

Saline/Estuarine: any aqueous sample from an ocean or estuary, or other salt-water source such as the Great Salt Lake.

Non-aqueous Liquid: any organic liquid with <15% settleable solids.

Biological Tissue: any sample of a biological origin such as fish tissue, shellfish, or plant material. Such samples shall be grouped according to origin.

Solids: includes soils, sediments, sludges and other matrices with >15% settleable solids.

Chemical Waste: a product or by-product of an industrial process that results in a matrix not previously defined.

Air and Emissions: whole gas or vapor samples including those contained in flexible or rigid wall containers and the extracted concentrated analytes of interest from a gas or vapor that are collected with a sorbent tube, impinger solution, filter, or other device. (NELAC)

The component or substrate (e.g., soil, air or charcoal tube) that contains the analyte of interest. (AIHA LQAP)

Matrix Spike (spiked sample or fortified sample): a sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available. Matrix spikes are used, for example, to determine the effect of the matrix on a method's recovery efficiency. (QAMS)

An aliquot of sample, or sample media, spiked with a known concentration of target analyte(s). The spiking occurs prior to sample preparation and analysis. (AIHA LQAP)

Matrix Spike Duplicate (spiked sample or fortified sample duplicate): a second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte. (QAMS)

May: denotes permitted action, but not required action.

Measurement Quality Objectives (MQOs): The desired sensitivity, range, precision, and bias of a measurement.

Method: see Test Method

Method Blank: An unexposed sampling media or reagent(s), not taken to the field or shipped, but carried through the complete sample preparation and analytical procedure. The blank is used to assess possible background contamination from the analytical process. This blank may also be referred to as a laboratory blank. (AIHA LQAP)

Method Detection Limit (MDL): the minimum concentration of a substance (an analyte) that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte. (40 CFR Part 136, Appendix B)

The minimum concentration of an analyte that, in a given matrix and with a specific method, has a 99 percent probability of being identified, qualitatively or quantitatively measured, and reported to be greater than zero. (AIHA LQAP)

Method Performance: A general term used to document the characteristics of a method. These characteristics usually include method detection limits, linearity, precision, accuracy and bias and uncertainty of measurement. See Acceptance Limits. (AIHA LQAP)

Must: denotes a requirement that must be met. (Random House College Dictionary)

National Accreditation Database: the publicly accessible database listing the accreditation status of all laboratories participating in NELAP. (NELAC)

National Institute of Standards and Technology (NIST): an agency of the US Department of Commerce's Technology Administration that is working with EPA, States, NELAC, and other public and commercial entities to establish a system under which private sector companies and interested States can be accredited by NIST to provide NIST-traceable proficiency testing (PT) to those laboratories testing drinking water and wastewater. (NIST)

National Environmental Laboratory Accreditation Conference (NELAC): a voluntary organization of State and Federal environmental officials and interest groups purposed primarily to establish mutually acceptable standards for accrediting environmental laboratories. A subset of NELAP. (NELAC)

National Environmental Laboratory Accreditation Program (NELAP): the overall National Environmental Laboratory Accreditation Program of which NELAC is a part. (NELAC)

National Voluntary Laboratory Accreditation Program (NVLAP): a program administered by NIST that is used by providers of proficiency testing to gain accreditation for all compounds/matrices for which NVLAP accreditation is available, and for which the provider intends to provide NELAP PT samples. (NELAC)

Negative Control: measures taken to ensure that a test, its components, or the environment do not cause undesired effects, or produce incorrect test results. (NELAC)

NELAC Standards: the plan of procedures for consistently evaluating and documenting the ability of laboratories performing environmental measurements to meet nationally defined standards established by the National Environmental Laboratory Accreditation Conference. (NELAC)

NELAP Recognition: the determination by the NELAP Director that an accrediting authority meets the requirements of the NELAP and is authorized to grant NELAP accreditation to laboratories. (NELAC)

Nonconformity: Noncompliance with any quality assurance policy, procedure, or specification. Nonconforming work results from an analysis event in which the QC results are not within acceptance limits and/or method specifications are not met. (AIHA LQAP)

Non-governmental Laboratory: any laboratory not meeting the definition of the governmental laboratory. (NELAC)

Performance Audit: the routine comparison of independently obtained qualitative and quantitative measurement system data with routinely obtained data in order to evaluate the proficiency of an analyst or laboratory. (NELAC)

Performance Based Measurement System (PBMS): a set of processes wherein the data quality needs, mandates or limitations of a program or project are specified and serve as criteria for selecting measurement processes which will meet those needs in a cost-effective manner. (NELAC)

Policy: An organization's written statement of commitment to implement a management program element. (AIHA LQAP)

Positive Control: measures taken to ensure that a test and/or its components are working properly and producing correct or expected results from positive test subjects. (NELAC)

Precision: the degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves; a data quality indicator. Precision is usually expressed as standard deviation, variance or range, in either absolute or relative terms. (NELAC)

The degree to which a set of observations or measurements of the same property, usually obtained under similar conditions, conform to themselves. Precision is often expressed as standard deviation, variance or range, in either absolute or relative terms. (AIHA LQAP)

Preventive Action: A planned activity to identify, recognize and control potential sources of nonconformity and to introduce needed improvements. (AIHA LQAP)

Procedure: A written set of instructions that describe how to implement a policy requirement, or how to carry out a specific task. (AIHA LQAP)

Preservation: refrigeration and/or reagents added at the time of sample collection (or later) to maintain the chemical and/or biological integrity of the sample. (NELAC)

Primary Accrediting Authority: the agency or department designated at the Territory, State or Federal level as the recognized authority with responsibility and accountability for granting NELAC accreditation for a specified field of testing. (NELAC)[1.5.2.3]

Proficiency Analytical Testing (PAT): Refers to any proficiency analytical testing program(s), such as the programs established under the Analytical Quality Programs. See Inter-laboratory Comparisons. (AIHA LQAP)

Proficiency Testing: a means of evaluating a laboratory's performance under controlled conditions relative to a given set of criteria through analysis of unknown samples provided by an external source. (NELAC)[2.1]

Proficiency Testing Oversight Body/Proficiency Testing Provider Accreditor (PTOB/PTPA): an organization with technical expertise, administrative capacity and financial resources sufficient to implement and operate a national program of PT provider evaluation and oversight that meets the responsibilities and requirements established by NELAC standards. (NELAC)

Proficiency Testing Program: the aggregate of providing rigorously controlled and standardized environmental samples to a laboratory for analysis, reporting of results, statistical evaluation of the results and the collective demographics and results summary of all participating laboratories. (NELAC)

Proficiency Testing Study Provider: any person, private party, or government entity that meets stringent criteria to produce and distribute NELAC PT samples, evaluate study results against published performance criteria and report the results to the laboratories, primary accrediting authorities, PTOB/PTPA, and NELAP. (NELAC)

Proficiency Test Sample (PT): a sample, the composition of which is unknown to the analyst and is provided to test whether the analyst/laboratory can produce analytical results within specified acceptance criteria. (QAMS)

Protocol: a detailed written procedure for field and/or laboratory operation (e.g., sampling, analysis) that must be strictly followed. (EPA-QAD)

Quality: The suitability of a product or service for use, as perceived by the user. (AIHA LQAP)

Quality Assurance: an integrated system of activities involving planning, quality control, quality assessment, reporting and quality improvement to ensure that a product or service meets defined standards of quality with a stated level of confidence. (QAMS)

An integrated system of activities involving planning, quality control, quality assessment, reporting, and quality improvement to ensure a product or service meets defined standards of quality within a stated level of confidence. (AIHA LQAP)

Quality Assurance [Project] Plan (QAPP): a formal document describing the detailed quality control procedures by which the quality requirements defined for the data and decisions pertaining to a specific project are to be achieved. (EPA-QAD)

Quality Control: the overall system of technical activities whose purpose is to measure and control the quality of a product or service so that it meets the needs of users. (QAMS)

Technical activities whose purpose is to measure and control the quality of a product or service so that it meets the needs of users. The aim is to provide quality that is satisfactory, adequate, dependable and economical. (AIHA LQAP)

Quality Control Sample: an uncontaminated sample matrix spiked with known amounts of analytes from a source independent from the calibration standards. It is generally used to establish intra-laboratory or analyst specific precision and bias or to assess the performance of all or a portion of the measurement system. (EPA-QAD)

Quality Manager: The Quality Manger is responsible for implementation of the Quality Management System with direct access to the highest levels of management. The Quality Manger is responsible for planning and organizing audits.

Quality Management System: System to establish a quality policy and quality objectives and to achieve those objectives.

Quality Manual: a document stating the management policies, objectives, principles, organizational structure and authority, responsibilities, accountability, and implementation of an agency, organization, or laboratory, to ensure the quality of its product and the utility of its product to its users. (NELAC)

A document stating the quality policy, quality system and internal quality control procedures of the laboratory. (AIHA LQAP)

Quality System: a structured and documented management system describing the policies, objectives, principles, organizational authority, responsibilities, accountability, and implementation plan of an organization for ensuring quality in its work processes, products (items), and services. The quality system provides the framework for planning, implementing, and assessing work performed by the organization and for carrying out required QA and QC activities.

Quantitation Limits: levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported at a specified degree of confidence. (NELAC)
Range: the difference between the minimum and the maximum of a set of values. (EPA-QAD)
Raw Data: any original factual information from a measurement activity or study recorded in a laboratory notebook, worksheets, records, memoranda, notes, or exact copies thereof that are necessary for the reconstruction and evaluation of the report of the activity or study. Raw data may include photography, microfilm or microfiche copies, computer printouts, magnetic media, including dictated observations, and recorded data from automated instruments. If exact copies of raw data have been prepared (e.g., tapes which have been transcribed verbatim, data and verified accurate by signature), the exact copy or exact transcript may be submitted. (EPA-QAD)
Recognition: previously known as reciprocity. The mutual agreement of two or more parties (i.e., States) to accept each other's findings regarding the ability of environmental testing laboratories in meeting NELAC standards. (NELAC)[1.5.3]
Reference Material: a material or substance one or more properties of which are sufficiently well established to be used for the calibration of an apparatus, the assessment of a measurement method, or for assigning values to materials. (ISO Guide 30-2.1)
A material or substance, one or more properties of which are sufficiently homogeneous and well established to be used to monitor instrument and method performance. AIHA PAT samples may be used as reference materials. (AIHA LQAP)
Reference Method: a method of known and documented accuracy and precision issued by an organization recognized as competent to do so. (NELAC)
Reference Standard: a standard, generally of the highest metrological quality available at a given location, from which measurements made at that location are derived. (VIM-6.08)
A substance or reference material used to calibrate an instrument. Reference standards shall be NIST traceable or equivalent and of the highest quality available at the location. (AIHA LQAP)
Reference Toxicant: the toxicant used in performing toxicity tests to indicate the sensitivity of a test organism and to demonstrate the laboratory's ability to perform the test correctly and obtain consistent results (see Chapter 5, Appendix D, section 2.1f). (NELAC)
Relative Percent Difference (RPD): A term defined as RPD = ((R1 – R2)/R) x 100 where R1 – R2 represents the absolute difference of two (2) values and R represents the average of the two (2) values. (AIHA LQAP)
Relevant Degree: A program of collegiate study that is appropriate to the applicable accreditation program. (AIHA LQAP)
Replicate Analyses: the measurements of the variable of interest performed identically on two or more sub-samples of the same sample within a short time interval. (NELAC)
Reporting Limit: The lowest concentration of analyte in a sample that can be reported with a defined, reproducible level of certainty. This value is based on the low standard used for instrument calibration. For environmental lead analyses, the reporting limit must be at least twice the MDL. (AIHA LQAP)
Representativeness: Refers to the degree to which the data collected accurately reflect the population, group or medium being sampled.
Requirement: denotes a mandatory specification; often designated by the term "shall". (NELAC)
An essential criterion necessary for accreditation. (AIHA LQAP)

Resource Conservation and Recovery Act (RCRA): the enabling legislation under 42 USC 321 *et seq.* (1976), that gives EPA the authority to control hazardous waste from the "cradle-to-grave", including its generation, transportation, treatment, storage, and disposal. (NELAC)

Revocation: the total or partial withdrawal of a laboratory's accreditation by the accrediting authority. (NELAC)[4.4.3]

The formal, permanent removal of a laboratory's accreditation for noncompliance with AIHA accreditation requirements. (AIHA LQAP)

Removal of the accredited status of a laboratory if the laboratory is found to have violated the conditions for accreditation. (NIST)

Run: A set of consecutive measurements performed on different samples. (AIHA LQAP)

Safe Drinking Water Act (SDWA): the enabling legislation, 42 USC 300f *et seq.* (1974), (Public Law 93-523), that requires the EPA to protect the quality of drinking water in the U.S. by setting maximum allowable contaminant levels, monitoring, and enforcing violations. (NELAC)

Sample: for instrumental analyses, a sample is defined as an analytical determination. Thus a Continuing Calibration Verification Standard (CCV) is analyzed after every ten determinations, regardless of the type of sample (QC sample or test sample). For those test methods that require the analysis of an Initial or Continuing Calibration Blank (ICB or CCB) after the ICV or CCV analysis, the ICB or CCB is not counted as a determination. In addition, if a reagent/solvent blank analysis (rinse blank) is performed to ensure that carryover from a highly concentrated sample has not contaminated the system, this is not counted as a determination. For certain analyses (i.e., GC/MS), the requirement to analyze a CCV is per number of hours, not per number of determinations.

Sample Log: A document where sample identification, date received, customer, etc., are noted when samples arrive at the laboratory. The log is part of the sample tracking system. See Sample Tracking. (AIHA LQAP)

Sample Tracking: procedures employed to record the possession of the samples from the time of sampling until analysis, reporting, and archiving. These procedures include the use of a Chain of Custody Form that documents the collection, transport, and receipt of compliance samples to the laboratory. In addition, access to the laboratory is limited and controlled to protect the integrity of the samples. (NELAC)

A document system of following a sample from receipt at the laboratory, through sample processing and analysis, to final reporting. The system includes unique numbering, or bar coding labels, and the use of a Sample Log. (AIHA LQAP)

Secondary Accrediting Authority: the Territorial, State or federal agency that grants NELAC accreditation to laboratories, based upon their accreditation by a NELAP-recognized Primary Accrediting Authority. See also **Recognition** and **Primary Accrediting Authority**. (NELAC)[1.5.2.3]

Selectivity: (Analytical chemistry) the capability of a test method or instrument to respond to a target substance or constituent in the presence of non-target substances. (EPA-QAD)

Sensitivity: the capability of a method or instrument to discriminate between measurement responses representing different levels (e.g., concentrations) of a variable of interest. (NELAC)

Shall: denotes a requirement that is mandatory whenever the criterion for conformance with the specification requires that there is no deviation. This does not prohibit the use of alternative approaches or methods for implementing the specification so long as the requirement is fulfilled. (ANSI)

Should: denotes a guideline or recommendation whenever noncompliance with the specification is permissible. (ANSI)
Spike: a known mass of target analyte added to a blank sample or sub-sample; used to determine recovery efficiency or for other quality control purposes. (NELAC)
SRM (NIST Standard Reference material): A reference material certified and distributed by the National Institute of Standards and Technology.
Standard: the document describing the elements of laboratory accreditation that has been developed and established within the consensus principles of NELAC and meets the approval requirements of NELAC procedures and policies. (ASQC)
A substance or material with properties believed to be known with sufficient accuracy to permit its use to evaluate the same property of another. In chemical measurements, it often describes a solution or substance commonly prepared by the analyst to establish a calibration curve or the analytical response function of an instrument. (AIHA LQAP)
Standard Administrative Procedure (SAP): a written procedure that details administrative operations that thoroughly prescribes actions to be taken
Standard Operating Procedures (SOPs): a written document which details the method of an operation, analysis or action whose techniques and procedures are thoroughly prescribed and which is accepted as the method for performing certain routine or repetitive tasks. (QAMS)
A written document that details the procedures of an operation; an analysis or action whose techniques and procedures are thoroughly prescribed, and which are accepted as the procedure for performing certain routine or repetitive tasks. (AIHA LQAP)
Standard Reference Material (SRM): a certified reference material produced by the U.S. National Institute of Standards and Technology or other equivalent organization and characterized for absolute content, independent of analytical method. (EPA-QAD)
A certified reference material produced by the U.S. National Institute of Standards and Technology (NIST) and characterized for absolute content independent of analytical method. It is accompanied by a certificate that reports the results of the characterization and the intended use of the material. (AIHA LQAP)
Standardization: The process of establishing the quantitative relationship between a known mass of target material and the measurement system (example, instrument response). See Calibration and Calibration curve. The term may also refer to activities that establish provisions for common and repeated use of accreditation policies to achieve an optimum level of conformity. (AIHA LQAP)
Statistical Minimum Significant Difference (SMSD): the minimum difference between the control and a test concentration that is statistically significant; a measure of test sensitivity or power. The power of a test depends in part on the number of replicates per concentration; the significance level selected, e.g., 0.05, and the type of statistical analysis. If the variability remains constant, the sensitivity of the test increases as the number of replicates is increased. (NELAC)
Stock Solution: A concentrated solution of analyte(s) or reagent(s) prepared and verified by prescribed procedure(s), and used for preparing calibration standards. See Calibration Standard. (AIHA LQAP)
Subsample: A representative portion of a sample; a subsample may be taken from any location or a field sample; in analytical chemistry, an “aliquot.” (AIHA LQAP)

Suggestion: Suggested activity or advice for improving laboratory performance often made during a site assessment. A recommendation is not a requirement. (AIHA LQAP)

Supervisor (however named): the individual(s) designated as being responsible for a particular area or category of scientific analysis. This responsibility includes direct day-to-day supervision of technical employees, supply and instrument adequacy and upkeep, quality assurance/quality control duties and ascertaining that technical employees have the required balance of education, training and experience to perform the required analyses. (NELAC)

Surrogate: a substance with properties that mimic the analyte of interest. It is unlikely to be found in environment samples and is added to them for quality control purposes. (QAMS)

Suspension: temporary removal of a laboratory's accreditation for a defined period of time, which shall not exceed six months, to allow the laboratory time to correct deficiencies or area of noncompliance with the NELAC standards. (NELAC)[4.4.2]

A temporary removal of the accredited status of a laboratory when it is found to be out of compliance with specific program requirements. (AIHA LQAP)

Technical Director: individual(s) who has overall responsibility for the technical operation of the environmental testing laboratory. (NELAC)

Technical Systems Audit: A thorough, systematic, onsite, qualitative evaluation of facilities, equipment, personnel, training, procedures, record keeping, data validation, data management and reporting aspects of a total quality system. (AIHA LQAP)

Technology: a specific arrangement of analytical instruments, detection systems, and/or preparation techniques.

Test: a technical operation that consists of the determination of one or more characteristics or performance of a given product, material, equipment, organism, physical phenomenon, process or service according to a specified procedure. The result of a test is normally recorded in a document sometimes called a test report or a test certificate. (ISO/IEC Guide 2-12.1, amended)

A technical operation that consists of determining one or more elements in a sample according to a specified procedure. (AIHA LQAP)

Test Method: an adoption of a scientific technique for a specific measurement problem, as documented in a laboratory SOP or published by a recognized authority. (NELAC)

Specified technical procedure for performing a test. See Standard Operating Procedure (AIHA LQAP)

Testing Laboratory: a laboratory that performs tests. (ISO/IEC Guide 2-12.4)

Test Sensitivity/Power: the minimum significant difference (MSD) between the control and test concentration that is statistically significant. It is dependent on the number of replicates per concentration, the selected significance level, and the type of statistical analysis (see Chapter 5, Appendix D, section 2.4.a). (NELAC)

Tolerance Chart: A chart in which the plotted quality control data is assessed via a tolerance level (e.g. +/- 10% of a mean) based on the precision level judged acceptable to meet overall quality/data use requirements instead of a statistical acceptance criteria (e.g. +/- 3 sigma) (applies to radiobioassay laboratories). (ANSI)

Toxic Substances Control Act (TSCA): the enabling legislation in 15 USC 2601 *et seq.*, (1976), that provides for testing, regulating, and screening all chemicals produced or imported into the United States for possible toxic effects prior to commercial manufacture. (NELAC)

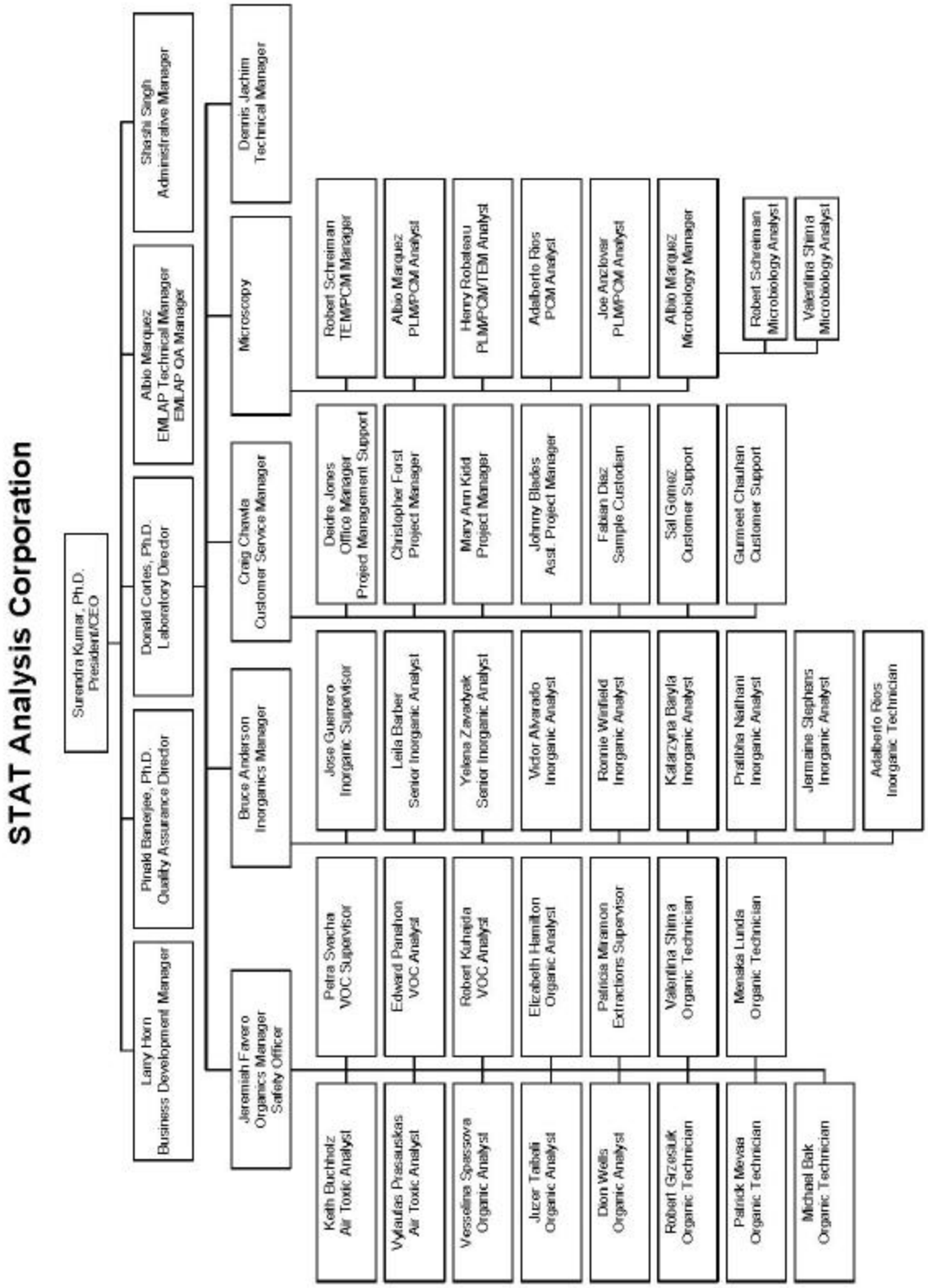
Traceability: Property of the result of a measurement or the value of a standard whereby it can be related to stated references, usually international or national standards, through an unbroken chain of comparisons all having stated uncertainties. (NIST)
The process of documenting the value of a reference material or standard as related to NIST standards or equivalent through an unbroken chain of comparisons with stated uncertainties. (AIHA LQAP)
Uncertainty of Measurement: Result of the evaluation aimed at characterizing the range within which the true value of a test result is estimated to lie, generally within a given likelihood. (AIHA LQAP)
Parameter, associated with the result of a measurement that characterizes the dispersion of the values that could reasonably be attributed to the measurand. (NIST)
United States Environmental Protection Agency (EPA): the federal governmental agency with responsibility for protecting public health and safeguarding and improving the natural environment (i.e., the air, water, and land) upon which human life depends. (US-EPA)
Validation: the process of substantiating specified performance criteria. (EPA-QAD)
The process of confirming specified method performance criteria. (AIHA LQAP)
Verification: confirmation by examination and provision of evidence that specified requirements have been met. (NELAC)
NOTE: In connection with the management of measuring equipment, verification provides a means for checking that the deviations between values indicated by a measuring instrument and corresponding known values of a measured quantity are consistently smaller than the maximum allowable error defined in a standard, regulation or specification peculiar to the management of the measuring equipment.
The result of verification leads to a decision either to restore in service, to perform adjustment, to repair, to downgrade, or to declare obsolete. In all cases, it is required that a written trace of the verification performed shall be kept on the measuring instrument's individual record.
Confirmation by examination and provision of evidence that specified requirements have been met. (AIHA LQAP)
Voting Member: officials in the employ of the Government of the United States, and the States, the Territories, the Possessions of the United States, or the District of Columbia and who are actively engaged in environmental regulatory programs or accreditation of environmental laboratories. (NELAC)
Work Cell: a well-defined group of analysts that together perform the method analysis. The members of the group and their specific functions within the work cell must be fully documented. (NELAC)

Appendix 1

Summary of Changes from Rev 08

- Most Sections revised to replace “client” with “customer” and “nonconformance” with “nonconformity.”
- A paragraph describing STAT’s policy regarding use of NVLAP term, logo, and symbol has been added in the Policy statement.
- The organization chart, the document master list, and the equipment list were updated. .
- Minor editorial revisions

APPENDIX 2: Organizational Chart



APPENDIX 3: DOCUMENT MASTER LIST
ADMINISTRATIVE SOPs

SOP Number	STAT SOP
ADMINISTRATIVE PROCEDURES	
005	SOP 005 Document Control
006	SOP 006 Management Review of Quality System
100	SOP 100 SOP on SOPs
230	SOP QA 230 Corrective Action
240	SOP 240 Archiving
1000	SOP 1000 Control and Use of Laboratory Notebooks
1010	SOP 1010 Analytical Standards and Reagents Receipt and Preparation
1020	SOP QA 1020 Laboratory Glassware Cleaning
1040	SOP 1040 General Laboratory Practices
1210	SOP 1210 Method Detection Limits
1220	SOP 1220 Internal Quality Assurance Audit
1230	SOP 1230 Training
1250	SOP 1250 Data Review
1255	SOP 1255 Manual Integration
1270	SOP 1270 Uncertainty
SAFETY DEPARTMENT	
003	SOP QA 003 Chemical Hygiene Plan
1130	SOP 1130 Waste Disposal
CUSTOMER SERVICE DEPARTMENT	
220	SOP 220 Customer Service
300	SOP 300 Sample Receiving and Login Procedures
1330	SOP 1330 Purchasing
INFORMATION TECHNOLOGY DEPARTMENT	
1400	SOP 1400 LIMS
1500	SOP 1500 Computer Network

APPENDIX 3: DOCUMENT MASTER LIST (cont.'d)
NELAC APPROVED TEST METHODS

Laboratory Test Method	STAT SOP
SW846 9095A	SOP 2010 Paint Filter Liquids Test by EPA Method 9095A
SW846 1311	SOP 2125 Leaching Procedures (Toxicity Characteristic Leaching Procedure (EPA Method 1311))
SW846 1312	SOP 2125 Leaching Procedures (Synthetic Precipitation Leaching Procedure (EPA Method 1312))
SW846 3005A	SOP 3005 SW848 3005 Acid Digestion of Waters for Total Recoverable or Dissolved Metals for Analysis by FLAA, ICP, or ICP-MS
SW846 3620B	SOP 3060 Florisil Clean up for PCBs and Pesticides (EPA Method 3620B)
SW846 3660B	SOP 3070 Sulfur & Sulfuric Acid/Permanganate Cleanup for PCBs and Pesticides (EPA Method 3660B & 3665A)
SW846 3665A	SOP 3070 Sulfur & Sulfuric Acid/Permanganate Cleanup for PCBs and Pesticides (EPA Method 3660B & 3665A)
SW846 3050B	SOP 3110 SW846 3050B Acid Digestion of Sediment, Sludges, and Soils for Metals Analysis by FLAA, ICP, or ICP-MS
SW846 3050B	SOP 3115 Extraction of High Volume Filters
SW846 3630C	SOP 3330 Silica Gel Cleanup for Semi-Volatile Organics (EPA Method 3630C)
SW846 3510C	SOP 3500 Extractions of Samples for Semi-Volatile Organic Analyses (EPA Methods 3510C, 3520C, 3540, 3545, 3550B, 3580A, 8151A)
SW846 3540	SOP 3500 Soxhlet Extraction: Extractions of Samples for Volatile and Semi-Volatile Organics (EPA Methods 3510C, 3520C, 3540, 3545, 3550B, 3580A, 8151A)

APPENDIX 3: DOCUMENT MASTER LIST (cont.'d)
NELAC APPROVED TEST METHODS

Laboratory Test Method	STAT SOP
SW846 3545	SOP 3500 Pressurized Fluid Extraction: Extractions of water nonsoluble or slightly soluble Semi-Volatile Organics (EPA Methods 3510C, 3520C, 3540, 3545, 3550B, 3580A, 8151A)
SW846 3550B	SOP 3500 Extractions of Samples for Semi-Volatile Organic Analyses (EPA Methods 3510C, 3520C, 3550B, 3580A, 8151A)
SW846 3580A	SOP 3500 Extractions of Samples for Semi-Volatile Organic Analyses (EPA Methods 3510C, 3520C, 3550B, 3580A, 8151A)
SW846 8151A	SOP 3500 Extractions of Samples for Semi-Volatile Organic Analyses (EPA Methods 3510C, 3520C, 3550B, 3580A, 8151A)
SW846 9012A	SOP 3610 Total and Amenable Cyanide: Distillation by EPA 9012A
SW846 Ch. 7	SOP 36154 Reactive Cyanide and Sulfide: Distillation by SW 846, Chapter 7.
SW846 9065	Phenolics: Distillation by EPA 9065.
SW846 8260B	SOP 4000 Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS) (EPA Methods 5030B/5035/ 8260B)
SW846 8270C	SOP 4020 Semi-Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS) (EPA Method 8270C)
SW846 8081A	SOP 4050 Organochlorine Pesticides & PolyChlorinated Biphenyl by Gas Chromatography/Electron Capture Detector (EPA Methods 8081A/8082)
SW846 8082	SOP 4050 Organochlorine Pesticides & PolyChlorinated Biphenyl by Gas Chromatography/Electron Capture Detector (EPA Methods 8081A/8082)

APPENDIX 3: DOCUMENT MASTER LIST (cont.'d)
NELAC APPROVED TEST METHODS

Laboratory Test Method	STAT SOP
ASTM Method D-4059	SOP 4051 PolyChlorinated Biphenyl by Gas Chromatography/Electron Capture Detector (ASTM Method D-4059)
SW846 8321A	SOP 4080 ChloroPhenoxy Herbicides by HPLC (EPA Method 8321A)
SW846 8015M	SOP 4090 Total Petroleum Hydrocarbons by GC/FID
SW846 1010	SOP 4105 Ignitibility by EPA 1010/ ASTM D93-02 Pensky-Martens Closed Cup and ASTM D1310 Tag Open Cup- DRAFT
SW846 9040B	SOP 4210 pH of Aqueous, Soil and Waste Samples by EPA Method 9040B, 9045C, 150.1
SW846 9045C	SOP 4210 pH of Aqueous, Soil and Waste Samples by EPA Method 9040B, 9045C, 150.1
SW846 8270C SIM	SOP 4500 Polynuclear Aromatic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS) with Selective Ion Monitoring (SIM) (EPA Method 8270C SIM)
SW846 6020	SOP 4510 Metals Analysis by Inductively Coupled Plasma- Mass Spectrometry (EPA Method 6020 and EPA Method IO-3.5)
SW846 7470A	SOP 4530 Mercury in Water, Solid or Semisolid Water (Manual Digestion/Automated Analysis Cold-Vapor Technique (EPA Method 7470A & 7471A)
SW846 7471A	SOP 4530 Mercury in Water, Solid or Semisolid Water (Manual Digestion/Automated Analysis Cold-Vapor Technique (EPA Method 7470A & 7471A)
SW846 3060A	SOP 4600 Automated Hexavalent Chromium Analysis by EPA Method 7196A and 3060A
SW846 7196A	SOP 4600 Automated Hexavalent Chromium Analysis by EPA Method 7196A and 3060A

APPENDIX 3: DOCUMENT MASTER LIST (cont.'d)
NELAC APPROVED TEST METHODS

Laboratory Test Method	STAT SOP
SW846 9012A	SOP 4610 Total and Amenable Cyanide: Distillation by 9012A
SW846 Chapter 7.3.3.2	SOP 4615 Reactive Cyanide and Sulfide: Distillation by SW846 Chapter 7
SW846 9065	SOP 4620 Phenolics 4AAP: Distillation by EPA 9065
EPA 415.1	SOP 4630 Total Organic Carbon By EPA 415.1
SW846 9012A	SOP 4710 Automated Cyanide Analysis by EPA 9012A
SW846 9066	SOP 4715 Automated Phenols – Analysis by EPA 9066
846 9034	SOP 4725 Automated Sulfide Analysis by EPA 376.2 and EPA 9034
EPA 410.4	SOP 4260 Chemical Oxygen Demand by EPA 410.4
SW846 9023	TOX, EOX in Soils and Waters by SW846 9023 and 9020-Draft

APPENDIX 3: DOCUMENT MASTER LIST (cont'd)
AIHA TEST METHODS

Laboratory Test Method	STAT SOP
NIOSH 7300	SOP 4515 Elements by ICP-MS by NIOSH 7300 -DRAFT
NIOSH 6009	SOP 4535 Mercury in Air Monitoring Cartridges by - NIOSH 6009
NIOSH 7082	SOP 4550 Lead Analysis of Lead by Atomic Absorption Direct Aspiration (NIOSH 7082, EPA IO-3.2, and EPA 7420)
OSHA 07, NIOSH (5515, 1400, 1501, 1500, 2000, 5503)	SOP 4700 Organic Vapors in Air Monitoring Cartridges by Gas Chromatography
NIOSH 7400	SOP 5100 Asbestos and Other Fibers by PCM
NIOSH 5515	SOP 4701 Polynuclear Aromatic Hydrocarbon in Air Monitoring Cartridges by GC/MS with Selective Ion Monitoring
OSHA 0500, 0600	SOP 4040 Sampling And Analysis of Ambient Air for Total Suspended Particulate Matter (SPM) And PM_{10} Using High Volume (HV) Sampler
SOP 6110	SOP 6110 Analysis of Non-Viable Microbiological Air Samples
SOP 6120	SOP 6120 Analysis of Viable Microbiological Air Samples
SOP 6210	SOP 6210 Analysis of Non-Viable Microbiological Samples by Direct Examination
SOP 6220	SOP 6220 Analysis of Viable Microbiological Swab and Bulk Samples
SOP 6310	SOP 6310 Preparation of Media
SOP 6410	SOP 6410 Microscope Alignment and Adjustment

APPENDIX 3: DOCUMENT MASTER LIST (cont.'d)
AMBIENT AIR TEST METHODS (ORDEQ/NELAC)

Laboratory Test Method	STAT SOP
EPA IO-3.1	SOP 3115 Extraction of High Volume Filters
SW846 3510, 3550B, 3580A	SOP 3500 Extractions of Samples for Semi-Volatile Organic Analyses (EPA Methods 3510C, 3520C, 3550B, 3580A, 8151A)
EPA TO-14A/15	SOP 4010 Volatile Organic Compounds in Ambient Air by 2-Stage Thermal Desorption/Gas Chromatography/Mass Spectrometry (GC/MS) (EPA Method TO-14A/TO-15)
EPA TO-14A/15	SOP 4011 Flow Calibration of Passive Air Sampling Equipment
EPA TO-13A	SOP 4030 Determination of Polycyclic Aromatic Hydrocarbons in Ambient Air Using Gas Chromatography/ Mass Spectrometry by EPA TO-13A
EPA IO-3.1	SOP 4040 Sampling And Analysis of Ambient Air for Total Suspended Particulate Matter (SPM) And PM_{10} Using High Volume (HV) Sampler
EPA IO-3.5	SOP 4510 Metals Analysis by Inductively Coupled Plasma- Mass Spectrometry (EPA Method 6020 AND EPA Method IO-3.5)
IO-3.2, EPA 7420	SOP 4550 Analysis of Lead by Atomic Absorption Direct Aspiration (NIOSH 7082, EPA IO-3.2, and EPA 7420)

APPENDIX 3: DOCUMENT MASTER LIST (cont.'d)
NIST/NVLAP METHODS

5100	SOP 5100 Phase Contrast Microscopy (PCM) Analysis
5200	SOP 5200 Polarized Light Microscopy (PLM) Analysis
5330	SOP 5300 Transmission Electron Microscopy (TEM) Sample Analysis

APPENDIX 3: DOCUMENT MASTER LIST (cont.'d)
OTHER TEST METHODS

Laboratory Test Method	STAT SOP
ASTM E1664	SOP 2000 Total Recoverable Oil & Grease by ASTM E1664 and EPA 9071B - DRAFT
SW846 9071B	SOP 2000 Total Recoverable Oil & Grease by ASTM E1664 and EPA 9071B - DRAFT
ATSM D4979	SOP 2040 Color, Order, Physical Description by ASTM D4979 - DRAFT
ASTM 5058-90	SOP 2080 Compatibility of Screening Analysis - DRAFT
ASTM 3987-85	SOP 2125 Leaching Procedures (ASTM D3987-85 Leaching Procedure)
EPA350.1	SOP 3250 Ammonia Distillation by EPA 350.1 - DRAFT
ASTM D93-80	SOP 4105 Ignitibility by EPA 1010 Pensky-Martens Closed Cup and ASTM D93-80 Open Cup – DRAFT
SW846 9050A	SOP 4200 Conductivity (Specific Conductance)
EPA 150.1	SOP 4210 pH of Aqueous, Soil and Waste Samples (EPA Method 9040B, 9045C, 150.1)
EPA 310.1	SOP 4230 Acidity and Alkalinity of Aqueous, Soil and Waste Samples by EPA 310.1 and ASTM M2310 B - DRAFT
ASTM M2310 B	SOP 4230 Acidity and Alkalinity of Aqueous, Soil and Waste Samples by EPA 310.1 and ASTM M2310 B - DRAFT
EPA 350.1	SOP 4250 Ammonia as N in Soil and Water by EPA 350.1 DRAFT
EPA 410.4	SOP 4260 Chemical Oxygen Demand by EPA 410.4
EPA 325.2	SOP 4280 Chloride in Soil and Water by EPA 325.2 - DRAFT

APPENDIX 3: DOCUMENT MASTER LIST (cont.'d)
OTHER TEST METHODS

Laboratory Test Method	STAT SOP
EPA 340.2	SOP 4290 Fluoride in Soil and Water by EPA 340.2 - DRAFT
ASTM D2937	SOP 4300 Density and Specific Gravity for Solids and Liquids by ASTM D2937 and D854 - DRAFT
ASTM D854	SOP 4300 Density and Specific Gravity for Solids and Liquids by ASTM D2937 and D854 - DRAFT
EPA 353.1	SOP 4400 Nitrates and Nitrites in Soils and Water by EPA 353.1, EPA 353.2 and EPA 354.1 - DRAFT
EPA 353.2	SOP 4400 Nitrates and Nitrites in Soils and Water by EPA 353.1, EPA 353.2 and EPA 354.1 - DRAFT
EPA 354.1	SOP 4400 Nitrates and Nitrites in Soils and Water by EPA 353.1, EPA 353.2 and EPA 354.1 - DRAFT
EPA 365.2	SOP 4450 Ortho-phosphate in Soils and Waters by EPA 365.2 - DRAFT
EPA 160.4	SOP 4480 % Ash, FOC, % Solids and % Moisture by EPA 160.4, ASTM D2974, and ASTM D2216 - DRAFT
ASTM D2974	SOP 4480 % Ash, FOC, % Solids and % Moisture by EPA 160.4, ASTM D2974, and ASTM D2216 - DRAFT
ASTM D2216	SOP 4480 % Ash, FOC, % Solids and % Moisture by EPA 160.4, ASTM D2974, and ASTM D2216 - DRAFT
EPA 160.1	SOP 4490 Total Dissolved, Total Settleable Solids, and Total Solids by EPA 160.1 and EPA 160.2 - DRAFT
EPA 160.2	SOP 4490 Total Dissolved, Total Settleable Solids, and Total Solids by EPA 160.1 and EPA 160.2 – DRAFT
EPA 376.2	SOP 4725 Automated Sulfide Analysis by EPA 376.2 and EPA 9034

APPENDIX 3: DOCUMENT MASTER LIST (cont.'d)

SOFTWARES

Semivolatile - Compact Discs
3Com EtherCD Version 5.1
3Com Fast EtherLink Server Adapter Software Release 2.0 Customized for Dell
Agilent 5973N MSD Maintenance Collection Rev. A.00.00
Agilent 6890 GC/ALS Service Information
Agilent 6890 Series GC Service Information
Agilent 6890N Series GC User Information
Agilent 7683B Automatic Liquid Sampler User Information
Agilent G1701DA User Information
Agilent HW User Info Kit 5975
Agilent LC ChemStation Spectral S/W Module Rev. A.09.01
Agilent MSD ChemStaion Software User Information
Agilent MSD ChemStation MNL Kit Rev. D.02.00
Agilent MSD Productivity Chemsta SW Core Rev. D.02.00
Agilent MSD Productivity ChemStation Revision D.01.02
Agilent MSD Productivity ChemStation Revision D.02.00 SP1
Agilent MSD Productivity ChemStation Software Rev. C.00.00
Agilent MSD Productivity ChemStation Software Rev. C.00.01
Agilent MSD Reference Collection
Agilent MSD Reference Collection Rev D.00.00
Agilent Technologies ALS Controller Software Utility
Agilent Technologies Recovery CD-ROM for HP Compaq DC7100 Windows XP SP2
Dell Dimension ResourceCD
Dell E770s Color Monitor Quick Setup
Dionex Consumables/Instrumentation Manuals and Literature
Dionex Reference Library: Manuals, Technical Documents, Applications
D-Link DFE-530TX+ Driver version 2.02 User's Manual
D-Link DFE-530TX+ Fast Ethernet Adapter Driver Program MAY.10.2000
D-Link DFE-530TX+ Fast Ethernet Adapter Driver Program OCT.01.2000
Gateway System CD Information Guide
Gateway System Restoration CD Version 9.9
Government Institutes CFRs Environmental, Health and Safety
HP 5973 Mass Selective Detector Reference Collection Rev. A.00.00

APPENDIX 3: DOCUMENT MASTER LIST (Contd)

HP 6890 Plus Service Information November 1997
HP Analytical HP-IB Drivers for 82341C
HP Analytical MSD Productivity ChemStation Software A.03.01 Update
HP Analytical MSD Productivity ChemStation Software A.03.02
HP Analytical MSD Productivity ChemStation Software Rev. A.03.00
HP Analytical MSD Productivity ChemStation Software Rev. B.00.01
HP Analytical MSD Productivity ChemStation Software Rev. B.01.00
HP CD-Writer Installation Software
HP Chemstation for Windows 95 Revision A.06.03
HP Chemstation G1034 Version C.03.00
HP ChemStation Plus Family Rev. A.07.01
HP ChemStation System Emergency Boot Floppy Windows NT 4.0
HP ChemStation System Emergency Recovery CD
HP ChemStation Update Revision A.06.03 to A.06.04
HP Compaq Business Desktop Documentation CD
HP Flat Panel Monitor Software and reference library
HP G1033A NIST1998 MS Library Rev. D.00.00
HP I/O and Security software and documentation
HP Kayak XA PC Workstation Drivers and Utilities
HP Kayak XA PC Workstation HP ConfigTailor 1.2
HP Kayak XA PC Workstation HP ConfigTailor 1.2
HP LaserJet 2400 series
HP LaserJet 4000 series Printing System & Utilities
HP MusicMatch, cd-labeller II, ACID Xpress, ArcSoft
HP Operating System CD Microsoft Windows XP PRO SP2
HP Windows NT 4.0 Emergency Repair Disk
Localized Language CD-ROM for the MSD Productivity ChemStation
Microsoft Internet Explorer Starter Kit
Microsoft MSDN Windows 95 versions, Add-ons for Windows 95
Microsoft Office 2000 Professional
Microsoft Office 2000 Small Business
Microsoft Windows 98 Second Edition
Microsoft Windows NT 4.0 Debug/Check Build
Microsoft Windows NT Service Packs
Microsoft Windows NT WorkStation 4.0
Microsoft Windows NT WorkStation Certificate of Authenticity
Microsoft Works Suite 2000
MSDSonline MSDS Advantage v4.5
Restek Compendium of Methods for the Determination of Toxic Organic Compounds
Roxio Easy CD & DVD Creator Basic Edition
Roxio Easy Media Creator Basic Edition

APPENDIX 3: DOCUMENT MASTER LIST(Contd)

Symantec Norton Ghost 9.0
TurboLinux Server 6.0 Lite
Agilent 6890N Series GC Service Information
Agilent 6890N Series GC User Information
Teledyne Instruments Tekmar AutoCan TekLink v.1.10 Rev A
Teledyne Instruments Tekmar Velocity Manual Rev. B
Teledyne Instruments Tekmar VOC TekLink 2.4 Rev. B
WINEDS 3.22. WinDISS80201. High Performance XRay Microanalysis. User's Guide.

NETWORK SOFTWARES

Excel spread sheet for Microbiology: Rev. 00; My Network/STAT Server/Micro
Excel spread sheet for PCM: Rev.00;My Network/STAT Server/PCM
GC-FID:ChemStation Model G1701AA Version A.03.00
GC (PCB-PEST 1):ChemStation Model G1701CA Version C.00.00
GC (PCB-PEST 2):ChemStation Model G1701CA Version C.00.00
SVOC 1 GCMS: ChemStation Model G 1034C Version C.03.00
SVOC 3 GCMS:ChemStation Model G1701CA Version C.00.00
SVOC 3 GCMS:ChemStation Model G1701CA Version C.00.00
GC (PCB-PEST 3):ChemStation G1710DA D.02.00
SVOC 5 GCMS:ChemStation G1710DA D.02.00
HPLC 1 LC:ChemStation for LC G2180AA A.09.03
VOA 1 GCMS:ChemStation G1701BA Version B.00.00
VOA 2 GCMS:ChemStation G1701AA Version A.03.00
VOA 3 GCMS:ChemStation G1701CA Version C.00.00
VOA 4 GCMS:ChemStation G1701CA Version C.00.00
VOA 5 GCMS:ChemStation G1701DA 0.01.02
ChemStation Data Analysis, G1710DA D.01.02
Mercury Analyzer:Cetec Tech M 6000; Version 1.5.2.7
Perkin-Elmer AA:Version 3
ICPMS 1 and 2:Chem Station Model G1834A Version A01.07
Auto sampler Cetec Version A01.00
Spreadsheet, //HARRISON/D/STAT Files/Methods/AIHA/AIHA-PAT-Rounds.xls
Spreadsheet, //HARRISON/D/STAT Files/Methods/AIHA/AIHA-Workorders-Rounds.xls

APPENDIX 3: DOCUMENT MASTER LIST (cont.'d)

GUIDANCE DOCUMENTS

40CFR Part 136

40 CFR Part 763, Subpart E. Asbestos-containing materials in Schools; Final Rule and Notice.

AIHA Analytical Accreditation Board (AAB)

AIHA LQAP Policy Document, current revision.

American Society for Quality Control (ASQC), Definitions of Environmental Quality Assurance Terms, 1996

American Society for Testing and Materials, Annual Book of ASTM Standards, Part 31, 1987; Water: Atmospheric Analysis, ASTM, Philadelphia, PA

American National Standards Institute (ANSI), Style Manual for Preparation of Proposed American National Standards, Eighth Edition, March 1991

ANSI/ASQC E4, 1994

ANSI N42.23-1995, Measurement and Associated Instrument Quality Assurance for Radiobioassay Laboratories

Compendium Method IO-3.5 Compendium of Methods for the Determination of Inorganic Compounds in Ambient Air: Determination of Metals in Ambient Particulate Matter Using Inductively Coupled Plasma/ Mass Spectrometry (ICP/MS), U.S. EPA, June 1999.

ISO/IEC 17025: 2005 General requirements for the competence of testing and calibration laboratories

International Vocabulary of Basic and General Terms in Metrology (VIM): 1984. Issued by BIPM, IEC,

Manufacturers' Equipment Instruction Manuals---Various

Microscopical Identification of Asbestos, McCrone Research Institute, Chicago, IL, 2002.

National Environmental Laboratory Accreditation Conference (NELAC), Current version at date of signing, USEPA Office of Research and Development, Washington, DC EPA600/R-99-068

NIOSH Method 6009 Mercury, NIOSH Manual of Analytical Methods (NMAM), Fourth Edition, 8/15/94

APPENDIX 3: DOCUMENT MASTER LIST (cont.'d)

GUIDANCE DOCUMENTS

NIOSH Method 7082 "LEAD by FAAS" Issue 2 August 15, 1994.

NIOSH Manual of Analytical Methods (NMAM), Fourth Edition, 8/15/1994

NIOSH Method 1501 Hydrocarbons, Aromatic

NIOSH Method 5503 Polychlorobiphenyls

NIOSH Method 1400 Alcohols

NIOSH Method 2000 Methanol

NIOSH Method 1500 Hydrocarbons, 36 – 126 °C BP

NIOSH Method 7400 "Asbestos and Other Fibers by PCM" Issue 2: August 15, 1994

NIOSH 9002 Asbestos (bulk) by PLM, August, 1994.

National Institute of Standards and Technology (NIST) Handbook 150, NVLAP Procedures and General Requirements. July 2006.

NIST Handbook 150-3, NVLAP Bulk Asbestos Analysis. July 2006.

NIST Handbook 150-13, NVLAP Airborne Asbestos Analysis. July 2006.

NIST Technical Note 1297, 1994 Edition. Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results, Barry N. Taylor and Chris E. Kuyatt.

NISTIR 5951, Guide for Quality Control on the Qualitative and Quantitative Analysis of Bulk Asbestos Samples: Version 1 by Jennifer R. Verkouteren and David L. Duewer, March 1997

OSHA Method #007 Organic Vapors

Refractive Index Liquid Calibration using Optical Glass Standards by Shu-Chun Su, Ph.D., May 1996.

State of Illinois Title 35: Environmental Protection Subtitle A: General Provisions Chapter II: Environmental Protection Agency Part 186: Accreditation of Laboratories for Drinking Water, Waste Water and Hazardous Waste Analyses

APPENDIX 3: DOCUMENT MASTER LIST (cont.'d)

GUIDANCE DOCUMENTS

U.S. EPA SW-846 "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods" Update III, December 1996

U.S. EPA 747-R-95-001 Residential Sampling for Lead: Protocols for Dust and Soil Sampling, March 1995 USEPA Pollution Prevention and Toxics (7404)

U.S. EPA Contract Laboratory Program Statement of Work for Organic Analysis" Revision OLM04.2 May 1999, US. Environmental Protection Agency. Office of Solid Waste, Washington DC 20460.

U.S. EPA IO 3.2 Determination of Metals in Ambient Particulate Matter Using Atomic Absorption (AA) Spectroscopy, June 1999.

US EPA Quality Assurance Management Section (QAMS), Glossary of Terms of Quality Assurance Terms, 8/31/92 and 12/6/95

EPA 600/M4-82-020. Interim Method for the Determination of Asbestos in Bulk Insulation Samples, December, 1982.

EPA 600/R-93/116. Method for the Determination of Asbestos in Bulk Building Materials. July 1993.

US EPA (1987), Interim Transmission Electron Microscopy Analytical Methods-Mandatory and Nonmandatory Section to Determine Completion of Response Action, Appendix A to Subpart B. 40 CFR Part 763.

Walter C McCrone, *Asbestos Identification*. McCrone Research Institute, Chicago, IL. 1987.

Webster's New World Dictionary of the American Language

Note: External source documents are kept on shelves in individual laboratories. Some of the documents are also accessed through the world wide web.

APPENDIX 3: DOCUMENT MASTER LIST (cont.'d)

REFERENCE TEXT (MICROBIOLOGY)

Title:	Ed.:	Author/Editor:	Publisher:	City/State:
A Laboratory Guide to Common Penicillium Species		Pitt, John I.	Food Science Australia	
Applications in General Microbiology: A Laboratory Manual	6th Ed.	Kerr and McHale	Hunter Textbooks, Inc.	
Atlas of Clinical Fungi	2nd Ed.	de Hoog, G.S, et al.	Centraalbureau voor Schimmelcultures	Utrecht, The Netherlan
Dermatiaceous Hyphomycetes		Ellis, M.B.	Commonwealth Mycological Institute	Kew, Surrey, England
Fungi and Food Spoilage	2nd Ed.	Pitt, JI and Hocking, AD	Aspen Publishers, Inc.	Gaithersburg, Marylan
Guidelines on Assessment and Remediation of Fungi in Indoor Environments		New York City Dept. of Health		
Identification of Common Aspergillus Species		Klich, Maren	Centraalbureau voor Schimmelcultures	Utrecht, The Netherlan
Identifying Filamentous Fungi: A Clinical Laboratory Handbook		St-Germain, Guy	Star Publishing Company	
Indoor Environmental Quality Guidance and Reference Manual		Martin, James	Martin Consulting	
Introduction to Food- And Airborne Fungi	6th Ed.	Samson, Robert A. and Hoekstra, Ellen S.	Centraalbureau voor Schimmelcultures	Utrecht, The Netherlan
Introduction to Microbiology and the Clinical Microbiology Laboratory		Engelkirk, Paul	Hunter Textbooks, Inc.	
Medically Important Fungi: A Guide to Identification	3rd Ed.	Larone, Davise	ASM Press	Washington, DC
Microbiological Aspects of Biofilms and Drinking Water		Percival, Steven et al.	CRC Press	
Microbiological Examination of Water and Wastewater		Csuros, Maria and Csaba	Lewis Publishers	
Microbiological Methods for Monitoring The Environment: Water and Wastes		EPA	EPA Doc# EPA-600/8-78-017	
Microbiology	4th Ed.	Prescott, Harley, and Klein	WCB McGraw-Hill	
Study Guide to Accompany Microbiology	4th Ed.	Rascati, Ralph	WCB McGraw-Hill	
Mold Remediation in Schools and Commercial Buildings		USEPA	EPA Doc# EPA 402-K-01-001	
Moulds: Isolation, Cultivation, Identification		Malloch, David		
Myxomycetes: A Handbook of Slime Molds		Stephenson, Steven and Stempen, Henry	Timber Press	Portland, Oregon
Pictorial Atlas of Soil and Seed Fungi	2nd Ed.	Watanabe, Tsuneo	CRC Press	
Field Guide for the Determination of Biological Contaminants in Environmental Samples		Dillon, Heinsohn, and Miller	AIHA Press	Fairfax, VA
Compendium of Soil Fungi	Vol.I	Domsch, KH, and W. Gams	IHW-Verlag	
Compendium of Soil Fungi	Vol. II	Domsch, KH, and W. Gams	IHW-Verlag	
Bioaerosols: Assessment and Control		Macher, Janet	ACGIH	Cincinnati, OH
How to Identify Mushrooms to Genus III: Microscopic Features		Largent, David	Mad River Press Inc.	Eureka, CA
Fungal Contamination in Public Buildings: A Guided to Recognition and Management		Federal-Provincial Committee on Environmental and Occupational Health		Ottawa, Ontario
The Preservation and Maintenance of Living Fungi	2nd Ed.	D. Smith and A.H.S. Onions	CAB International	UK

APPENDIX 3: DOCUMENT MASTER LIST (cont.'d)

EQUIPMENT INSTRUCTION MANUALS

Inorganic Manuals

Name		Location
Agilent 7500 ICPMS		
	Option Instruction Manual IM	under Cetac
	Chemstation Operators Manual OM	under Cetac
	Integrated Sample Intro System	under Cetac
	Customer Maintenance Parts List	under Cetac
	Installation Guide	under Cetac
	Operator's Manual	under Cetac
	Application Handbook	Inorganic Manager's Office
	Manual EM Voltage and Discriminator Adjustment	Inorganic Manager's Office
Beckman 300Series pH/mV/ISE OM		by pH meter
Flash tester	Hotplate OM series 237	Wet Chem Folder
Cole Palmer pH Meter	pH/mV/degrees C	Wet Chem Folder
Adjustable Vol Repipet Jr. Dispenser		Wet Chem Folder
Bausch and Lomb Spec 20	old copy	Wet Chem Folder
	new spec 20 copy	Wet Chem Folder
Beckman Refillable Electrodes		Wet Chem Folder
Midi-Stil Distillation OM		Wet Chem Folder
Conductivity OM/Cert.of Cal		Wet Chem Folder
ZHE OM		Wet Chem Folder
Hach COD Reactor	45600/49100	Wet Chem Folder
Lachat QuIckChem 8000		
	Installation and Tutorial Manual	under Lachat
	ASX-500 Autosampler 510 OM	under Lachat
	ASX-500 Autosampler	under Lachat
	QuickCHem Methods Manual	under Lachat
	Hardware Installation and System OM	under Lachat
Hach Water Analysis Handbook		under Lachat

APPENDIX 3: DOCUMENT MASTER LIST (cont.'d)

Cetec Mercury Analyzer		under Cetec
	ASX-500 Autosampler	under Cetec
	M-6000 A Mercury Analyzer Catalog	under Cetec
	ASX-500 Autosampler 510 OM	under Cetec
	M-6000A Mercury Analyzer OM	under Cetec
	M-6000A Mercury Analyzer Software Manual	under Cetec
Modblock Instruction Manual		under Cetec
Perkin Elmer AA		
	AS-90 Autosampler Installation Giude	under AA monitor
	Analytical Methods Manual	under AA monitor
	Installing AA WinLab on Windows 95	under AA monitor
	Concepts, Instrumentation and Techniques in A A	under AA monitor
	Guide to AA100/300 AA spectrometers	under AA monitor

Asbestos Manuals

Plasma Asher Manual	Asbestos laboratory
High Vacuum Evaporator Manual	Asbestos laboratory
Jeol Manual	Asbestos laboratory
Hood	With the Hood

Note: Asbestos manuals are in the asbestos Laboratory

Organic Manuals-General

Barnstead International Repipet II Dispensers
Barnstead International Variable Speed Extraction Mixer Model:6000-1
Barnstead/Thermolyne Repipet Jr. Dispensers
Beckman Instruments Futura Refillable Combination Electrodes
Beckman pH Meter
Branson Ultrasonics Model 250/450 Sonifer Instruction Manual
Clay Adams Compact II Centrifuge Model Nos: 420225 & 420227
Coleman Cordless Drills
Concoa Regulators
Dehumidifier Use & Care Guide

APPENDIX 3: DOCUMENT MASTER LIST (cont.'d)

High Velocity Air Circulator
HP LaserJet 4050 & 4050N Printers
Internal/External Digital Thermometer
Lindberg/BlueM 1100 C Box Furnace Model:BF51800
Mettler PM100, PM200, PM300, PM400, PM600, PM2000, PM4000
Mettler Toledo BD Balances
Millipore Dispensing Pressure Vessels
Millipore OM100 Operation & Maintenance Instructions
Millipore Rotary Agitator
NitroVap-1LV & NitroVap-2LV Nitrogen Generators
Pensky Martens Flash Testers 74537MAN
RapidVap Vacuum & N2 Evaporation Systems
VWR Scientific Water Baths Models: 1200,1201,1202,1203,1204,1205
VWR Vanlab Heat Block
Wheaton Science Hand Operated Crimpers
Wheaton Science Hand Operated Decapper

Note: General Organic manuals are kept in the Semivolatile Laboratory

Organic Manuals -SVOC

Agilent 1100 Series Fluorescence Detector
Agilent 1100 Series Quaternary Pump
Agilent 1100 Series Standard, Micro and Preparative Autosamplers
Agilent 1100 Series Thermostatted Column Compartment
Agilent 1100 Series Vacuum Degasser
Agilent 1100 Series Variable Wavelength Detector
Agilent 5973N MSD 6890 Series GC Quick Reference
Agilent 5973Network Mass Selective Detector Hardware Installation Manual
Agilent 5973Network Mass Selective Detector Hardware Manual
Agilent 6890 Series GC Operating Manual Volume 1 - General Information
Agilent 6890 Series GC Operating Manual Volume 2 - Detectors
Agilent 6890 Series GC Operating Manual Volume 2 – Inlets
Agilent 6890 Series GC Site Prep and Installation
Agilent Custom Reports Software Getting Started
Agilent Environmental Analysis Software Getting Started
Agilent G1701CA MSD Productivity ChemStation Software Installation Manual
Agilent G1701DA GC/MSD ChemStation Drug Analysis Software Getting Started
Agilent G1701DA GC/MSD ChemStation Getting Started
Agilent G1701DA MSD ChemStation 5973 MSD Quick Reference
Agilent G1701DA MSD ChemStation Drug Analysis Software Getting Started
Agilent G1701DA MSD Productivity ChemStation Software Ver. D.01.00 or later
Agilent G1701DA MSD Productivity ChemStation Software Ver. D.02.xx
Agilent MS Operation Software Revision A.03.00
Agilent MSD ChemStation Mnl Kit Rev. D.03.00

APPENDIX 3: DOCUMENT MASTER LIST (cont.'d)

Agilent MSD Data Analysis ChemSta Core SW Rev. D.03.00
Applications for diode-array detection in HPLC
Dell Dimension L Series Reference and Troubleshooting Guide
Dell Dimension Systems Setup Guide
Dell E770s Color Monitor Quick Setup Guide
Dell Getting Started Microsoft Windows 98
Hewlett Packard HP 5971A MSD Hardward Manual
Hewlett Packard Understanding Your HP Chemstation
HP 5973 MSD HP 6890 Series GC Quick Reference
HP 6890 Module Installing Your GC ChemStation
HP 6890 Series GC Operating Manual Volume 2. Inlets
HP 6890 Series GC Operating Manual Volume 3. Detectors
HP 6890 Series GC Site Preparation and Installation Manual
HP 7683 Automatic Liquid Sampler Installation Guide
HP 7683 Automatic Liquid Sampler Operation Guide
HP Automatic Liquid Samplers Sampling Techniques Handbook
HP Custom Reports Software Getting Started
HP Electron Capture Detectors Information for General Licensees
HP Environmental Software Getting Started
HP G1032C EnviroQuant Software
HP G1034C MS ChemStation Software Using and Writing Macros
HP G1701AA MSD ChemStation Software Installation Manual
HP Hydrogen Carrier Gas Safety Guide
HP Kayak XA PC Workstation User's Guide
HP The Micro-Cell Electron Capture Detector Operating Manual
HP Using an HP ChemStation in Windows 95
HPLC - Agilent 1100

Note: SVOC manuals are kept in the Semivolatile Laboratory

ORGANIC MANUALS - Volatiles

Agilent 5973N & 5973Inert Mass Selective Detector
Agilent 5973N MSD 6890 Series GC Quick Reference
Agilent 5973N MSD Local Control Panel (LCP) Quick Reference
Agilent 5973Network Mass Selective Detector – Hardware Installation Manual
Agilent 5973Network Mass Selective Detector – Hardware Manual
Agilent 5973Network Mass Selective Detector Site Preparation Manual
Agilent 6890 Series GC Operating Manual Volume 1 - General Information
Agilent 6890 Series GC Operating Manual Volume 2 – Inlets
Agilent 6890 Series GC Operating Manual Volume 3 - Detectors
Agilent 6890 Series GC Site Prep and Installation
Agilent Custom Reports Software Getting Started
Agilent Environmental Analysis Software Getting Started
Agilent G1701CA MSD Productivity Software Installation Manual

APPENDIX 3: DOCUMENT MASTER LIST (cont.'d)

Agilent HP G1032C EnviroQuant Software EnviroForms User's Guide
Branson UltraSonic Cleaners, Models 1510, 2510, 3510, 5510, 8510
Gow-Mac Model 21-070 & 21-072 Mini Gas Leak Detector
Granville-Phillips 59864A & 59864B Ionization Gauge Controller Instruction Manual
HP 02842A, 02842W 19-inch color monitor
HP 1090 Series II/L Liquid Chromatographs Using Your HP1090
HP 5973 Mass Selective Detector hardware manual
HP 5973 MSD HP 6890 Series GC Quick Reference
HP 6890 Series GC Operating Manual 1. General Information
HP 6890 Series GC Operating Manual 2. Inlets
HP 6890 Series GC Operating Manual 3. Detectors
HP 6890 Series GC Site Preparation and Installation Manual
HP Custom Reports Software Getting Started
HP Environmental Data Analysis User's Guide
HP Environmental Software Getting Started
HP G1032C EnviroQuant Software - EnviroForms User's Guide
HP G1701BA Productivity ChemStation Software Installation Manual
HP Hydrogen Carrier Gas Safety Guide
HP Kayak XA PC WorkStation User's Guide
HP LaserJet 4000 and 4000N Printers Getting Started Guide
HP LaserJet 4000, 4000T, 4000N & 4000TN Printers User's Guide
HP Procurve Switch 408
HP Using an HP ChemStation in Windows NT
HP5890 Series II GC Operating Manual Cool On-column Inlet Manual
Tekmar 2016/2032 Purge & Trap Autosampler User Manual
Tekmar 3000 Purge and Trap Concentrator User Manual
Tekmar 3100 Purge & Trap Concentrator User Manual
Tekmar ALS 2016/ALS 2032 User Manual
Tekmar LSC 2000 User Manual
Teledyne Velocity XPT Sample Concentrator
Varian Archon Purge & Trap Autosampler System Operation Manual
Varian Archon Purge & Trap Autosampler System Operator's Manual

Note: Volatile manuals are kept in the Volatiles Laboratory

APPENDIX 4: INSTRUMENTATION

Equipment	Manufacturer	Model #	Serial #	Dept.
GC/MS (SVOC-1)	Hewlett Packard	5890 Series II GC	2950A27820	SVOC
		5971U MSD	3050A01584	
		6890 AS	3409A34948-3	
GC/MS (SVOC-2)	Agilent	6890N GC	US00033560	SVOC
		5973N MSD	US9014004	
		7683N AS	US95310985	
GC/MS (SVOC-3)	Agilent	6890N GC	US00037515	SVOC
		5973N MSD	US03340461	
		7683N AS	US01012145	
GC/MS (SVOC-4)	Agilent	6890N GC	US00042823	SVOC
		5973N MSD	US10440761	
		7683N AS	US11618674	
GC/MS (SVOC-5)	Agilent	6890N GC	CN52734690	SVOC
		5975N MSD	US52430277	
		7683N AS	CN5272615	
GC/FID	Hewlett Packard	5890 Series II GC	3140A39325	SVOC
		6890 AS	3113G06781-3	
GC/ECD PCB1	Agilent	6890N GC 7683N AS	US00034720 US00411387	PCB
GC/ECD PCB2	Agilent	6890N GC 7683N AS	CN10445022 CN44731379	PCB
GC/ECD PCB3	Agilent	6890N GC 7683 AS	CN10606009 CN62239870	PCB
GC/MS (VOC-1)	Hewlett Packard	6890 GC	US00023185	VOC
		5973 MSD	US82311186	
GC/MS (VOC-2)	Hewlett Packard	5890 Series Plus GC	2939A08878	VOC
		5971 MSD	3050A01916	
GC/MS (VOC-3)	Agilent	6890N GC	US00033670	VOC
		5973N MSD	US03340480	
GC/MS (VOC-4)	Agilent	6890N GC	US00042820	VOC
		5973N MSD	US10440768	
GC/MS (VOC-5)	Agilent	6890 GC	CN10516053	Air Toxics
	Agilent	5973 MS	US44621448	
	Tekmar	14-ACAN-000 AS	US05130007	
GC/MS (VOC-6)	Agilent	6890 GC	CN 10716027	Air Toxics
		5975C MS	US 71235770	

APPENDIX 4: INSTRUMENTATION

Equipment	Manufacturer	Model #	Serial #	Dept.
		Autocan 12	US 07100004	
VOA-7 (GC FID/PID)	Agilent	6890	US00001664	Air Toxics
	Tekmar	14-3100-OEL	241003	
	Varian	Archon	13383	
GCFID	HP	5890	3033A31565	Air Toxics
HPLC 1	Waters	600 Controller	SX5MM0449M	SVOC
		Pump	MX5KM3223M	
		717 Autosampler	MX5EM4621M	
HPLC 2	Agilent 1100	G1311A Pump	DE14917955	SVOC
		G1313A Autosampler	DE14918512	
		G1322A Degasser	DE14918512	
		G1316A Column Heater	DE14926164	
		G1314A VWD	JP11616431	
		G1321A Fluorescence Det.	DE14904016	
Hot Plate	VWR	Dynatherm	33918	ASB
Purified HEPA Filter Enclosure	Labconoco	3730000	02022032A-31	ASB
Sonicator	Branson	2510	RLA1203942170	ASB
Balance-2	Mettler Toledo	B303	1114032438	WC
Analytical Balance-6	Mettler	AE160	B81560	LEAD
Autosampler	Perkin-Elmer	AS90	507910 (8621)	LEAD
Block Digestors	CPI	05 C0530	293	LEAD
FLAA	Perkin-Elmer	PE Analyst 300	041S9110115	LEAD
Pyromultimagnestir	Labline	1268	058950057	LEAD
Analytical Balance-3	Mettler	AE 50	L88569	METALS
Autosampler on ICP-MS1	CETAC	ASX510	090007A5X5	METALS
Autosampler on ICP-MS2	Cetac	ASX510	020230ASX	METALS
Block Digestors	CPI Int.	-	A	METALS
Block Digestors	CPI Int.	-	B	METALS
Chiller on ICP-MS1	Neslab	M75	102025049	METALS
Chiller on ICP-MS2	Neslab	CFT-100	100175035	METALS
Kwikool AC	Kwikool	SWAC 2411	4480	METALS
High Vacuum Pump	Edwards	E2M5	17915F	METALS
ICP-MS-1	Agilent	7500i	JP93200201	METALS
ICP-MS-2	Agilent	7500i	JP13200437	METALS

APPENDIX 4: INSTRUMENTATION

Equipment	Manufacturer	Model #	Serial #	Dept.
Mercury Analyzer	CETAC	M-6000A	060003MAS	METALS
Water Bath	VWR	1204	23005	METALS
Class Safety Enclosure	Labconoco	3730001	020220239A	MICRO
Colony Counter	Leica	3327	0002411463YPO003	MICRO
Conductivity Meter	VWR	61161-362	230355432	MICRO
Crystal Panel Viewer	Becken-Dickison	BD-BBL	050604-1499	MICRO
Fluorescence Analysis Chamber	Spectriline	CM-10	147858	MICRO
Fluorescence Analysis Chamber	UVP	CC-10	95-00724	MICRO
Fume Enclosure	Mystaire	100		MICRO
Fume Enclosure	Mystaire	FE100		MICRO
Furnace	Thermolyne	48000	480911020760	MICRO
Hot plate	VWR	Dynatherm	0687	MICRO
Hot plate	VWR	Dynatherm	0686	MICRO
Hot Plate/ Stirrer	VWR	371	2258	MICRO
Incubator (I-1)	VWR	1510E	120060-2	MICRO
Incubator (I-2)	VWR	1516E	04070804	MICRO
Microscope	Olympus	CX31	RBSFA 2M03757	MICRO
Microscope	Olympus	CH2	7L0064	MICRO
Microscope	Olympus	BH-2	223905	MICRO
Microscope	Olympus	BH-2	221905	MICRO
Microscope	Olympus	BH-2	217318	MICRO
Mini Vortex	VWR	945300	14263	MICRO
pH /Temp. Meter 340	Beckman	511210	4585	MICRO
Refrigerator 15	Kenmore	253.6072101	WA32201606	MICRO
Sealer Index	Quanti-Tray	89-10894-02	3510R	MICRO
Smart Cycler II	Cephid	900-0057	200306	MICRO
Refrigerator #10	Jordan	AB-4-6	PR52858-99H	RECEIVE
Refrigerator #6	Jordan	AB-4-6	PR52857-99H	RECEIVE
Refrigerator #8	Jordan	AB-4-6	PR5381-00A	RECEIVE
Autosampler	Varian	8200	8200-09311	STORAGE
Autosampler	Varian	SPS-5	95061148	STORAGE

APPENDIX 4: INSTRUMENTATION

Equipment	Manufacturer	Model #	Serial #	Dept.
Autosampler (VOC1)	Varian	Archon	13037	STORAGE
FLAA	Varian	SpectrAA 200	31-100838-00	STORAGE
Hot plate	Thermolyne	Cimarec-3	66196070461	STORAGE
HPLC Pump	Hewlett Packard	1050		STORAGE
Power Pack	Varian	SIPS/PP1	94111272	STORAGE
Purge & Trap (VOC2)	HP	1909	3432A10143	STORAGE
Sample introduction	Varian	SIPS 1	95021096	STORAGE
Sonicator	Branson	450	BI0009670	STORAGE
Spect 20	Baush & Lomb	33.31.72	1152868	STORAGE
TCLP tumblers	Millipore	Agitator 10	455VS4045	STORAGE
TCLP tumblers	Millipore	Agitator 10	455VS4049	STORAGE
Water Bath	Precision Scientific	180	26AX-6	STORAGE
Desktop Centrifuge	Becton-Dickinson	Compact II	31000253	SVOC
Fume enclosure	Labconco	69000	020697466M	SVOC
Fume enclosure	Labconco	69000	020697440M	SVOC
GC/ECD	Varian	3600	3600-02846	SVOC
Heaters	Glas Col	TM106	158714a to 29A	SVOC
Mini Vortex	VWR	1945300	23007	SVOC
N2 Solvent Concentrator	Labconco	79100-00	991292324C	SVOC
N2 Solvent Concentrator	Labconco	79100-00	000593233D	SVOC
N2 Solvent Concentrator	Labconco	79100-00	000893763E	SVOC
N2 Solvent Concentrator	Labconco	79100-00	000893764E	SVOC
Refrigerator #11	Kenmore	253.611121	4A30721853	SVOC
Refrigerator #78	GE	TAX4DNCAWH	32373	SVOC
Refrigerator 13	Kenmore	253.6072101	WA2001629	SVOC
Sonicator	Branson	450	BI120061	SVOC
Sonicator	Branson	450	BI30158	SVOC
Sonicator	Branson	450	BI99063085	SVOC
Top Loading Balance-4	Mettler Toledo	PM300/49	F64687	SVOC
Autosampler (VOC2)	Varian	Archon	13037	VOC
Autosampler (VOC3)	Varian	Archon	13176	VOC

APPENDIX 4: INSTRUMENTATION

Equipment	Manufacturer	Model #	Serial #	Dept.
Autosampler (VOC4)	Varian	Archon	13553	VOC
Autosampler (VOC1)	Varian	Archon	13553	VOC
Flow Meter	Agilent	ADM 1000	US06L31632	VOC
Freezer #0	GE	FUM5SAARWH	H2115897	VOC
Freezer #12	Kenmore	253.234.24101	WB32231534	VOC
Freezer #9	GE	FUM5SAARWH	V21100784	VOC
Fume enclosure	Labconco	6900000	020697464M	VOC
Purge & Trap (VOC1)	Tekmar	3100	US 01107021	VOC
Purge & Trap (VOC3)	Tekmar	3000	98019001	VOC
Purge & Trap (VOC4)	Tekmar	14-8900-00T	US04356005	VOC
Refrigerator #14	Kenmore	56491601100	30200594	VOC
Refrigerator #8	Jordan	AB-4-G	PR53581-00A	VOC
Sonicator	Branson	2510	RLA070151006D	VOC
Balance-1	Mettler Toledo	PB403-S	1129192065	VOC
Vacuum Pump for VOC 2	Edwards	E2M2	68877	VOC
Gas leak detector	GPW-MAC	21-070	S20308	Air Tox
Gas leak detector	GPW-MAC	21-050	J47706	VOC
Dessicator (D-1)	Nalgene	5317-0180	Cat. 24987-056	WET
Analytical Balance-9	Mettler-Toledo	AB304-S	1125191416	WET
Box Furnace	Lindberg Blue	BF51828C-1	009L-516875-OL	WET
COD Reactor	Hach	4500	0107000022043	WET
Conductivity Meter	VWR	61161-362	230109686	WET
Digital Hygrometer/Thermometer	Control Company	35519-049	240130982	WET
Digital Hygrometer/Thermometer	Control Company	35519-049	240160719	WET
Environ Chamber	Environmental Chamber Company	Tenney TH Jr	11863-528	WET
Flash Point	Precision	74537	S03198	WET
Hot Plate/ Stirrer	VWR	325	0868	WET
Hot Plate/ Stirrer	VWR	325	0869	WET
Magnetic stirrer	VWR	VWR 200	58940-158	WET

APPENDIX 4: INSTRUMENTATION

Equipment	Manufacturer	Model #	Serial #	Dept.
Mini-Cyanide Distillation System	RGW Instruments	R-3166MS-100	2	WET
pH/mV/Temp Meter Series 20	Cole Palmer	570002-30	EP20/18094	WET
Phi240 pH/Temp Meter	Beckman	Phi-340	3532	WET
QuickChem FIA	Lachat	8000	A83000-1663	WET
Refrigerator #1	Frigidaire	MRT188BSCW6	BA009009793	WET
Refrigerator #2	Frigidaire	MRT188BSCW6	BA91700637	WET
Refrigerator #3	Frigidaire	FPDA181PLO	BA13108023	WET
Spect 20	Baush & Lomb	33.31.72	0115280	WET
Stirrer	VWR	205	7251	WET
Stirrer	VWR	941006	6090	WET
Stirrer	VWR	941006	6096	WET
Stirrer	VWR	941006	6097	WET
Stirrer	VWR	941006	6085	WET
Stirrer	VWR	941006	6093	WET
Stirrer	VWR	941006	6094	WET
TCLP tumblers	Analytical Technologies	42RBFC1-E3	0685CPF0018	WET
TCLP tumblers	Millipore	Agitator 10	455RY4029	WET
TOC/TOX	Euroglass	TOC 1200	2000.137	WET
Balance-12	Mettler	PB1502-S	1126341459	WET
Top Loading Balance-7	Mettler	BD202	4846	WET
Top Loading Balance-8	Mettler	PB602	1113242526	WET
Balance-11	Mettler-Toledo		1129140668	WET
Balanca-10	Mettler	AB104-S	1128422933	SVOA
Balance-13	Mettler	PB403	1129262406	Air Tox
Transite Oven	Blue M	11TA	S3585	WET
XYZ Autosampler	Lachat	ASX 500	020122 ASX	WET

APPENDIX 4: INSTRUMENTATION (Contd.)

Manufacturer	Equipment	Model #	Serial #	Lab
Olympus	Microscope	CX31	2M03757	Micro
Olympus	Microscope	CX21	4J00403	Micro
Bransonic	Ultrasonic Bath	2210R-MT	RLA94060-072C	ABS
JEOL	Electron Microscope	JEM-100CX II	EM156150-260	ABS
JEOL	Vacuum Evaporator	JEE-4X	EM300059-376	ABS
Ladd	Carbon rod Sharpener	30285	89-01-014	ABS
Olympus	Microscope	CH-2	9H0036	ABS
Olympus	PLM scope	BH-2	H62105-00214	ABS
Olympus	PLM scope	BH-2	HS2805-2000	ABS
Olympus	Stereoscope		399597	ABS
Olympus	Stereoscope	SZX2	344125	ABS
SPI	Plasma Asher	11005	1586	ABS
Thermolyne	Muffle Furnace	48000	480911020760	ABS
Olympus	PCM Microscope	CH-2	H92607-0318	ABS
Oxford	PCM filter fixer	QuickFix	10931	ABS
VWR	Hot plate / Stirrer	371	2258	ABS
VWR	Hotplate	Dylatherm	33918432 (cat.#)	ABS
VWR	Hotplate	Dylatherm	33918432 (cat.#)	ABS
VWR	Mini Vortex	945300	14203	ABS
VWR	Water Bath	1203	1103897	ABS
VWR	Incubator 1	NA	1200602	Micro

VWR	Incubator 2	NA	04070804	Micro
VWR	Incubator 3	NA	04007506	Micro
Edwards	High Vacuum Pump	E2M5	17915F	ABS
Thermolyne	Furnace	48000	480911020760	ABS

APPENDIX 5
Sample Bottles and Preservation

WATER

METALS

Parameter	Container	Preservative	Holding Time
General, dissolved	Plastic	Filtered on site, HNO_3 to pH<2	6 months
General, total	Plastic	HNO_3 to pH<2	6 months
Chromium, hexavalent	Plastic	Cool 4°C	24 hours
Mercury	Plastic	HNO_3 to pH<2	28 days

CONVENTIONAL PARAMETERS

Parameter	Container	Preservative	Holding Time
Acidity	Plastic	Cool 4°C	14 days
Alkalinity	Plastic	Cool 4°C	14 days
Ammonia	Plastic	H_2SO_4 to pH<2, Cool 4°C	28 days
BOD	Plastic	Cool 4°C	48 hours
Bromide	Plastic	None	28 days
Chloride	Plastic	None	28 days
Chlorine	Plastic	Cool 4°C	Analyze Immediately
Chromium, Hexavalent	Plastic	Cool 4°C	24 hours
COD	Plastic	H_2SO_4 to pH<2, Cool 4°C	28 days

APPENDIX 5 (cont'd)
Sample Bottles and Preservation

CONVENTIONAL PARAMETERS

Parameter	Container	Preservative	Holding Time
Color	Plastic	Cool 4°C	48 hours
Conductivity	Plastic	Cool 4°C	28 days
Cyanide, Total or Amenable	Plastic	NaOH to pH>12, Cool 4°C	14 days
Cyanide, Reactive	Plastic	NaOH to pH>12, Cool 4°C	14 days
Fluoride	Plastic	None	28 days
Hardness, Total	Plastic	$HN0_3$ to pH<2	6 months
Nitrate/Nitrite	Plastic	H_2S0_4 to pH<2, Cool 4°C	28 days
Nitrate	Plastic	Cool, 4°C	48 hours
Nitrite	Plastic	Cool, 4°C	48 hours
Oil & Grease	Glass	H_2SO_4 to pH<2, Cool 4°C	28 days
pH	Plastic	None	Analyze Immediately
Phenols	Glass	H_2S0_4 to pH<2, Cool 4°C	28 days
Phosphorus, Ortho	Plastic	Cool 4°C	48 hours
Phosphorus, Total	Plastic	H_2S0_4 to pH<2, Cool 4°C	28 days
Silica	Plastic	Cool 4°C	28 days
Solids, Dissolved	Plastic	Cool 4°C	7 days
Solids, Suspended	Plastic	Cool 4°C	7 days
Solids, Total	Plastic	Cool 4°C	7 days
Solids, Settleable	Plastic	Cool 4°C	48 hours

APPENDIX 5 (cont'd)
Sample Bottles and Preservation

CONVENTIONAL PARAMETERS

Parameter	Container	Preservative	Holding Time
Solids, Volatile	Plastic	Cool 4°C	7 days
Sulfate	Plastic	Cool 4°C	28 days
Sulfide	Plastic	NaOH to pH>9, Cool 4°C	7 days
Sulfide, Reactive	Plastic	NaOH to pH>9, Cool 4°C	7 days
Sulfite	Plastic	None	Analyze Immediately
Surfactants, MBAS	Plastic	Cool 4°C	48 hours
Turbidity	Plastic	Cool 4°C	48 hours
Total Organic Carbon (TOC)	Plastic	H_2S0_4 to pH<2, Cool 4°C	28 days
Total Organic Halogens (TOX)	Glass	H_2S0_4 to pH<2, Cool 4°C	28 days

ORGANICS

Parameter	Container	Preservative	Holding Time
HPLC Pesticides (Aldicarb / Carbonfuran)	Glass vial	1.2 mL Chloroacetic acid Cool 4°C	28 Days
EDB/DBCP	Glass vial	Cool 4°C	28 Days
Endothall	Glass	Cool 4°C	7 days extraction 1-day analysis
Pesticides and PCBs	Glass	Cool 4°C	7 days extraction 40 days analysis
Petroleum Hydrocarbons	Glass	H_2S0_4 to pH<2, Cool 4°C	28 days

APPENDIX 5 (cont'd)
Sample Bottles and Preservation

ORGANICS

Parameter	Container	Preservative	Holding Time
Phenoxyacid Herbicides	Glass	Cool 4°C	7 days extraction 40 days analysis
Phthalate Esters	Glass	Cool 4°C	7 days extraction 40 days analysis
Polynuclear Aromatic Hydrocarbons	Glass	Cool 4°C	7 days extraction 40 days analysis
GC/MS Semivolatiles	Glass	Cool 4°C	7 days extraction 40 days analysis
Total Petroleum Hydrocarbons	Glass	Cool 4°C	7 days extraction 40 days analysis
Volatile Organics	40 ml Glass	HCl to pH<2	14 days

SOIL

ALL PARAMETERS

Parameter	Container	Preservative	Holding Time
All except VOA	2, 4, 8 or 32 oz Glass	Cool 4°C	See individual SOP
Volatile Organics	ENCORE*	Cool 4°C	48 Hours
Volatile Organics	$NaHSO_4$/ Methanol	Cool 4°C	14 Days

*Or equivalent

APPENDIX 5 (cont'd)
Sample Bottles and Preservation

AMBIENT AIR

ALL PARAMETERS

Parameter	Container	Preservative	Holding Time
Metals, Lead	Filters (glass or quartz)	None	180 days
PAHs, PCBs, Pesticides, or Halogenated Dioxins and Furans	Cartridge: PUF Cartridge: XAD-2 Cartridge: PUF/XAD-2 sandwich	None	7 days extraction 40 days analysis
Aldehydes/Ketones	Cartridge: DNPH	None	14 days extraction 30 days analysis
Volatile Organics	Canisters	None	30 days
	Sorbent Tubes	None	30 days
	Tedlar Bags	None	30 days, but recommend in 24 hrs.
Phosgene, Phenols or Cresols	Impinger Tubes	None	7 days extraction 40 days analysis

Appendix 6: STAT Analysis Sample Acceptance Policy

Chain of Custody Requirements: All samples must be submitted with a completed Chain-of-Custody (COC) form filled out in ink. Please print legibly. The following information should be included:

1) Customer Information: Company name and contact information.
2) Customer Project Name or Number
3) Sampler's name.
4) Sample identification or location.
5) Date and Time of collection.
6) Matrix type.
7) Preservation type: Including chemical preservation as well as thermal preservation. Environmental samples require thermal preservation and the temperature requirement for shipment/storage is 0.1-6ºC.
8) Total number of containers.
9) Requested analyses or reference to quote or other documentation specifying analysis.
10) Turn Around Time.
11) Special remarks: Includes any additional sample analysis requirements such as reporting limits, if the samples are considered hazardous or contaminated, etc.
12) Signatures including date/time of all persons who have handled or possessed the samples.
13) If applicable, Purchase Order number, quote or other billing information.

Sampling/Container Requirements:

1) All samples must be labeled properly with unique identification in indelible ink, on water-resistant labels and correspond with the information on the COC. Date and time of sampling and preservation type should also be present on the label. Deviations between the sample number on the COC and sample containers will be noted on the sample receipt checklist.
2) All samples must be received in appropriate containers required by the analytical test methods and be received in good condition without any signs of damage or contamination.
3) Containers must have sufficient sample volume for analysis, with proper preservation. If QC is required (MS/MSD), additional sample must be submitted. Chemical preservation (pH) is checked at log in or by the analyst. Insufficient volume and improper preservation will be noted on the sample receipt checklist. Please see attachment for container and volume requirements.
4) All samples should be received within the analytical test method specified holding times. Hold time violations will be noted in the analytical report. For analysis with short hold time, please submit the sample with adequate time for analysis and notify your project manager when the sample will be arriving.

NOTE: Sample containers provided by STAT Analysis may contain small amounts of chemical preservatives as required by the analytical test method and labeled as such. Please take necessary precautions when using these sample bottles. Be sure to cap bottles tightly before shipment.

When shipping samples to STAT Analysis:

1) Enclose completed COC form in sealed zip-lock bag in order to prevent water damage from melting ice.
2) Ensure that the sample cooler is sealed properly with tape to avoid opening while in transit.
3) Ensure that there is enough ice or cooling material (ice is preferred over 'Blue Ice') in order to maintain required temperature preservation (0.1-6ºC). Samples received out of temperature compliance will be noted on the COC or sample receipt checklist.
4) Ensure that there is enough packing material in cooler to prevent damage to sample containers while in transit. Fill empty space in the cooler with bubble wrap or other packing material.
5) Be sure that samples containers are properly sealed so that water from melting ice does not enter the sample container. Shipping sample containers in sealed zip-lock bags can help prevent this.
6) Use extra packing material when shipping water samples. It is best to individually wrap glass water containers with bubble wrap or packing paper and then place in zip-lock bags.

NOTE: Samples that do not meet the above criteria will be flagged in an unambiguous manner defining the nature and substance of the variation. This will be noted on the final report.

Appendix 7
Ethics Policy and Data Integrity Agreement

Ethics Policy and Data Integrity Agreement

It is STAT Analysis Corporation's responsibility to produce data that is scientifically valid, defensible, and of known and documented quality in accordance with all applicable federal, State, and local laws and regulations consistent with accepted professional and analytical practices in a manner that justifies the public trust. STAT Analysis Corporation conducts all business with integrity and in an ethical manner. It is the responsibility of each staff member, manager, director, and owner to perform their duties with the highest ethical standards and professional conduct to ensure compliance with this Quality Manual and related documentation.

The STAT Analysis Corporation laboratory has a Quality Assurance Manual designed to insure that work performed in the laboratory is accurate, precise, complete, comprehensive, reproducible and reflects the need of the customer/client while satisfying the requirements of appropriate State and Federal regulations. STAT Analysis Corporation will not offer any analysis for which we cannot demonstrate consistent quality and defensible analyses.

Any allegation of misconduct will be promptly investigated in an unbiased and confidential manner by an investigative team designated by the President/CEO. The investigation including any supporting documentation, actions and resolution will be recorded and archived by the QA Manager.

I. I understand the high standards of integrity required of me with regard to the duties I perform and the data I report in connection with my employment at STAT Analysis Corporation.

II. I state that I am free from any commercial, financial or other pressures and do not have any conflicts of interests, which might adversely affect my duties at STAT Analysis Corporation. Laboratory analysts will not have any direct customer contact except with the approval of laboratory management, this includes but is not limited to telephone calls, emails, facsimiles, audits, etc.

III. I agree that in the performance of my duties at STAT Analysis Corporation:
   a. I agree to read, understand, sign and comply with all the policies and procedures detailed in the latest revisions of the Quality Assurance Plan and SOPs at all times;
   b. I will not intentionally report data that are not the actual values obtained without collaborating data acceptable to the laboratory's Standard Operating Procedures. All modifications will be properly documented;
   c. I will not invent data (dry lab) this includes raw data, support equipment calibrations; quantitative reports, LIMS etc.
   d. I will not adjust the area of a peak in chromatography to bypass QC criteria (peak shaving or adding);
   e. I shall not intentionally report the dates and times of data analyses that are not the actual dates and times of data analyses (time traveling);
   f. I shall not intentionally represent another individual's work as my own;
   g. I understand that if my job includes supervisory responsibilities, I shall not instruct, request, or direct any subordinate to perform any laboratory practice, which is unethical or improper.

IV. I will not compare or disclose results for any Performance Testing (PT) sample, or other similar QA or QC requirements, with any employee of any other laboratory, prior to the required submission date of the results to the person, organization, or entity supplying the PT sample.

V. I will not divulge customer names or their results outside of the company except to those parties designated as an approved customer representative.

VI. I agree to inform STAT Analysis Corporation of any accidental or intentional reporting of non-authentic data by other employees or by myself in a timely manner. I understand that if any manager or representative of management instructs, requests, or directs me to perform any of the aforementioned improper laboratory practices (I – V), or if I am in doubt or uncertain as to whether or not such laboratory practices are proper, I will not comply, but I must immediately report such event to all appropriate members of management including my manager, the Laboratory Director, the QA Manager and President/CEO, excluding such individuals who participated in such perceived improper instruction, request, or directive.

I understand that failure to follow company policies and procedures, and failure to follow federal, State and local law, may result in discipline, up to and including termination. If I have knowledge of a non-compliant incident and do not report it, I will be subject to disciplinary measures up to and including termination. If I retaliate or in any way punished another employee for reporting a violation, I will be subject to discipline, up to and including termination.

_____

(Employee's Signature) (Dated)

_____

(Print Name)

_____

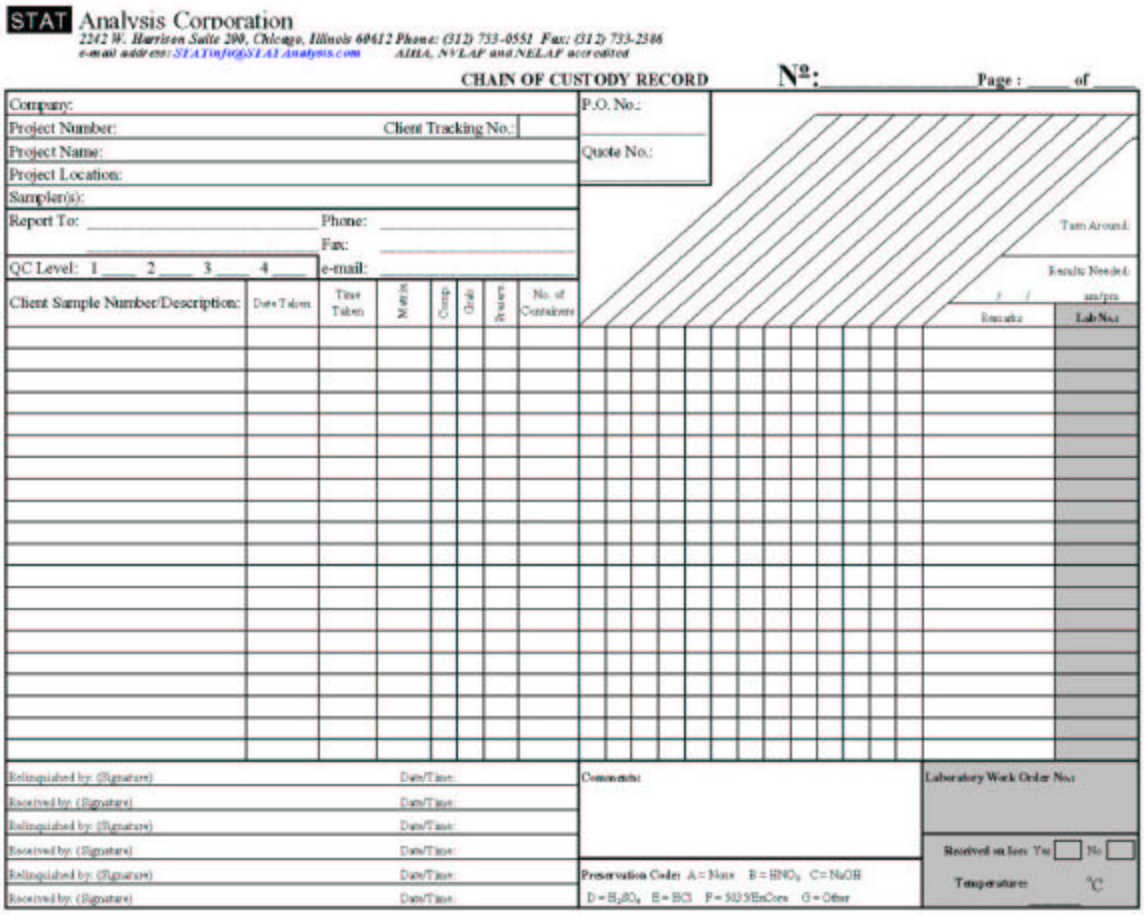
(Witness Signature) (Dated)

_____

(Print Name)

NOTE: This Ethics Policy/Data Integrity Agreement must be signed at the time of hire and re-signed between January 1 and January 15 of every year. Such signature is a condition of continued employment and failure to sign will result in immediate termination of employment.

ATTACHMENT 1
Example Chain of Custody for NELAC Samples



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2242 W. Harrison Suite 200, Chicago, Illinois 60612 Phone: (312) 733-0551 Fax: (312) 733-2386
e-mail address: STATinfo@STATAnalysis.com AIHA, NVLAP and NELAP accredited

CHAIN OF CUSTODY RECORD Nº: _____ Page : ____ of ____

Company:
Project Number: Client Tracking No.:
Project Name:
Project Location:
Sampler(s):
Report To: _____ Phone: _____
Fax: _____
QC Level: 1 ____ 2 ____ 3 ____ 4 ____ e-mail: _____

P.O. No.:
Quote No.:

Turn Around:
Results Needed: / / am/pm

Client Sample Number/Description:	Date Taken	Time Taken	Matrix	Comp	Grab	Preserv	No. of Containers	Remarks	Lab No.

Relinquished by: (Signature) Date/Time:
Received by: (Signature) Date/Time:
Relinquished by: (Signature) Date/Time:
Received by: (Signature) Date/Time:
Relinquished by: (Signature) Date/Time:
Received by: (Signature) Date/Time:

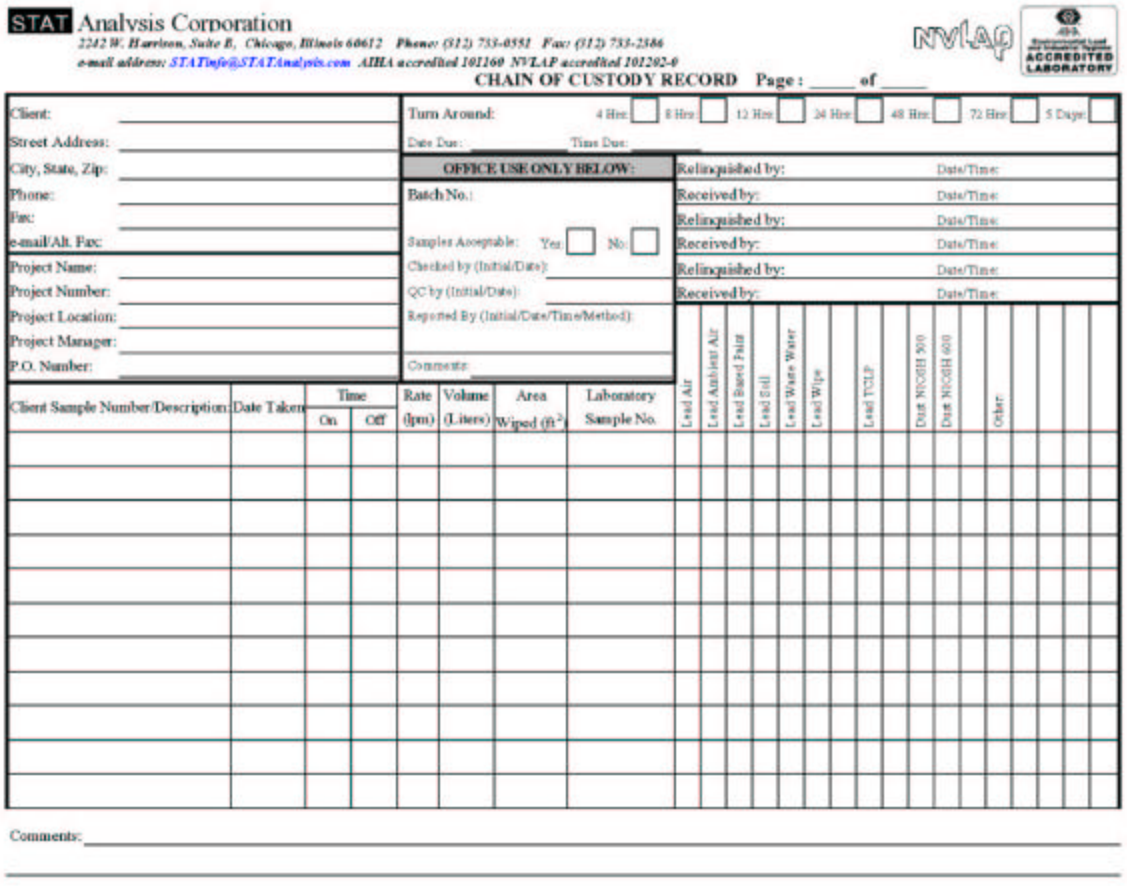
Comments:

Preservation Code: A = None B = HNO_3 C = NaOH
D = H_2SO_4 E = HCl F = 5035/EnCore G = Other

Laboratory Work Order No.:

Received on Ice: Yes ☐ No ☐
Temperature: ____ °C

ATTACHMENT 2
Example Chain of Custody for Pb AIHA Samples



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e-mail address: STATinfo@STATAnalysis.com AIHA accredited 101160 NVLAP accredited 101202-0

CHAIN OF CUSTODY RECORD Page : _____ of _____

Client:
Street Address:
City, State, Zip:
Phone:
Fax:
e-mail/Alt. Fax:
Project Name:
Project Number:
Project Location:
Project Manager:
P.O. Number:

Turn Around: 4 Hrs. 8 Hrs. 12 Hrs. 24 Hrs. 48 Hrs. 72 Hrs. 5 Days:
Date Due: Time Due:

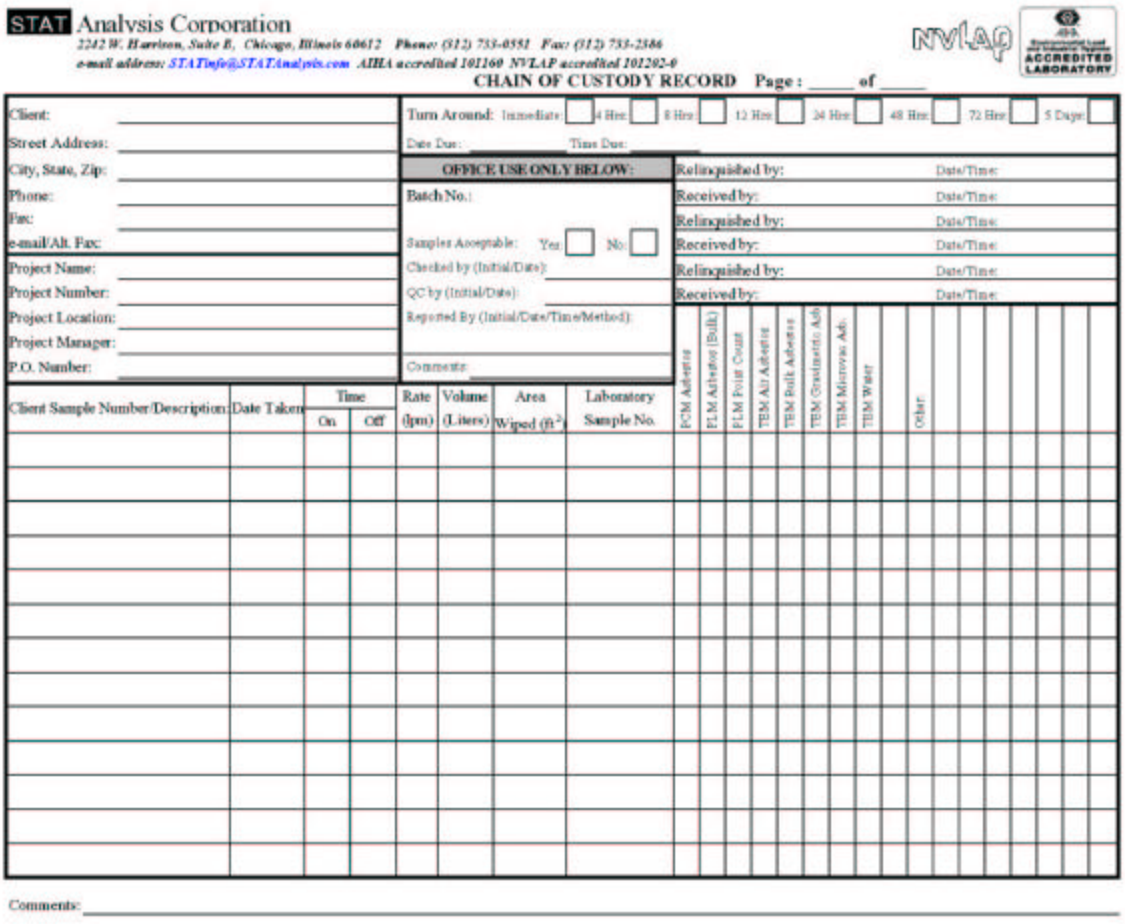
OFFICE USE ONLY BELOW:
Batch No.:
Samples Acceptable: Yes: No:
Checked by (Initial/Date):
QC by (Initial/Date):
Reported By (Initial/Date/Time/Method):
Comments:

Relinquished by: Date/Time:
Received by: Date/Time:
Relinquished by: Date/Time:
Received by: Date/Time:
Relinquished by: Date/Time:
Received by: Date/Time:

Client Sample Number/Description	Date Taken	Time On	Time Off	Rate (lpm)	Volume (Liters)	Area Wiped (ft^2)	Laboratory Sample No.	Lead Air	Lead Ambient Air	Lead Based Paint	Lead Soil	Lead Waste Water	Lead Wipe	Lead TCLP	Dust NIOSH 500	Dust NIOSH 600	Other

Comments:

ATTACHMENT 3
Example Chain of Custody for Asbestos Samples



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NVLAP ACCREDITED LABORATORY

CHAIN OF CUSTODY RECORD Page: _____ of _____

Client:
Street Address:
City, State, Zip:
Phone:
Fax:
e-mail/Alt. Fax:
Project Name:
Project Number:
Project Location:
Project Manager:
P.O. Number:

Turn Around: Immediate ☐ 4 Hrs ☐ 8 Hrs ☐ 12 Hrs ☐ 24 Hrs ☐ 48 Hrs ☐ 72 Hrs ☐ 5 Days ☐
Date Due: Time Due:

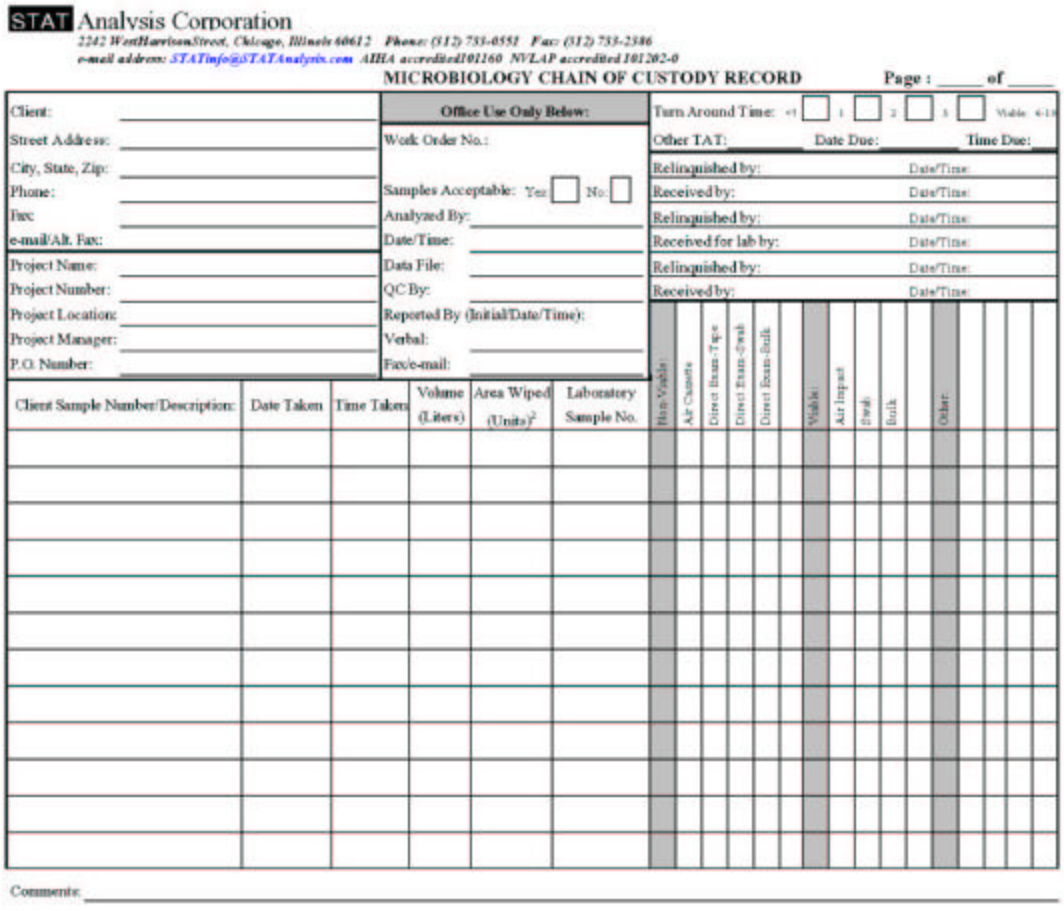
OFFICE USE ONLY BELOW:
Batch No.:
Samples Acceptable: Yes ☐ No ☐
Checked by (Initial/Date):
QC by (Initial/Date):
Reported By (Initial/Date/Time/Method):
Comments:

Relinquished by: Date/Time:
Received by: Date/Time:
Relinquished by: Date/Time:
Received by: Date/Time:
Relinquished by: Date/Time:
Received by: Date/Time:

Client Sample Number/Description	Date Taken	Time On	Time Off	Rate (lpm)	Volume (Liters)	Area Wiped (ft^2)	Laboratory Sample No.	PCM Asbestos	PLM Asbestos (Bulk)	PLM Point Count	TEM Air Asbestos	TEM Bulk Asbestos	TEM Qualitative Adh.	TEM Microvac Adh.	TEM Water		Other							

Comments: _____

ATTACHMENT 4
Microbiology Chain of Custody



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MICROBIOLOGY CHAIN OF CUSTODY RECORD Page : _____ of _____

Client:
Street Address:
City, State, Zip:
Phone:
Fax:
e-mail/Alt. Fax:
Project Name:
Project Number:
Project Location:
Project Manager:
P.O. Number:

Office Use Only Below:
Work Order No.:
Samples Acceptable: Yes ☐ No ☐
Analyzed By:
Date/Time:
Data File:
QC By:
Reported By (Initial/Date/Time):
Verbal:
Fax/e-mail:

Turn Around Time: <1 ☐ 1 ☐ 2 ☐ 3 ☐ Visible 4-10
Other TAT: Date Due: Time Due:
Relinquished by: Date/Time:
Received by: Date/Time:
Relinquished by: Date/Time:
Received for lab by: Date/Time:
Relinquished by: Date/Time:
Received by: Date/Time:

Client Sample Number/Description:	Date Taken	Time Taken	Volume (Liters)	Area Wiped (Units)^2	Laboratory Sample No.	Non-Viable:	Air Cassette	Direct Exam-Tape	Direct Exam-Swab	Direct Exam-Bulk		Viable:	Air Impact	Swab	Bulk		Other:				

Comments: _____

Attachment 5
Example of Notice of Confidentiality for E-mail

Craig

From: "Craig Chawla" <CChawla@STATAnalysis.com>
To: <CChawla@STATAnalysis.com>
Sent: Thursday, September 18, 2003 3:41 PM
Subject: Confidentiality Statement

Craig Chawla
STAT Analysis Corporation
(312) 563-0371

The information contained in this e-mail message and any attachments is confidential information intended only for the use of the individual or entities named above. If the reader of this message is not the intended recipient you are hereby notified that any dissemination, distribution, or copying of this communication is strictly prohibited. If you have received this communication in error, please notify us immediately by e-mail at the originating address.

9/18/2003

Attachment 6
Example of Notice of Confidentiality for Facsimiles

STAT Analysis Corporation:
2201 West Campbell Park Drive, Chicago, Illinois 60612-3547
Tel: 312.733.0551; Fax: 312.733.2386; e-mail address: STATinfo@STATAnalysis.com

NVLAP AIHA Environmental Lead and Industrial Hygiene ACCREDITED LABORATORY

Fax Cover Sheet

DATE: **TIME:**

TO: **PHONE:**
FAX:

COMPANY:

FROM: Craig Chawla **PHONE:** (312) 563-0371
FAX: (312) 733-2386

RE:

No. of Pages Including This Page:

NOTICE OF CONFIDENTIALITY

The information contained in this facsimile message is intended only for the confidential use of the designated recipient(s) named above. This message may contain proprietary information, and / or may be a consultant / client communication, and as such is privileged and confidential. If the reader of this message is not the intended recipient or an agent responsible for delivering it to the intended recipient, you are hereby notified that you have received this document in error, and that any review, dissemination, distribution, or copying of this message is strictly prohibited. If you have received this note in error, please notify us immediately and return the original message to us by mail at our expense.

STANDARD OPERATING PROCEDURE 3005:

SW846 3005A Acid Digestion of Waters for Total Recoverable or Dissolved Metals for Analysis by FLAA, ICP or ICP-MS

Revision 01
Effective Date: May 10, 2005

Author: **Dennis Jachim**

Printed Name	Signature/Date
Bruce Anderson **Inorganics Manager**	_____
Dennis Jachim **Technical Manager**	_____
Laurie Fetterman **QA Manager**	_____
Donald Cortes **Laboratory Director**	_____

This Standard Operating Procedure has been prepared for the sole use of STAT Analysis Corporation.

Copy Number: _____

The absence of a Copy Number indicates this is an uncontrolled copy of the document supplied for information only.

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1. Identification of Test Method

SW846 3005A Acid Digestion of Waters for Total Recoverable or Dissolved Metals for Analysis by FLAA, ICP, or ICP-MS.

2. Applicable Matrix or Matrices

This method is applicable to the following matrices: waters, and SPLP and TCLP extracts.

3. Detection Limits

Detection limits for this method are not applicable. Please refer to the analytical SOP 4510 Metals Analysis by Inductively Coupled Plasma-Mass Spectrometry and SOP 4550 Analysis of Lead by atomic Absorption Direct Aspiration for the corresponding detection limits.

4. Scope and Application

4.1 This digestion procedure is used for the preparation of aqueous samples, mobility-procedure extracts, and wastes that contain suspended solids for analysis by FLAA, ICP or ICP-MS. The procedure is used to determine total recoverable metals.

Samples prepared by this SOP may be analyzed for the following:

Aluminum	Magnesium
Antimony	Manganese
Arsenic	Molybdenum
Barium	Nickel
Beryllium	Potassium
Boron	Selenium
Cadmium	Silver
Calcium	Sodium
Chromium	Thallium
Cobalt	Tin
Copper	Titanium
Iron	Vanadium
Lead	Zinc

4.2 When analyzing for total dissolved metals, filter the sample at the time of collection, prior to acidification with nitric acid.

4.3 This method is restricted to use by or under the supervision of analysts experienced in the digestion process. Each workcell/ analyst must demonstrate the ability to generate acceptable results with this method.

5. Summary of Test Method

5.1 Total recoverable metals – The entire sample is acidified at the time of collection with nitric acid. At the time of analysis the sample is heated with acid and substantially reduced in volume. The digestate is filtered (optional) and diluted to volume and is then ready for analysis.

5.2 Dissolved metals – The sample is filtered through a 0.45 µm filter. Samples for dissolved metals do not need to be digested as long as the acid concentrations have been adjusted to the same concentration as in the standards.

5.3 Method Modifications

5.3.1 The laboratory uses this procedure to digest samples for ICP-MS analysis.

5.3.2 The laboratory uses slightly different concentrations of acids to perform the digestion due to the use of ICP-MS.

5.3.3 The laboratory uses this preparation procedure for the analysis of boron, tin and titanium. These analytes are not originally covered in the scope of EPA 3005A.

6. Definitions

The STAT Analysis Corporation Quality Assurance Manual (QAM) contains the definitions of standard terms used in this SOP.

7. Interferences

The analyst should be cautioned that this digestion procedure might not be sufficiently vigorous to destroy some metal complexes.

8. Safety

8.1 General laboratory protection (safety glasses, lab coat, disposal latex/nitrile gloves) should be worn at all times when handling samples or reagents. Use extreme caution when handling concentrated acids.

8.2 The digestion, and all reagent additions must be performed in a fume hood.

8.3 The potential health hazards from the samples cannot be determined. Therefore, exposure to the samples should be minimized to the extent possible.

8.4 Other safety precautions must be conducted in accordance with the Chemical Hygiene Plan. Other actions can also be applied if deemed necessary. A reference file of material safety data sheets (MSDS) is available in each room for personnel involved in an analysis using chemicals.

9. Equipment and Supplies

9.1 The following apparatus is recommended for performing this procedure. Equivalent items can be used, if with their use, the analytical and QA/QC requirements in this SOP can be met.

9.1.1 Polypropylene Digestion Vessels or equivalent, graduated 70 mL

9.1.2 25 mm Polypropylene ribbed watch glasses, or equivalent.

9.1.3 Thermometer capable of measuring to at least 125°C with suitable precision and accuracy.

9.1.4 Filter paper – Whatman No. 41 or equivalent.

9.1.5 0.45 micron filter disks (Whatman Paradisc (13mm)) and 10 mL syringe (used for dissolved metals analysis)

9.1.6 Disposable tubes, approximately 15 mL

9.1.7 CPI ModBlock block digestor or equivalent – Adjustable and able to maintain a temperature of 90-100°C.

9.1.8 Funnel or equivalent.

9.1.9 Autopipetter: 0.010 to 0.10 mL, 0.10 to 1.0 mL, 1.0 to 5.0 mL

9.1.10 Acid dispensers, repipet 1-10 mL, 1-5 mL

9.1.11 pH paper, wide range

9.1.12 Graduated cylinder – 1 Liter

9.1.13 150 mL glass Pyrex® Griffin beakers or equivalent

9.1.14 40 to 50 mm glass ribbed watch glass

9.1.15 Thermolyne Cimarec Model 3 hot plate or equivalent

10. Reagents and Standards

The following reagents and standards are required to perform this procedure. When instructions are given on how to prepare a specific volume of a reagent or standard, larger or smaller volumes can be prepared as needed so long as the final concentrations remain the same. Any other deviations from the reagents or standards listed in this SOP could be detrimental to the quality of the data produced. Such deviations would have to be approved and documented (see SOP 230 Corrective Action). Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. If the purity of a reagent is questionable, analyze the reagent to determine the level of impurities. The reagent blank must be less than the RL in order to be used.

10.1 Instructions for labeling and record keeping of reagents and standards are contained in SOP 1010 Analytical Standards and Reagent Receipt and Preparation.

10.2 Reagents – In methods where the purity of reagents is not specified, analytical reagent grade shall be used. Reagents of lesser purity than those specified by the test method shall not be used.

10.3 Reagent Water - Reagent water will be interference free. All references to water in the method refer to reagent water unless otherwise specified. An in-house water system is used.

10.4 Nitric acid (concentrated), HNO_3 – Trace Metal Grade, and analyzed to determine level of impurities. If method blank is < RL, the acid can be used.

10.5 Nitric Acid 1:1 – Place 20 Liter carboy in sink. Add approximately 9 Liters of reagent water. Slowly add Nitric Acid (4-2.5 Liter bottles) to the carboy at a rate of one bottle every minute. Bring up to the 20 Liter mark with reagent water. Mix well. ***Note: Lab coats, gloves, safety glasses, and a face shield must be worn when preparing the 1:1 Nitric Acid.***

10.6 Hydrochloric acid (concentrated), HCL - Trace Metal Grade, and analyzed to determine level of impurities. If method blank is < RL the acid can be used.

10.7 ICPMS LCS and Matrix Spiking Solution: Spike 1 mL of the working spike solution per 50 mL of sample.

10.8 FLAA Spike Solution - Spike 0.5 mL of the lead ICV/CCV stock intermediate per 50 mL of sample.

11. Sample Collection, Preservation, Shipment and Storage

All samples are stored away from all standards, reagents, food and other potentially contamination sources in order to prevent cross contamination.

11.1 Sample Collection: 250 mL or 500 mL plastic bottle

11.1.1 Total recoverable metals – All samples must be acidified at the time of collection with HNO_3 (~ 5 mL/L) to pH <2.

11.1.2 Dissolved metals – All samples must be filtered through a 0.45-µm filter and then acidified at the time of collection with HNO_3 (~ 5 mL/L) to pH <2. (If the unpreserved sample is filtered in the laboratory, a blank and a laboratory control sample must also be filtered, and analyzed with the batch.)

11.2 Sample Storage: Samples may be chilled to 0.1 - 6°C or stored at room temperature.

11.3 Digestate Storage: store at room temperature

11.4 Holding time is 180 days from time of sample collection.

12. 0 Quality Control

The following details the QC requirements that apply to this analysis. Each Quality Control Indicator (QCI) provides information pertaining to either method or individual sample performance. Our goal is to produce defensible data of known and documented quality.

The results of these QCI samples are used to assess the acceptability of data.

12.1 Blanks

Method Blank analysis is performed to determine if any contamination is present in the analytical process and is used to evaluate acceptance of the batch of samples. A method blank shall be prepared once per preparation batch of 20 or less samples per matrix type. If more than 20 samples are prepared a second blank shall be prepared after the twentieth sample. The method blank shall be processed through all preparatory steps used for the samples, including cleanup procedures. The blank shall be analyzed using the same instrument and conditions as the samples.

12.2 Laboratory Control Sample (LCS)

The LCS is used to evaluate the performance of the total analytical system, including all preparation and analysis steps. The LCS shall be prepared once per preparation batch of 20 or less samples per matrix type. If more than 20 samples are prepared a second LCS shall be prepared after the twentieth sample. The LCS shall be processed through all preparatory steps used for the samples, including cleanup procedures. The LCS shall be analyzed using the same instrument and conditions as the samples. Refer to Section 10.7 for instructions.

12.3 Duplicates

Duplicates of field samples or of the LCS must be prepared in compliance with the method requirements and client directives. Note: the analysis of the Matrix Spike Duplicate (MSD) is used as a substitute for the laboratory duplicate. In those cases when there is insufficient sample to perform either a duplicate analysis or MSD analysis, the duplicate analysis of the LCS (LCS/LCSD) is used to judge the precision of the analytical results.

12.4 Matrix Spike and Matrix Spike Duplicate (MS/MSD)

MS/MSDs indicate the effect of the sample matrix on the precision and accuracy of the results generated using the selected method. This information does not determine the validity of the entire batch. MS/MSDs must be analyzed at a minimum of 1 per 20 samples per matrix per preparation procedure, or as specified by the required test method.

Samples chosen for matrix spiking are rotated among different clients and/or different client projects. This is accomplished through communication between the Department Manager and the analyst. In addition, designated samples, as indicated by client request or contract requirement, are matrix spiked.

The MS/MSD pair shall be processed through all preparatory steps used for the samples. They shall be analyzed using the same instrument and conditions as the samples. Refer to Section 10.7 and section 10.8 for sample spiking instructions for ICP-MS and FLAA, respectively. Some clients may require different spiking levels; these specific needs are documented on the request for analysis forms.

13. Calibration and Standardization

Support Equipment

Autopipettes - Check autopipette to ensure standardization is within control limits (see SOP General Laboratory Practices 1040 for Pipette Calibration).

Thermometers – Check the thermometer to ensure the calibration has not expired (see SOP 1040 General Laboratory Practices for Thermometer Calibration). Check the thermometer during the analysis and record the corrected temperature in the preparation logbook.

14. Procedure

14.1 Block Digestion

14.1.1 Initial Set-up:

14.1.1.1 Turn on power switch

14.1.1.2 Use SELECT button to choose A

14.1.1.3 Push and hold down the ENTER button until OFF appears

14.1.1.4 Select temperature using UP (▲) and DOWN (▼) arrows

14.1.1.5 Push the ENTER button until the status light starts to flash

14.1.1.6 If you want to turn B on, use the SELECT button to choose B and repeat steps 14.1.3 to 14.1.5

14.1.1.7 Status light will stop flashing when the correct temperature is reached

14.1.1.8 Place the dedicated temperature digestion vessel (a vessel filled with water to monitor the temperature of samples) in the block. Allow the temperature to equilibrate. Adjust the thermostat if the temperature is not correct (95°C ± 5°C or 194 to 212°F). Record the corrected temperature reading in the prep logbook.

14.1.2 Transfer an aliquot of well-mixed sample to a sample digestion vessel and fill to the 50-mL mark. Record the sample volume in the prep logbook.

NOTE: All steps requiring the use of acids must be conducted under a fume hood using appropriate laboratory safety equipment.

14.1.3 Add 3 mL of 1:1 HNO_3 and 1 mL of concentrated HCL. Record the reagent identification in the prep logbook. Place the digestion vessel into the block digestor, attach watch glass and heat the sample to 95°C ± 5°C (or 194 to 212°F) until the volume has been reduced to less than one-half (approximately 3 to 6 hours). Record the "start" time in the prep logbook.

CAUTION: Do not boil. Antimony is easily lost by volatilization from hydrochloric acid media.

14.1.4 Remove the vessel and allow it to cool. Wash down the vessel walls and watch glass with water and, when necessary, filter the sample to remove silicates and other insoluble material that could clog the nebulizer. Record the "End Time" in the sample Prep logbook.

14.1.4.1 Filtration using Whatman no. 41 filter paper should be done only if there is concern that insoluble materials may clog the nebulizer; this additional step is liable to cause sample contamination unless the filter and filtering apparatus are thoroughly cleaned and pre-rinsed with 1:1 HNO_3, followed by reagent water. Filter the entire sample, and rinse the filter with reagent water.

14.1.5 Adjust the final volume to the 50 mL mark with reagent water, cap, and mix well.

14.2 Beaker Digestion

14.2.1 Turn on the hot plate. Place the temperature beaker (a beaker filled with water to monitor the temperature of samples) on the hot plate. Allow the temperature to equilibrate. Adjust the thermostat if the temperature is not correct (95°C ± 5°C or 194 to 212°F). Record the temperature reading in the prep logbook.

14.2.2 Transfer an aliquot of well-mixed sample to a labeled 70-mL polypropylene sample digestion vessel and fill to the 50-mL mark. Record the sample volume in the prep logbook.

14.2.3 Pour the 50 ml of sample into a clean pre-labeled 150 ml beaker. Rinse the vessel and cap and save the labeled 70-mL polypropylene sample digestion vessel.

NOTE: All steps requiring the use of acids must be conducted under a fume hood using appropriate laboratory safety equipment.

14.2.4 Add 3 mL of 1:1 HNO_3 and 1 mL of concentrated HCL. Record the reagent identification in the prep logbook. Place the beaker on the hot plate, cover with a 50-mm glass ribbed watch glass and heat the sample to 95°C ± 5°C (or 194 to 212°F) until the volume has been reduced to less than one-half (approximately 1.5 to 2 hours). Record the "start" time in the prep logbook.

CAUTION: Do not boil. Antimony is easily lost by volatilization from hydrochloric acid media.

14.2.5 Remove the beaker and allow it to cool. Wash down the beaker walls and watch glass with water and, when necessary, filter the sample to remove silicates and other insoluble material that could clog the nebulizer. Record the "End Time" in the sample Prep logbook.

14.2.5.1 Filtration using Whatman no. 41 filter paper should be done only if there is concern that insoluble materials may clog the nebulizer; this additional step is liable to cause sample contamination unless the filter and filtering apparatus are thoroughly cleaned and pre-rinsed with 1:1 HNO_3, followed by reagent water. Filter the entire sample, and rinse the filter with reagent water.

14.2.6 Transfer the sample back into the labeled 70-mL polypropylene sample digestion vessel. Rinse the beaker with reagent water and bring to a final volume of 50 mL.

15. Data Reduction, Calculations and Loading

15.1 The procedure for uploading data into the LIMS system is detailed in SOP 1400 LIMS.

16. Method Performance

Demonstration of Capability (DOC)

All parameters of interest must meet the method acceptance criteria before actual sample analysis begins. See SOP 1230 Training for the procedure to perform and document the DOC. The DOCs for the analysts performing this method are located in the analysts' training form folders located in the QA office files.

16.1 ICP-MS Metals

A quality control (QC) reference concentrate is required containing elements at an approximate concentration of 10 to 250 µg/L for aqueous samples using the LCS solution (SOP 4510 Metal Analysis by Inductively Coupled Plasma- Mass Spectrometry). Note: The LCS solution may need several different dilutions to accommodate all the analytes. The QC reference sample is made using stock standards prepared independently from those used for calibration.

For each analyte calculate the mean recovery (X) and standard deviation (s) and the average % Recovery (%R). Compare X and s and %R with the corresponding acceptance criteria for accuracy and precision, respectively. Note: For aqueous samples, X must be within 10 ± 2 µg/L to 250 ± 50 µg/L and s must be less than 2 and 50 µg/L and %R must be within 100 ± 20%. These limits are taken from established in-house criteria If X and s and %R for all analytes meet the acceptance criteria, the system performance is acceptable and analysis of actual samples can begin. If X or %R falls outside the range for accuracy, or s exceeds the precision limit, then the system performance is unacceptable for that analyte and corrective action must be taken.

16.2 Lead by FLAA

Four Quality Control (QC) reference concentrates are required containing lead at 1 mg/L. They are made (using the LCS solutions and materials in Section 10.9.6) as described in section 12.2 of SOP 4550 Analysis of Lead by Atomic Absorption Direct Aspiration (NIOSH 7082, EPA IO-3.2, and EPA 7420). The QC reference samples are made using stock standards prepared independently from those used for calibration.

Calculate the mean recovery (X) and standard deviation (s) and the average % Recovery (%R). Compare X and s and %R with the corresponding acceptance criteria for accuracy and precision, respectively. For aqueous samples, X must be within 1 ± 0.2 mg/L and s must be less than 0.2 mg/L and %R must be within 100 ± 20%. These limits are taken from

established in-house criteria If X and s and %R for all analytes meet the acceptance criteria, the system performance is acceptable and analysis of actual samples can begin. If X or %R falls outside the range for accuracy, or "s" exceeds the precision limit, then the system performance is unacceptable for that analyte and corrective action must be taken.

Comparison to Reference Method Data

Not applicable to this SOP

In-House Control Limits

Not applicable to this SOP

17. Pollution Prevention

The preparation of excessive volumes of laboratory reagents and standards shall be avoided so that waste and potential for pollution are minimized. Samples, reagents and standards shall be disposed in compliance with the lab waste disposal program, SOP 1130 Waste Disposal. With the consent of the client, the samples may be returned to their origin for treatment.

Uncontaminated paper waste, glass and cans should be separated for recycling. Laboratory staff is required to protect the laboratory's and our clients' business information when disposing of recycled paper or waste from the facility.

18. Data Assessment and Criteria for Quality Control Measures

The laboratory must maintain records to document the quality of data that is generated. Ongoing quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. The data review is conducted according to SOP 1250 Data Review.

Record any samples not properly preserved, any holding time exceeded, or deviations from this SOP in the logbook.

19. Corrective Actions for Out-Of-Control Data

The process for handling unacceptable and out of control data is found in SOP 230 Corrective Action. Corrective action, if necessary, will be implemented by the department manager. Possible actions include:

1) Review standards digestion logbooks. Check all sample data entries and ensure all support equipment checks are properly recorded.
2) Re-Analyze the samples as directed by the department manager.
3) Perform routine preventative maintenance following manufacturer's specification. Record all maintenance in the maintenance logbook.

20. Contingencies for Handling Out-Of-Control Or Unacceptable Data

Every effort is made to prevent problems from occurring. When out of control or unacceptable data occurs the first option is to identify the problem and reanalyze the samples within the holding times. When this is not possible, the QA Manager and/or the Laboratory Director will review data and discusses options with the client. Re-analysis or reporting the data with qualifications are alternatives. Out-of-control or unacceptable data reported to the client must include the data qualifier, flag and discussion on the rationale for reporting.

20.1 The process for handling unacceptable and out of control data is found in the Laboratory QAM Section 11. The reporting of data that is out of control must be approved and documented by Quality Assurance Manager and either the Technical Manager or the Laboratory Director.

20.2 Client Requested Modifications: See applicable analytical SOP.

21. Waste Management

The STAT Analysis Corporation SOP 1130 Waste Disposal identifies proper waste management practices for the chemicals and biological materials used in this procedure. Samples are stored and discarded accordance with SOP 1130 Waste Disposal.

22. References

22.1 Method 3005A, U.S. EPA SW-846 "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods" Update III, December 1996.
22.2 STAT Analysis Corporation Quality Assurance Manual
22.3 STAT SOP 003 Chemical Hygiene Plan
22.4 STAT SOP 230 Corrective Action
22.5 STAT SOP 1000 Control and Use of Laboratory Notebooks
22.6 STAT SOP 1010 Analytical Standards and Reagent Receipt and Preparation
22.7 STAT SOP 1020 Laboratory Glassware Cleaning
22.8 STAT SOP 1040 General Laboratory Practices
22.9 STAT SOP 1130 Waste Disposal
22.10 STAT SOP 1210 Method Detection Limits
22.11 STAT SOP 1230 Training
22.12 STAT SOP 1250 Data Review
22.13 STAT SOP 1400 LIMS
22.14 STAT SOP 4510 Metals Analysis by Inductively Coupled Plasma- Mass Spectrometry
22.15 STAT SOP 4550 Analysis of Lead by Atomic Absorption Direct Aspiration (NIOSH 7082, EPA IO-3.2, and EPA 7420)

23. Forms, Figures, Tables, Diagrams, Flowcharts, Attachments or Validation Data

Attachment 1: ICP-MS Preparation Logbook
Attachment 2: Pb Preparation Logbook

ATTACHEMNT 1: ICP-MS Preparation Logbook

Logbook # 23-0007

STAT ANALYSIS

ICP-MS Prep Logbook

Start Time:

End Time:

Temperature:

Thermometer ID#:

Matrix: W = Water, S = Soil, T = TCLP, D = Dissolved

Sp = SPLP, Wp = Wipe, A = Air

Analyst	Date	Sample #	Bottle #	Matrix	Sample Wt./Vol. (g or mls)	Final Volume (mls)	Spike Volume (mls)	Spike Solution ID#	Comments

Reagent ID#s

HNO_3: _____

H_2O_2: _____

HCl: _____

Reviewed by /Date: _____

Attachment 2: Pb Preparation Logbook

Logbook22-0019

STAT ANALYSIS

Lead Prep Logbook

Matrix A = Air, Wp = Wipes, S = Soil, T= TCLP, P= Paint, WW= Waste Water, AA = Ambient Air

Analyst(s)	Date	Start time	End time	Client	Sample #	Count	Matrix	Sample Wt/ Vol (g or mls)	Final Vol (mls)	Spike Amount (g or mls)	Spike Solution ID#	Temp °C	Area / Volume	TAT	Comments

Acid Reagent #: _____ Page 1 of 200 Reviewed by/Date: _____

STANDARD OPERATING PROCEDURE 3110:

SW846 3050B Acid Digestion of Sediments, Sludges, and Soils for Metals Analysis by FLAA, ICP, or ICP-MS

Revision 03
Effective Date: December 24, 2002

Author: **Dennis Jachim**

Printed Name	Signature/Date
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1. Identification of Test Method

SW846 3050B Acid digestion of Sediments, Sludges, and Soils for Metals Analysis by FLAA, ICP, or ICP-MS.

2. Applicable Matrix or Matrices

This method is applicable to the following matrices: sediments, soils and sludges.

3. Detection Limits

Detection limits for this method are not applicable. Please refer to the analytical SOPs 4510 ICP/MS and 4100 ICP for corresponding detection limits.

4. Scope and Application

4.1 Samples prepared by this method may be analyzed by ICP-AES for all the listed metals as long as the detection limits are adequate for the required end-use of the data. Alternative determinative techniques may be used if they are scientifically valid and the QC criteria of the method, including those dealing with interferences, can be achieved. Other elements and matrices may be analyzed by this method if performance is demonstrated for the analytes of interest, in the matrices of interest, at the concentration levels of interest. The recommended determinative techniques for each element are listed below:

FLAA/ICP-AES		ICP-MS
Aluminum	Magnesium	Arsenic
Antimony	Manganese	Barium
Barium	Molybdenum	Beryllium
Beryllium	Nickel	Cadmium
Cadmium	Potassium	Chromium
Calcium	Silver	Cobalt
Chromium	Sodium	Iron
Cobalt	Thallium	Lead
Copper	Vanadium	Molybdenum
Iron	Zinc	Selenium
Lead		Thallium

In addition, all of the above listed elements plus Boron and Tin are analyzed using ICP-MS.

4.2 This method is not a total digestion technique for most samples. It is a very strong acid digestion that will dissolve almost all elements that could become "environmentally available." By design, elements bound in silicate structures are not normally dissolved by this procedure, as they are not usually mobile in the environment. If absolute total digestion is required an alternate digestion procedure must be used.

5. Summary of Test Method

5.1 For the digestion of samples, a representative 0.8-1.2 gram (wet weight) or 0.5 gram (dry weight) sample is digested with nitric acid (HNO_3 and hydrogen peroxide (H_2O_2).

5.2 Hydrochloric acid (HCl) is added to the digestate and the sample is refluxed. The digestate is then diluted to a final volume of 50 mL.

5.3 If required, a separate sample aliquot shall be dried for a total percent solids determination.

5.4 Method Modifications

5.4.1 The laboratory uses this procedure to digest samples for ICP/MS analysis.
5.4.2 The laboratory uses slightly different concentrations of acids to perform the digestion.

6. Definitions

The STAT Analysis Corporation Quality Assurance Manual (QAM) contains the definitions of standard terms used in this SOP.

7. Interferences

Sludge samples can contain diverse matrix types, each of which may present it's own analytical challenge. Spiked samples and any relevant standard reference material should be processed in accordance with the quality control requirements given in Section 12 to aid in determining whether Method 3050B is applicable to a given waste.

8. Safety

8.1 General laboratory protection (safety glasses, lab coat, disposal latex/nitrile gloves) should be worn at all times when handling samples or reagents. Use extreme caution when handling concentrated acids.

8.2 The digestion, and all reagent additions must be performed in a fume hood.

8.3 The potential health hazards from the samples cannot be determined. Therefore, exposure to the samples should be minimized to the extent possible.

8.4 Other safety precautions must be conducted in accordance with the Chemical Hygiene Plan. Other actions can also be applied if deemed necessary. A reference file of material safety data sheets (MSDS) is available in each room for personnel involved in an analysis using chemicals.

9. Equipment and Supplies

9.1 The following apparatus is recommended for performing this procedure. Equivalent items can be used, if with their use, the analytical and QA/QC requirements in this SOP can be met.

9.1.1 Polypropylene Digestion Vessels or equivalent, graduated 70 mL and 100 mL

9.1.2 Polypropylene ribbed watch glasses, or equivalent.

9.1.3 Drying ovens – able to maintain 30°C ± 4°C.

9.1.4 Thermometer capable of measuring to at least 125°C with suitable precision and accuracy.

9.1.5 Filter paper – Whatman No. 41 or equivalent.

9.1.6 Disposable tubes, approximately 15 mL

9.1.7 Analytical balance – capable of accurate weighings to 0.01 g.

9.1.8 CPI ModBlock block digestor or equivalent – Adjustable and able to maintain a temperature of 90-100°C.

9.1.9 Funnel or equivalent.

9.1.10 Autopipetter: 0.010 to 0.10 mL, 0.10 to 1.0 mL, 1.0 to 5.0 mL

9.1.11 Acid dispensers, repipet 1-10 mL, 1-5 mL

9.1.12 Teflon Boiling chips

9.1.13 Wooden Spatula

9.1.14 Graduated cylinder – 1 Liter

10. Reagents and Standards

The following reagents and standards are required to perform this procedure. When instructions are given on how to prepare a specific volume of a reagent or standard, larger or smaller volumes can be prepared as needed so long as the final concentrations remain the same. Any other deviations from the reagents or standards listed in this SOP could be detrimental to the quality of the data produced. Such deviations would have to be approved and documented (see SOP 230 Corrective Action). Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. If the purity of a reagent is questionable, analyze the reagent to determine the level of impurities. The reagent blank must be less than the RL in order to be used.

10.1 Instructions for labeling and record keeping of reagents and standards are contained in SOP 1010 Standard and Reagent Preparation.

10.2 Reagents – In methods where the purity of reagents is not specified, analytical reagent grade shall be used. Reagents of lesser purity than those specified by the test method shall not be used.

10.3 Reagent Water - Reagent water will be interference free. All references to water in the method refer to reagent water unless otherwise specified. An in-house water system is used.

10.4 Nitric acid (concentrated), HNO_3 - Trace Metal Grade, and analyzed to determine level of impurities. If method blank is < RL, the acid can be used.

10.5 Nitric Acid 1:1 – Place 20 Liter carboy in sink. Add approximately 9 Liters of reagent water. Slowly add Nitric Acid (4-2.5 Liter bottles) to the carboy at a rate of one bottle every minute. Bring up to the 20 Liter mark with reagent water. Mix well. ***Note: Labcoat, gloves, safety glasses, and a face shield must be worn when preparing the 1:1 Nitric Acid.***

10.6 Hydrochloric acid (concentrated), HCL – Trace Metal Grade, and analyzed to determine level of impurities. If method blank is < RL the acid can be used.

10.7 Hydrogen Peroxide (30%), H2O2 – Oxidant should be high purity, and analyzed to determine level of impurities. If method blank is < RL, the peroxide can be used.

10.8 ICPMS LCS and Matrix Spiking Solution: Spike 1 mL of the working spike solution per sample.

11. Sample Collection, Preservation, Shipment and Storage

All samples are stored away from all standards, reagents, food and other potentially contamination sources in order to prevent cross contamination.

11.1 Sample Collection: 4 oz glass jar

11.2 Sample Storage: Samples may be chilled to 4°C or stored at room temperature.

11.3 Digestate Storage: store at room temperature

11.4 Holding time is 180 days from time of sample collection.

12. Quality Control

The following details the QC requirements that apply to this analysis. Each Quality Control Indicator (QCI) provides information pertaining to either method or individual sample performance. Our goal is to produce defensible data of known and documented quality.

The results of these QCI samples are used to assess the acceptability of data.

12.1 Blanks

Method Blank analysis is performed to determine if any contamination is present in the analytical process and is used to evaluate acceptance of the batch of samples. A method blank shall be prepared once per preparation batch of 20 or less samples per matrix type (see Section 6 for definition of a prep batch). If more than 20 samples are prepared a second blank shall be prepared after the twentieth sample. The method blank shall be processed through all

preparatory steps used for the samples, including cleanup procedures. The blank shall be analyzed using the same instrument and conditions as the samples.

12.2 Laboratory Control Sample (LCS)

The LCS is used to evaluate the performance of the total analytical system, including all preparation and analysis steps. The LCS shall be prepared once per preparation batch of 20 or less samples per matrix type. If more than 20 samples are prepared a second LCS shall be prepared after the twentieth sample. The LCS shall be processed through all preparatory steps used for the samples, including cleanup procedures. The LCS shall be analyzed using the same instrument and conditions as the samples. Refer to Section 10.8 for instructions.

12.3 Duplicates

Duplicates of field samples or of the LCS must be prepared in compliance with the method requirements and client directives. Note: the analysis of the Matrix Spike Duplicate (MSD) is used as a substitute for the laboratory duplicate. In those cases when there is insufficient sample to perform either a duplicate analysis or MSD analysis, the duplicate analysis of the LCS (LCS/LCSD) is used to judge the precision of the analytical results.

12.4 Matrix Spike and Matrix Spike Duplicate (MS/MSD)

MS/MSDs indicate the effect of the sample matrix on the precision and accuracy of the results generated using the selected method. This information does not determine the validity of the entire batch. MS/MSDs must be analyzed at a minimum of 1 per 20 samples per matrix per preparation procedure, or as specified by the required test method. If an MS/MSD pair is not analyzed in the preparation batch, an LCS/LCSD pair is analyzed.

Samples chosen for matrix spiking are rotated among different clients and/or different client projects. This is accomplished through communication between the Department Manager and the analyst. In addition, designated samples, as indicated by client request or contract requirement, are matrix spiked.

The MS/MSD pair shall be processed through all preparatory steps used for the samples. They shall be analyzed using the same instrument and conditions as the samples. Refer to Section 10.8 for instructions. Some clients may require different spiking levels, these specific needs are documented on the request for analysis forms.

13. Calibration and Standardization

Support Equipment

Autopipettes - Check autopipette to ensure standardization is within control limits (see SOP 1040 for Pipette Calibration).

Thermometers – Check the thermometer to ensure the calibration has not expired (see SOP 1040 for Thermometer Calibration). Check the thermometer during the analysis and record the corrected temperature in the preparation logbook.

14. Procedure

14.1 Block Digestor Initial Set-up:

14.1.1 Turn on power switch

14.1.2 Use SELECT button to choose A

14.1.3 Push and hold down the ENTER button until OFF appears

14.1.4 Select temperature using UP (▲) and DOWN (▼) arrows

14.1.5 Push the ENTER button until the status light starts to flash

14.1.6 If you want to turn B on, use the SELECT button to choose B and repeat steps 14.1.3 to 14.1.5

14.1.7 Status light will stop flashing when the correct temperature is reached

14.1.8 Place the dedicated temperature digestion vessel in the block. Allow the temperature to equilibrate. Adjust the thermostat if the temperature is not correct (95°C ± 5°C or 194 to 212°F). Record the corrected temperature reading in the logbook.

14.2 Mix the sample thoroughly to achieve homogeneity. All equipment used for homogenization should be cleaned to minimize the potential of cross-contamination. For each digestion procedure, weigh to the nearest 0.01 g and transfer a 0.8-1.2 g sample (wet weight) or a 0.5 g sample (dry weight) to a digestion vessel. For samples with high liquid content, a larger sample size may be used as long as digestion is completed. For samples with limited quantity or suspected to contain high levels of metals, a smaller sample size may be used. Separate sample aliquots will be weighed out for MS/MSD analysis, and spiked with an appropriate spiking solution (Section 10.8). For Method Blank analysis, weigh out approximately 1 gram of the Teflon boiling chips. For LCS analysis, weigh out approximately 1 gram of the Teflon boiling chips, and spike with 1 mL of the Spiking Solution (Section 10.8). Record all weights in the prep logbook.

NOTE: All steps requiring the use of acids should be conducted under a fume hood using appropriate laboratory safety equipment.

14.3 Add 10 mL of 1:1 HNO_3, mix the slurry, and cover with a watch glass. Place the covered digestion vessel into the block digestor, heat the sample to 95°C ± 5°C (or 194 to 212°F) and reflux for approximately 1 hour. Record the "start" time and the reagent identification in the prep logbook.

NOTE: Do not allow the solution to go to dryness, as this may affect the recovery of certain analytes. If a sample goes to dryness, a new sample aliquot must be digested.

14.4 After the step in Section 14.3 has been completed and the sample has cooled for approximately 15 minutes, add 2 mL of 30% H_2O_2. Record the reagent identification in the prep logbook. Cover the vessel with a watch glass and return the covered vessel to the heat source for warming and to start the peroxide reaction. Care must be taken to ensure that losses do not occur due to excessively vigorous effervescence. Heat until effervescence subsides and cool the vessel (approximately 15 minutes).

14.4.1 Add 2 mL of 30% H_2O_2. Cover the vessel with a watch glass and return the covered vessel to the heat source for warming and to start the peroxide reaction. Care must be taken to ensure that losses do not occur due to excessively vigorous effervescence. Heat until effervescence subsides (approximately 15 minutes).

NOTE: Do not add more than a total of 4 mL 30% H_2O_2.

14.4.2 Continue heating the acid-peroxide digestate at 95°C ± 5°C (or 194 to 212°F) without boiling for 45 minutes. Maintain a covering of solution over the bottom of the vessel at all times. Note: As necessary, add minimal amounts (1-2 mL) of reagent water to maintain the covering of solution over the bottom of the vessel.

14.5 Let cool for 15 minutes. Add 1 mL of concentrated HCl and cover with a watch glass. Record the reagent identification in the prep logbook. Place the sample in the block digestor and reflux 15 to 30 minutes. Remove from heat and allow to cool.

NOTE: Do not allow the solution to go to dryness, as this may affect the recovery of certain analytes. If a sample goes to dryness, a new sample aliquot must be digested.

14.5.1 Wash down the vessel walls and watch glass with water and, when necessary, filter the sample to remove silicates and other insoluble material that could clog the nebulizer. Record the "End Time" in the sample Prep logbook.

14.5.1.1 Filtration using Whatman no. 41 filter paper should be done only if there is concern that insoluble materials may clog the nebulizer; this additional step is liable to cause sample contamination unless the filter and filtering apparatus are thoroughly cleaned and pre-rinsed with 1:1 HNO_3, followed by reagent water. Filter the entire sample, and rinse the filter with reagent water.

14.5.1.2 Adjust the final volume to the 50 mL mark with reagent water, cap, and mix well. The sample is now ready for analysis.

15. Data Reduction, Calculations and Loading

15.1 The procedure for uploading data into the LIMS system is detailed in SOP 1400 LIMS.

16. Method Performance

Demonstration of Capability (DOC)

All parameters of interest must meet the method acceptance criteria before actual sample analysis begins. See SOP 1230 Training for the procedure to perform and document the DOC. The DOCs for the analysts performing this method are located in the analysts' training form folders located in the QA office files.

A quality control (QC) reference concentrate is required containing elements at an approximate concentration of 500 to 12500 µg/Kg for soil samples using the LCS solution (SOP 4510). Note: The LCS solution may need several different dilutions to accommodate all the analytes. The QC reference sample is made using stock standards prepared independently from those used for calibration.

For each analyte calculate the mean recovery (X) and standard deviation (s) and the average % Recovery (%R). Compare X and s and %R with the corresponding acceptance criteria for accuracy and precision, respectively. Note: For soil samples, X must be within 500 ± 100 µg/Kg to 12500 ± 2500 µg/Kg and s must be less than 100 and 2500 µg/Kg and %R must be within 100 ± 20%. These limits are taken from established in-house criteria If X and s and %R for all analytes meet the acceptance criteria, the system performance is acceptable and analysis of actual samples can begin. If X or %R falls outside the range for accuracy, or s exceeds the precision limit, then the system performance is unacceptable for that analyte and corrective action must be taken.

Comparison to Reference Method Data

Not Applicable

In-House Control Limits

Not Applicable

17. Pollution Prevention

The preparation of excessive volumes of laboratory reagents and standards shall be avoided so that waste and potential for pollution are minimized. Samples, reagents and standards shall be disposed in compliance with the lab waste disposal program, SOP 1130. With the consent of the client, the samples may be returned to their origin for treatment.

Uncontaminated paper waste, glass and cans should be separated for recycling. Laboratory staff are required to protect the laboratory's and our clients' business information when disposing of recycled paper or waste from the facility.

18. Data Assessment and Criteria for Quality Control Measures

The laboratory must maintain records to document the quality of data that is generated. Ongoing quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. The data review is conducted according to SOP 1250 Data Review.

Record any holding time exceedences or deviations from this SOP in the logbook.

19. Corrective Actions for Out-Of-Control Data

The process for handling unacceptable and out of control data is found in SOP 230 Corrective Action. Corrective action, if necessary, will be implemented by the department manager. Possible actions include:

1) Review standards digestion logbooks. Check all sample data entries and ensure all support equipment checks are properly recorded.
2) Re-Analyze the samples as directed by the department manager.
3) Perform routine preventative maintenance following manufacturer's specification. Record all maintenance in the maintenance logbook.

20. Contingencies for Handling Out-Of-Control Or Unacceptable Data

Every effort is made to prevent problems from occurring. When out of control or unacceptable data occurs the first option is to identify the problem and reanalyze the samples within the holding times. When this is not possible, the QA Manager and/or the Laboratory Director will review data and discusses options with the client. Re-analysis or reporting the data with qualifications are alternatives. Out of control or unacceptable data reported to the client must include the data qualifier, flag and discussion on the rationale for reporting.

20.1 The process for handling unacceptable and out of control data is found in the Laboratory QAM Section 11. The reporting of data that is out of control must be approved and documented by Quality Assurance Manager and either the Technical Manager or the Laboratory Director.

20.2 Client Requested Modifications: See SOP 4510 ICP/MS Analysis

21. Waste Management

The STAT Analysis Corporation Waste Disposal SOP 1130 [or Chemical Hygiene Plan] identifies proper waste management practices for the chemicals and biological materials used in this procedure. Samples are stored and discarded accordance with SOP 1130 Waste Disposal.

22. References

22.1 Method 3050B, U.S. EPA SW-846 "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods" Update III, December 1996
22.2 STAT SOPs 4510 Metals Analysis Using ICP/MS, 4100 Metals Analysis using ICP
22.3 STAT SOP 1040 General Laboratory Procedures
22.4 STAT SOP 1020 Glassware Cleaning
22.5 STAT SOP 1010 Standard and Reagent Preparation
22.6 STAT SOP 1000 Control and Use of Laboratory Notebooks
22.7 STAT SOP 230 Corrective Actions
22.8 STAT SOP 1400 LIMS

22.9 STAT SOP 1130 Waste Disposal
22.10 STAT SOP 003 Chemical Hygiene Plan
22.11 STAT SOP 1250 Data Review
22.12 STAT SOP 1230 Training
22.13 STAT SOP 1210 Method Detection Limits (MDLs)
22.14 STAT Analysis Corporation Quality Assurance Manual

23. Forms, Figures, Tables, Diagrams, Flowcharts, Attachments or Validation Data

Not applicable.

STANDARD OPERATING PROCEDURE 3500

Extractions of Samples for Organic Analyses (EPA Methods 3510C, 3520C, 3545, 3550B, 3580A, 8151A)

Revision 04
Effective Date: November 12, 2007

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1.0 IDENTIFICATION OF TEST METHOD

SOP Title: Extractions of Samples for Organic Analyses (EPA Methods 3510C, 3520C, 3545, 3550B, and 3580A, 8151A).

2.0 APPLICABLE MATRIX OR MATRICES

Aqueous samples, non-potable waters, soils, sludges and other solid waste samples are extracted using methylene chloride (dichloromethane) or hexane for organic analysis. Aqueous samples and non-potable waters are extracted using ether for herbicide analysis. Organic liquids or other non-aqueous waste samples, that may contain organic chemicals at a concentration greater than 20,000 mg/kg, are diluted with a suitable (miscible) solvent prior to analysis.

3.0 DETECTION LIMITS

Not applicable to the SOP.

4.0 SCOPE AND APPLICATION

4.1 This method describes procedures for isolating organic compounds from a variety of matrices including aqueous samples, non-potable waters, soils, sludges and other solid waste samples. The method also describes concentration techniques suitable for preparing the sample extract for analysis. The extract is then analyzed for compounds of interest according to the appropriate analytical procedure.

4.2 Separatory Funnel Extraction (EPA Method 3510C): For aqueous samples, the compounds of interest are removed from the water sample using an organic solvent that is immiscible with water. This method is applicable to the isolation and concentration of water-insoluble and slightly water-soluble organics in preparation for a variety of chromatographic procedures. See Table 1 for the list of these procedures.

4.3 Continuous Liquid-Liquid Extraction (EPA Method 3520C) is designed for aqueous sample extraction using organic solvents with a density greater than the sample. This method is applicable to the isolation and concentration of water-insoluble and slightly water-soluble organics in preparation for a variety of chromatographic procedures. See Table 1 for the list of these procedures.

4.4 Pressurized Fluid Extraction (EPA Method 3545) is a procedure for extracting nonvolatile and semi-volatile organic compounds from soils, sediments, sludge, and other solid waste samples using an organic solvent with high pressure and high temperature.

4.5 Sonication or ultrasonic extraction (EPA Method 3550B) is a procedure for extracting nonvolatile and semi-volatile organic compounds from soils, sludges, wipes and other solid waste samples using an organic solvent.

4.6 Waste Dilution (EPA Method 3580A) is a procedure for dilution of non-aqueous waste samples that are expected to contain elevated concentrations (greater than 20,000 mg/kg) of organic compounds.

4.7 Herbicide Extraction (EPA Method 8151A) is a procedure for extracting herbicides from aqueous samples using diethyl ether. The procedure is also used for extracting herbicides from soils, sludges, and other solid waste samples using an organic solvent.

4.8 This method is restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with this method.

5.0 SUMMARY OF TEST METHOD

5.1 Separatory Funnel Extraction (EPA Method 3510C): A measured volume of sample, usually 1 Liter, at a specified pH (see Table 1), is serially extracted with methylene chloride using a separatory funnel. The sample is serially extracted with ether for herbicide analysis (EPA Method 8151A). This procedure is abbreviated SEP FUN in the laboratory records.

5.2 Continuous Liquid-Liquid Extractor (EPA Method 3520C): A measured volume of sample, usually 1 Liter, at a specified pH (see Table 1), is extracted with methylene chloride using a continuous liquid-liquid extractor. This procedure is abbreviated L/L in the laboratory records.

5.3 Pressurized Fluid Extraction (EPA Method 3545): A 30 g sample is mixed with anhydrous sodium sulfate to form a free-flowing powder. The sample is transferred into a stainless steel extraction vessel. The vessel is placed onto the Dionex Accelerated Solvent Extractor (ASE-300) and extracted at high temperature (100 ºC) and high pressure (1500 psig) with dichloromethane. The extract is concentrated to an appropriate final volume. If necessary, the extract is exchanged into a different solvent compatible with the cleanup or determinative step to be used. The extract is then analyzed by the appropriate analytical instrumental procedure.

5.4 Sonication (EPA Method 3550B): The extraction procedure is divided into three sections, based on the expected concentration of organics in the sample or the sample matrix. The low concentration method (individual organic components of $\leq$ 20 mg/kg) uses a larger sample of 30 grams. This procedure is abbreviated SON in the laboratory records.

5.4.1 Low Concentration Method: A 30 g sample is mixed with anhydrous sodium sulfate to form a free-flowing powder. For herbicide analysis, adjust the pH of the sample to < 2.0 with concentrated hydrochloric acid or 85ml of 0.1M phosphate buffer.(EPA Method 8151A) This is solvent extracted three times using sonication. The extract is separated from the sample by filtration. The extract is ready for cleanup and/or analysis following concentration.

5.4.2 High Concentration Method: Approximately 3 g of sample is mixed with anhydrous sodium sulfate to form a free-flowing powder. For herbicide analysis, adjust the pH of the sample to < 2.0 with concentrated hydrochloric acid or 85ml of 0.1M phosphate buffer. (EPA Method 8151A) This is solvent extracted three times using sonication. The extract is separated from the sample by filtration. The extract is ready for cleanup and/or analysis following concentration.

5.4.3 Wipe Method: The wipe is placed into a 40mL solid cap VOA vial. Appropriate amounts of surrogate and solvent are added to the vial. The vial is then sonicated for 10 minutes in an ultrasonic bath.

5.5 For the three procedures listed above, the extract is isolated from the sample. If necessary, it is dried to remove traces of water and concentrated through a controlled evaporation process to a final volume of 1 to 10 mL. If necessary, the extract is exchanged into a different solvent compatible with the cleanup or determinative step to be used. The extract is then analyzed by the appropriate analytical instrumental procedure.

5.6 Waste Dilution (EPA Method 3580A): One gram of sample is weighed into a capped tube, and the sample is diluted to 10 mL with an appropriate solvent that is miscible with the waste sample. It is recommended that an aliquot of the diluted sample be cleaned up as per the appropriate method prior to analysis. This procedure is abbreviated WST DIL in the laboratory records.

5.7 Method Modifications: Soils (EPA Methods 3550B, 3545 and 8151A) are extracted initially using dichloromethane instead of a 50/50 V/V mixture of dichloromethane/acetone as recommended.

TABLE 1. Specific Aqueous Extraction Conditions for Various Determinative SOPs

Determinative Method	Initial Extraction pH	Secondary Extraction pH	Exchange solvent	Exchange solvent for cleanup	Vol. of extract required for cleanup (mL)	Final extract vol. for analysis (mL)
8081A/8082	as received	----	hexane	hexane	10.0	10.0
8270C (SVOC)	< 2	> 11	none	----	1.0	1.0
8270C (SIM)	as received	----	none	----	1.0	1.0
8321A (HERB)	<2	----	acetonitrile	acetonitrile	1.0	1.0
3545 (PNA)	as received	----	none	----	1.0	1.0
3545 (PCB)	as received	----	hexane	hexane	10.0	10.0
3580 (All)	as received	----	none	----	10.0	10.0

6.0 DEFINITIONS

The STAT Analysis Corporation Quality Assurance Manual (QAM) contains the definitions of standard terms used in this SOP.

Preparation batch - composed of one to 20 environmental samples of the same NELAC-defined matrix with a maximum time between the start of processing of the first and last sample in the batch to be 24 hours (NELAC).

7.0 INTERFERENCES

7.1 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of chromatograms. All these

materials must be demonstrated to be free from interferences under the conditions of the analysis, by analyzing reagent blanks.

7.2 The decomposition of some analytes has been demonstrated under basic extraction conditions required to separate analytes. Organochlorine pesticides may dechlorinate, phthalate esters may exchange, and phenols may react to form tannates. These reactions increase with increasing pH, and are decreased by the shorter reaction times available in Method 3510C. Method 3510C is preferred over Method 3520C for the analysis of these classes of compounds. However, the recovery of phenols may be optimized by using Method 3520C and performing the initial extraction at the acid pH.

7.3 For some soil extractions, elevated concentrations of petroleum hydrocarbons will prevent the extracts from being concentrated to a final volume of 1 ml. Judgment must be exercised to determine whether an elevated detection level and reduced surrogate concentration is preferred using a larger final volume or if the sample should be re-extracted using the high concentration method. In either case, elevated detection levels will be reported.

7.4 Phthalate esters contaminate many types of products commonly found in the laboratory. Plastics, in particular, must be avoided because phthalates are commonly used as plasticizers and are easily extracted from plastic materials. Serious phthalate contamination may result at any time if consistent quality control is not practiced.

7.5 Soap residue (e.g. sodium dodecyl sulfate), which results in a basic pH on glassware surfaces, may cause degradation of certain analytes. Specifically, Aldrin, Heptachlor, and most organophosphorus pesticides will degrade in this situation. This problem is especially pronounced with glassware that may be difficult to rinse (e.g., 500-mL round-bottom flask). These items should be hand-rinsed very carefully to avoid this problem.

7.6 Refer to the appropriate analytical SOP Section 7.0 for more information on interferences.

8.0 SAFETY

Proper personal protective equipment including safety glasses, nitrile gloves, a lab coat, and closed toe shoes are required during different parts of this method. Other safety precautions must be conducted in accordance with SAP 003 Chemical Hygiene Plan. Other actions can also be applied if deemed necessary. A reference file of Material Safety Data Sheets (MSDS) is available to all personnel involved in this method.

The organic solvents used in this method are considered hazardous. The use of solvents should be performed in the fume hood as much as possible. Hexane and ether are flammable liquids and should only be used in small quantities.

Caution should be exercised when using the separatory funnel. Pressure can build when performing the first extraction. After adding the methylene chloride or ether and performing the initial shake of the funnel, carefully vent the funnel into the fume hood.

9.0 EQUIPMENT AND SUPPLIES

The following apparatus is recommended for performing this procedure. Equivalent items can be used, if with their use, the analytical and QA/QC requirements in this SOP can be met.

All catalog numbers in this SOP are current as of the effective date and thereafter subject to change.

9.1 Separatory Funnel: 1 and 2 Liter, Glass or Teflon, with Teflon Stopcock

9.2 Extraction Mixer: Variable Speed, capacity: 4-2L extraction vessels, (Barnstead/Lab-Line Model 6000)

9.3 Extraction Vessels, 2-L self-venting separatory funnel with Teflon Stopcock (Barnstead/Lab-Line Model 6099-2)

9.4 Continuous liquid-liquid extractor - Equipped with 45/50 glass connecting joints requiring no lubrication. Includes extractor, condenser and 500 mL round bottom flask (Reliance Catalog Number R-3730-100, or equivalent)

9.4.1 Electric heating mantle for round bottom flasks: (Glas-Col Catalog Number TM 106)
9.4.2 Controller for electric heating mantle: (Glas-Col PowrTwin)
9.4.3 Chiller: Polyscience Model 1173

9.5 For sonication procedure:

9.5.1 A horn-type sonicator equipped with a titanium tip (Branson Sonifier 450). The disrupter must have a minimum power wattage of 300 watts, with pulsing capability. Follow the manufacturers instructions for preparing the disrupter for extraction of samples with low and medium/high concentration. Use a 3/4" horn for all concentration methods.
9.5.2 Sound box to fit around the sonicator

9.6 Balance: Top-loading, capable of accurately weighing 0.01 g.

9.7 Drying set-up: 100-mm stemless funnels

9.8 Qualitative fluted filter papers: grade 313, 15 cm (VWR 28333-043)

9.9 DMCS Treated Glass Wool: (Ohio Valley Specialty Chemicals Catalog Number 3352)

9.10 Labconco RapidVap closed-cell concentrator and Labconco Sample Receiving Tubes (600 mL).

9.11 Stainless Steel sample rack for Labconco Sample Receiving Tubes

9.12 Kuderna-Danish (K-D) Apparatus:

9.12.1 Concentrator tube: 10 or 15 mL, graduated, ground-glass joints
9.12.2 Evaporation flask: 500 mL, ground-glass jointed, with plastic clamps

9.12.3 Snyder column: Three-ball macro and Two-ball micro
9.12.4 Boiling Chips: Solvent extracted, approximately 10/40 mesh (teflon or equivalent).
9.12.5 Water Bath: Heated, with either bath balls or concentric ring covers to control loss of heat, capable of temperature control of up to 90^0C.

9.13 Glass vials: 2 mL capacity (for autosampler) with Teflon lined screw-cap or PTFE lined crimp tops and crimper.

9.14 pH Indicator Paper: universal range 0-14 pH

9.15 Mini-Vortexer

9.16 Beakers, glass: 400-mL heavy duty

9.17 Erlenmeyer Flask: 500 mL

9.18 Erlenmeyer Flask: 500 mL with ground glass stopper

9.19 Erlenmeyer Flask: 1 Liter widemouth

9.20 Syringes, milliliter, gastight, glass, Luer-Lok: appropriate sizes

9.21 Syringes, microliter, gastight, glass, fixed needle: appropriate sizes

9.22 Graduated Cylinders: appropriate sizes

9.23 Volumetric Flasks, Class A: appropriate sizes

9.24 Test Tubes: 15 mL screw cap Teflon lined

9.25 Test tube rack

9.26 Spatula: Stainless steel or Teflon.

9.27 Glass stirring rods

9.28 Disposable glass Pasteur pipettes, 1 mL

9.29 Teflon wash bottle

9.30 Adjustable autopipette dispenser: 10 mL

9.31 Aluminum foil

9.32 Electronic Timer

9.33 Nitrogen Generator, Parker/Balston Nitrovap Generator

9.34 Dionex Accelerated Solvent Extractor (ASE 300)

9.35 30mm Cellulose Filters

9.36 Ultra High Purity (UHP) Nitrogen

9.37 Precleaned, 250mL Clear Collection Bottles

9.38 Stainless Steel 100mL Extraction Cells

10.0 REAGENTS AND STANDARDS

The following reagents and standards are required to perform this procedure. When instructions are given on how to prepare a specific volume of a reagent or standard, larger or smaller volumes can be prepared as needed so long as the final concentrations remain the same. Any other deviations from the reagents or standards listed in this SOP could be detrimental to the quality of the data produced. Such deviations would have to be approved and documented (see SOP 230 Corrective Action). Equivalent items can be used, if with their use, the analytical and QA/QC requirements in this SOP can be met.

Instructions for labeling and record keeping of reagents and standards are contained in SOP 1010 Analytical Standards and Reagents Receipt and Preparation.

10.1 Analytical reagent grade chemicals shall be used in all tests. Unless otherwise indicated, all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.

10.2 Organic-free reagent water - All references to water in this SOP refers to Type II reagent water (in-house system).

10.3 Methylene chloride (Dichloromethane) – Pesticide quality (EM Science Catalog Number DX0831-1)

10.4 Hexanes - Pesticide quality (EM Science Catalog Number HX0298-1)

10.5 Acetone and Methanol - pesticide quality

10.6 Diethyl ether – stabilized with ethanol, pesticide quality

10.7 Acetonitrile – pesticide quality

10.8 Sodium sulfate: Anhydrous and reagent grade (EM Science Catalog Number SX0760E-5)

10.9 Sodium hydroxide solution (10 N), NaOH. Dissolve 40 g NaOH in water and dilute to 100 mL.

10.10 Sulfuric acid solution (1:1, v:v), H_2SO_4 (VWR Catalog Number VW3371-4)

10.11 Concentrated sulfuric acid

10.12 Concentrated hydrochloric acid

10.13 Sodium Chloride, granules

10.14 Copper granules

10.15 Surrogate Spiking Solutions: (summarized in Table 2). After preparation, these standards are stored at < -10°C in amber glass vials with a Teflon lined screw cap for up to 6 months. Store stock solutions according to manufacturer's instructions.

10.15.1 All pesticide and PCB (analytical SOP 4050 Organochlorine Pesticides & PCB's by GC/ECD) extractions are spiked with 1.0 mL of 1 µg/mL of TCMX/DCB. Prepare by adding 1.0 mL of 200 µg/mL stock solution (Supelco 4-8460) to a 200 mL volumetric flask with acetone.

10.15.2 All SVOC (analytical SOP 4020 Semi-Volatile Organic Compounds by GC/MS) extractions are spiked with 1.0 mL of a mix of 50 µg/mL Base/Neutral Surrogate Mix and 100 µg/mL Acids Surrogate Spike Mix. Prepare by adding 2.0 mL of 5000 µg/mL Base/Neutral Spike Mix (Supelco 4-7262) and 2.0 mL of 10000 µg/mL Acids Surrogate Spike Mix (Supelco 4-7261) to a 200 mL volumetric flask with methanol.

10.15.3 All PNA (analytical SOP 4500 PNA Compounds by GC/MS with SIM) extractions are spiked with 1.0 mL of a mix of 5.0 µg/mL Base/Neutral Surrogate Mix and 10.0 µg/mL Acids Surrogate Spike Mix. Prepare by adding 0.20 mL of 5000 µg/mL Base/Neutral Spike Mix (Supelco 4-7262) and 0.10 mL of 10000 µg/mL Acids Surrogate Spike Mix (Supelco 4-7261) to a 200 mL volumetric flask with methanol.

10.15.4 All Herbicide (analytical SOP 4080 Chlorophenoxy Herbicides By HPLC) extractions are spike with 1.0 mL of 1.0 µg/mL 2,4-Dichlorophenyl acetic acid (DCAA). Prepared by adding 2.0 mL of 0.1 mg/mL M-8150B-SS (Accustandard) to a 200 mL volumetric flask with acetone.

Table 2. Surrogate Spike Solutions

Analytical SOP	Surrogate Concentration	Surrogate Spike Stock *	Stock Amount (ml)	Solvent	Total Volume (ml)
SOP 4050 8081A/8082 (PCB/PEST)	1ug/ml	Supelco Pesticides Surrogate Spike	1.0 ml	Acetone	200 ml
SOP 4020 8270C (SVOC)	50 / 100 ug/ml	Supelco Semivolatiles Acid Surrogate HC / Semivolatile Base/Neutrals	2.0 ml each	Methanol	200 ml
SOP 4500 8270C-SIM (PNA)	5 ug/ml	Supelco Semivolatiles Acid Surrogate HC /	0.100 ml (acid) 0.200 ml	Methanol	200 ml

		Semivolatile Base/Neutrals	(b/n)		
SOP 4080 8151A (Herbicides)	1 ug/ml	AccuStandard M-8150B-SS	2.0 ml	Acetone	200 ml

* or equivalent

10.16 Matrix Spiking Solutions (summarized in Table 3). After preparation, these standards are stored at < -10°C in amber glass vials with a Teflon lined screw cap for up to 6 months. Store stock solutions according to manufacturer's instructions.

10.16.1 Pesticide (analytical SOP 4050 Organochlorine Pesticides & PCB's by GC/ECD) LCS, matrix spike and matrix spike duplicate extractions are spiked with 1.0 mL of 0.25 µg/mL Pesticide Matrix Spike solution. Prepare by adding 0.5 mL of a 2000 µg/mL CLP Organochlorine Pesticides Mix (Supelco 47426-U) and 0.5 mL of a 2000 µg/mL Hexachlorobenzene (Supelco 4-0008) to a 10 mL volumetric flask with acetone. Dilute this secondary standard by adding 0.25 mL of 50 µg/mL secondary CLP Pesticides Mix to a 50 mL volumetric flask with acetone.

10.16.2 PCBs (analytical SOP 4050 Organochlorine Pesticides & PCB's by GC/ECD) LCS, matrix spike and matrix spike duplicate extractions are spiked with 1.0 mL of 10.0 µg/mL Aroclor 1016/1260 Matrix Spike Solution. Prepare by adding 2.0 mL of 1000 µg/mL Aroclor 1016 (Supelco 4-8097) and 2.0 mL µg/mL Aroclor 1260 (Supelco 4-4809) to a 200 mL volumetric flask with acetone.

10.16.3 SVOC (analytical SOP 4020 Semi-Volatile Organic Compounds by GC/MS) LCS, matrix spike and matrix spike duplicate extractions are spiked with 1.0 mL of a mix of 50 µg/mL base/neutral compounds and 100 µg/mL acids compound mix. Prepare by adding 10.0 mL of 2.0 mg/mL Acid Composite Mix (AccuStandard CLP-HC-A-R), 5.0 mL of 2.0 mg/mL Base/Neutral Composite Mix (AccuStandard CLP-HC-BN-R), 5.0 mL of 2.0 mg/mL Composite Mix #3 (AccuStandard Z-014E-R3) and 5.0 mL of 2.0 mg/mL Benzidine & 3,3'-Dichlorobenzidine (AccuStandard Z-014F) to 200 mL volumetric flask with methanol.

10.16.4 PNA (analytical SOP 4500 PNA Compounds by GC/MS-SIM) LCS, matrix spike and matrix spike duplicate extractions are spiked with 1.0 mL of a 5.0 µg/mL PNA Mix. Prepare by adding 0.5 mL of 2000 µg/mL TCL Polynuclear Aromatic Hydrocarbon Mix (Supelco 48905-U), 0.5 mL of PNA Custom Mix (TACO Additions) (Supelco 20923178) and 0.5 mL of 2000 ug/ml Custom PNA Additions Mix (Supelco 20923656) to a 200 mL volumetric flask with methanol.

10.16.5 TPH (analytical SOP 4550 TPH in Soils and Waters) LCS, matrix spike and matrix spike duplicate extractions are spiked with 1.0 mL of a 1000.0 µg/mL TPH Mix. Prepare by adding 2.5 mL of 20 mg/mL Diesel Fuel #2 (AccuStandard FU-009-D-40X), 2.5 mL of 20 mg/mL Gasoline – Regular, Unleaded (AccuStandard GA-001-D-

40X) and 2.5 mL of 20 mg/mL SAE 10W30 Motor Oil (AccuStandard FU-026-D-40X) to a 50 mL volumetric flask with methanol.

10.16.6 Glycols (EPA Method 8015M) LCS, matrix spike and matrix spike duplicate extractions are spiked with 1.0 mL of a 100.0 µg/mL Glycols Spike Mix. Prepare by adding 1.0 mL of 2000 ug/mL Glycols Standard (Supelco 20827219) to a 20 mL volumetric flask with methanol.

10.16.7 Herbicides (analytical SOP 4080 Chlorophenoxy Herbicides By HPLC) LCS, LCSD, matrix spike, matrix spike duplicate extractions are spiked with 1.0 mL of a 1.0 – 10.0 µg/mL Herbicides Spike. Prepare by adding 1.0 mL of 100 - 1000 µg/mL Herbicide Custom Mix (Supelco 20923184) to a 100 mL volumetric flask with acetonitrile.

10.16.8 Phthalates (analytical SOP 4020 Semi-Volatile Organic Compounds by GC/MS) LCS, LCSD, matrix spike and matrix spike duplicate extractions are spiked with 0.5 mL of a 1000 µg/mL Phthalate Esters Mix (AccuStandard M-8061-R1) and 0.25 mL of Bisphenol A Custom Mix (Restek 560710). The spikes are added directly from the sealed ampule. Allow the ampule to warm to room temperature before removing spike from the ampule.

10.16.9 Internal Standards: All samples, LCS, matrix spike, matrix spike duplicate extractions for analysis of PNAs (SOP 4500) and SVOCs (SOP 4020) are spiked with 10 µL of the appropriate internal standard. Prepare the PNA internal standard by diluting 1.0 mL of HC Semivolatile Internal Standard Mix (Supelco 4-7906) to 10.0 mL with methylene chloride. Transfer the prepared internal standard into a screw top 1.0 mL vial equipped with a Mininert syringe valve. The remaining solution is stored in a 10 mL amber vial with a Teflon seal. Prepare the SVOC internal standard by transferring the entire contents of the HC Semivolatile Internal Standard Mix (Supelco 4-7906) ampule into a screw top 2.0 mL vial equipped with a Mininert syringe valve.

Table 3. Matrix Spike Solutions

Analytical SOP	Spike Concentration	Spike Stock *	Spike Amount (ml)	Solvent	Total Volume (ml)
SOP 4050 8081A (PEST)	50 µg/ml	Supelco CLP Pesticides Mix Hexachlorobenzene (solution #1)	0.250 ml	Acetone	10 ml
SOP 4050 8081A (PEST)	0.25 µg/ml	Solution #1 (from above)	0.250 ml	Acetone	50 ml
SOP 4050 8082 (PCB)	10 µg/ml	Supelco Aroclor 1016 Aroclor 1260	2.0 ml each	Acetone	200 ml
SOP 4020 8270C (SVOC)	50 / 100 µg/ml	Supelco Acid Composite Mix Base/Neutral Composite Mix Composite Mix #3 Benzidine & 3/3'- Dichlorobenzidine	10 ml Acid 5.0 ml each of others	Methanol	200 ml

SOP 4500 8270C-SIM (PNA)	5 µg/ml	Supelco TCL PNA Mix Custom PNA Additions Mix Custom Mix (TACO Additions)	0.5 ml each	Methanol	200 ml
SOP 4550 (TPH)	1000 µg/ml	AccuStandard #2 Diesel Fuel Unleaded Gasoline SAE 10W30 Motor Oil	2.5 ml	Methanol	50 ml
EPA 8015M (Glycols)	100 µg/ml	Supelco Custom Glycol Mix	1.0 ml	Methanol	20 ml
SOP 4080 (Herbicides)	1.0 – 10.0 µg/ml	Supelco Custom Mix	1.0 ml	Acetonitrile	100 ml
SOP 4020 8270C (Phthalates)	100 µg/ml	AccuStandard Phthalate Esters Restek Custom Bisphenol A Mix	0.5 mL (Accu) 0.25 mL (Restek)	N/A	N/A

* or equivalent

Table 4. Internal Standard Solutions

Analytical SOP	Spike Concentration	Spike Stock *	Spike Amount (ml)	Solvent	Total Volume (ml)
SOP 4020 8270C (SVOC)	4000 ug/ml	Supelco HC Semivolatile Internal Standard Mix	1.0 ml	-	1.0 ml
SOP 4500 8270C-SIM (PNA)	400 ug/ml	Supelco HC Semivolatile Internal Standard Mix	1.0 ml	Dichloro-methane	10.0 ml

* or equivalent

11.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

11.1 Containers used to collect samples for the determination of semivolatile organic compounds, pesticides, herbicides and PCBs are glass: 1 Liter bottles for water samples and various size jars for soil samples. They are equipped with screw caps with Teflon liners. Water samples containing residual chlorine should be field treated to remove the chlorine prior to collection. Non-aqueous samples for the waste dilution procedure may be collected in smaller glass jars. Plastic containers or lids may NOT be used for the storage of samples due to the possibility of sample contamination from the phthalate esters and other hydrocarbons within the plastic.

11.2 Samples must be stored under refrigeration at between 0.1 and 6.0°C. Extraction must be within 7 days from sampling date for water and 14 days for solids and non-aqueous samples. Sample extracts are stored in the dark at between 0.1 and 6.0°C and must be analyzed within 40 days of extraction.

11.3 No chemical preservation is required for this method.

11.4 All samples are stored away from all standards, reagents, food, and other potentially contaminating sources in order to prevent cross contamination.

11.5 Non-aqueous samples expected to have elevated concentrations or organic compounds must be stored away from other samples to prevent cross-contamination. Refrigeration of these samples is not required.

12.0 QUALITY CONTROL

The following details the QC requirements that apply to this analysis. Each Quality Control Indicator (QCI) provides information pertaining to either method or individual sample performance. Our goal is to produce defensible data of known and documented quality.

The results of these QCI samples are used to assess the acceptability of data.

12.1 Blanks

Method Blank analysis is performed to determine if any contamination is present in the analytical process and is used to evaluate acceptance of the batch of samples. A method blank shall be prepared once per preparation batch of 20 or less samples per matrix type (see Section 6 for definition of a prep batch). If more than 20 samples are prepared a second blank shall be prepared after the twentieth sample. The method blank shall be processed through all preparatory steps used for the samples, including cleanup procedures. The blank shall be analyzed using the same instrument and conditions as the samples.

12.2 Laboratory Control Sample (LCS)

The LCS is used to evaluate the performance of the total analytical system, including all preparation and analysis steps. The LCS shall be prepared once per preparation batch of 20 or less samples per matrix type. If more than 20 samples are prepared a second LCS shall be prepared after the twentieth sample. The LCS shall be processed through all preparatory steps used for the samples, including cleanup procedures. The LCS shall be analyzed using the same instrument and conditions as the samples. Refer to section 10.11 for preparation and concentration instructions.

12.3 Surrogates

Surrogates are used most often in organic chromatography methods and are chosen to reflect the chemistries of the targeted components of the method. Added prior to sample preparation/extraction, they provide a measure of recovery for every sample matrix.

Surrogate compounds must be added to all samples, standards, and blanks for all appropriate test methods. The addition of surrogate compounds to non-aqueous samples for waste dilution preparation is optional. Surrogate concentrations must be within the calibration range.

Surrogate compounds are chosen to represent the various chemistries of the target analytes in the method. They are often specified by the method and are deliberately chosen for their

being unlikely to occur as an environmental contaminant. Refer to section 10.10 for preparation and concentration instructions.

12.4 Duplicates

Duplicates of field samples or of the LCS must be prepared in compliance with the method requirements and client directives. Note: the analysis of the Matrix Spike Duplicate (MSD) is used as a substitute for the laboratory duplicate. In those cases when there is insufficient sample to perform either a duplicate analysis or MSD analysis, the duplicate analysis of the LCS (LCS/LCSD) is used to judge the precision of the analytical results.

12.5 Matrix Spike and Matrix Spike Duplicate (MS/MSD)

MS/MSDs indicate the effect of the sample matrix on the precision and accuracy of the results generated using the selected method. This information does not determine the validity of the entire batch. MS/MSDs must be analyzed at a minimum of once per matrix per preparation procedure, or 1 per 20 samples per matrix per preparation procedure, or as specified by the required test method. For case where the sample cannot be divided (e.g. wipes or air samples) and thus an MS/MSD pair cannot be prepared in the preparation batch, an LCS/LCSD pair is analyzed.

Samples chosen for matrix spiking are rotated among different clients and/or different client projects. This is accomplished through communication between the Project Manager, Department Manager and the analyst. In addition, designated samples, as indicated by client request or contract requirement, are matrix spiked.

The MS/MSD pair shall be processed through all preparatory steps used for the samples. They shall be analyzed using the same instrument and conditions as the samples. Refer to section 10.11 for preparation and concentration instructions. Some clients may require different spiking levels and/or target analytes, these specific needs are documented on the request for analysis forms.

13.0 CALIBRATION AND STANDARDIZATION

13.1 Sonicator - The sonication extraction device must have a minimum of 300 watts of power and be equipped with appropriate size disrupter horns. The horn must be properly maintained, including tuning according to the manufacturer's instructions prior to use, and inspection of the horn tip for excessive wear.

13.2 Bottle top dispensers - Check dispensers to ensure standardization is within control limits (see SOP 1040 General Laboratory Practices for Dispenser Calibration).

13.3 Balances - Be sure the balance is checked prior to use and performance criteria are met (see SOP 1040 General Laboratory Practices for Calibration of Balances).

14.0 PROCEDURE

Refer to Attachments 5 & 6 for simplified versions of these procedures.

14.1 AQUEOUS SAMPLES – SEPARATORY FUNNEL (EXTRACTION VESSEL) (Sections 14.1, see also sections 14.2 thru 14.5 for concentration steps)

14.1.1 Shake the sample bottle to suspend any sediment in the sample. Pour the bottle contents into a 1 liter graduated cylinder, measure the volume and pour into the separatory funnel (extraction vessel). Record the sample ID and the volume (record two significant figures) of the sample used for extraction. Option: Mark the water meniscus on the side of the sample bottle for later determination of sample volume (see 14.1.8).

NOTE: If high concentrations are anticipated, a smaller volume may be used. Measure the desired sample volume using a 1 liter graduated cylinder and then dilute to a final volume of 1 liter using reagent water. Record the sample ID and the volume (record two significant figures) of the sample used for extraction.

14.1.2 Add the 1 mL of the surrogate standards (section 10.15) to all samples, spikes, and blanks. For each sample selected for matrix spiking, add 1 mL of the matrix spiking solution (section 10.16). Swirl the separatory funnel (extraction vessel) to mix the spiking solutions into the water. Record the surrogate and spiking solution IDs.

14.1.3 Check Table 1 for the extraction pH. If a pH adjustment is necessary prior to extraction, adjust the pH to that indicated for the determinative method that will be used to analyze the extract. Add 2 mL of acid or 12 mL of base (sections 10.9 and 10.10) to the water and swirl to mix. Check the pH to ensure that the proper extraction pH has been obtained. Record the base or acid solution ID.

14.1.4 Rinse the graduated cylinder (or sample bottle) with approximately 60 mL of methylene chloride and transfer to the separatory funnel (extraction vessel). For herbicide analysis rinse with approximately 120 mL of diethyl ether.

14.1.5 If using the Extraction Mixer set the Speed to 30 and the Timer/Min to 2 minutes. Turn on the mixer. The caps on the extraction vessel automatically vent excess pressure.

14.1.6 Seal and vigorously shake the separatory funnel for approximately 2 minutes with periodic venting to release excess pressure. Use a ring stand to support the separatory funnel.

NOTE: Methylene chloride and diethyl ether create excessive pressure very rapidly; therefore initial venting into the fume hood should be done immediately after the separatory funnel has been sealed and inverted.

14.1.7 Allow the organic layer to separate from the water phase for about 2 minutes. If the emulsion interface between layers is more than one-third the size of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample and may include stirring, addition of sodium chloride, filtration of the emulsion through glass wool, centrifugation, or other physical methods.

14.1.8 Sample volume determination: Fill the sample bottle with tap water to the meniscus mark. Pour the water from the bottle into a 1 liter graduated cylinder. Record the sample ID and the volume (record two significant figures) of the sample used for extraction.

14.2 PROCEDURE IF LABCONCO RAPID-VAP IS TO BE USED FOR CONCENTRATION (see Labconco manual for more details on operation of the apparatus):

14.2.1 Place Labconco Sample Tube, with a stemless funnel containing a plug of glass wool filled 2/3 with sodium sulfate resting on the top, in the Sample Tube Rack and position the rack under the separatory funnel. Pre-rinse the sodium sulfate with acetone. For TPH and Herbicide extractions also pre-rinse the sodium sulfate with dichloromethane. Discard the rinsate.

14.2.2 Drain and dry the extract by passing it through the stemless funnel containing the plug of glass wool filled 2/3 with sodium sulfate into the Labconco Sample Tube.

14.2.3 Repeat the extraction twice more with additional approximately 60-mL portions of solvent (120-mL portions for Herbicides). Rinse the sodium sulfate thoroughly (approximately 10 to 20 mL) with extraction solvent.

14.2.4 If further pH adjustment and extraction is required (see Table 1), repeat sections 14.1.3 through 14.2.3.

14.2.5 Combine all the extracts. In some situations, separate concentration and analysis of the acid and base/neutral extracts may be preferable (e.g. if for regulatory purposes the presence or absence of specific acid or base/neutral compounds at low concentrations must be determined, separate extract analyses may be warranted).

14.2.6 Place the Labconco Sample Tubes in the appropriate position in the concentrator, place the polyethylene cap on the tube and select the appropriate program (For sample volume >300 mL use vortex speed 24 – 40 % and temperature 40°C. For sample volume <300 mL use vortex speed 70% and temperature 40°C.).

14.2.7 If a solvent exchange is required, add approximately 20 ml of hexane to the Sample Tube once the initial solvent has concentrated to approximately 10 mL. Concentrate the extract as described in section 14.2.6 to the desired final volume (1.0 mL for SOPs 4020 (SVOC by GC/MS) and 4500 (PNA Compounds by GC/MS) or 10 mL for SOP 4050 (Pesticides and PCB's by GC/ECD). Use a syringe to determine final volumes. If a final volume of 10 ml is required, pipet 10 ml of water into an empty test tube and mark the water meniscus on the side of the tube. Using this tube as a reference, bring the extract to a final volume of 10 ml. Record the final volume.

14.2.8 Using a 1.0 ml syringe, transfer exactly 1.0 mL of the concentrated extract to a clean crimp-top vial for analysis by SOP 4500 (8270C-SIM) and 4020 (8270C). Employ appropriate clean-up SOPs and transfer approximately 1.0 mL to a clean crimp-top vial for analysis by SOP 4050 Pesticides and PCB's by GC/ECD (8081A/8082).

14.2.9 For analysis by SOP 4500 (8270C-SIM) and 4020 (8270C) add 10 uL of internal standard solution immediately prior to capping the vial. Refer to Table 4 for appropriate internal standard and preparation.

14.3 PROCEDURE FOR HERBICIDES IF LABCONCO RAPID-VAP IS TO BE USED FOR CONCENTRATION (see Labconco manual for more details on operation of the apparatus):

14.3.1 Drain and the aqueous (bottom) layer into the 1.0 L flask and the ether (top) layer into the 500 mL Erlenmeyer flask with the ground glass stopper. Seal the 500 mL Erlenmeyer flask with the ground glass stopper.

14.3.2 Repeat the extraction twice more with additional approximately 120-mL portions of solvent.

14.3.3 Combine all the extracts. Add 45 –50 g of sodium sulfate pre-rinsed with dichloromethane into the 500 mL flask and mix the extract thoroughly with the sodium sulfate. Ensure that the sodium sulfate is free flowing. If the sodium sulfate is caked together, add additional sodium sulfate so that it is free flowing. Allow the extract to remain in contact with the sodium sulfate for a minimum of 2 hours.

NOTE: The drying step is very critical. Any moisture remaining in the ether will result in low recoveries. The 2 hour drying time is minimum; however, the extracts may be held overnight in contact with the sodium sulfate.

14.3.4 Place the Labconco Sample Tube, with a stemless funnel containing a plug of glass wool filled 2/3 with anhydrous sodium sulfate resting on top, in the Sample Tube Rack.

14.3.5 Drain and dry the extract by passing it through the stemless funnel containing the plug of glass wool filled 2/3 with anhydrous sodium sulfate into the Labconco Sample Tube.

14.3.6 Place the Labconco Sample Tubes in the appropriate position in the concentrator, place the polyethylene cap on the tube and select the appropriate program (For sample volume >300 mL use vortex speed 24 – 40 % and temperature 40°C. For sample volume <300 mL use vortex speed 70% and temperature 40°C.).

14.3.7 Add approximately 20 ml of the acetonitrile to the Sample Tube once the initial solvent has concentrated to 1 mL. Increase the block temperature to 50°C. Concentrate the extract as described in section 14.3.6 to the desired final volume (1.0 mL). Use a syringe to determine final volumes.

14.3.8 Using a 1.0 ml syringe transfer 1.0 mL of the concentrated extract to a clean crimp-top vial for analysis by SOP 4080 (Herbicides).

14.4 PROCEDURE IF KUDERNA DANISH/WATER BATH METHOD IS TO BE USED FOR SAMPLE COLLECTION AND CONCENTRATION: (use this procedure only if all of the Labconco RapidVaps are not functional)

14.4.1 Assemble a Kuderna Danish concentrator by attaching a 10 or 15-mL concentrator tube to a 500-mL evaporator flask.

14.4.2 Starting with step 14.2.2, decant and dry the extract by passing it through a stemless funnel containing a plug of glass wool filled 2/3 with anhydrous sodium sulfate pre-rinsed with acetone. Collect the dried extract in the Kuderna Danish concentrator.

14.4.3 Repeat the extraction steps 14.2.3, 14.2.4, and 14.2.5.

14.4.4 Add one or two clean boiling chips to the evaporative flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 mL methylene chloride to the top. Place the K-D apparatus on a hot water bath (80-90°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 10-15 minutes. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood with condensed solvent. If chambers flood, adjust the K-D apparatus so less is immersed. When the apparent volume of liquid reaches 4-6 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for about 10 minutes.

14.4.5 If a solvent exchange is required, momentarily remove the Snyder column, add 10 mL of the hexane and a new boiling chip (it is important to add the new chip), and re-attach the Snyder column. Concentrate the extract as described in section 14.3.4, raising the temperature of the water bath, if necessary, to maintain proper distillation.

14.4.6 Remove the Snyder column and, using approximately 0.5-2 mL of methylene chloride (or the exchange solvent hexane) rinse the flask and its lower joints. Collect the rinse in the concentrator tube. The extract may be further concentrated by using the technique outlined in section 14.3.7 or adjusted to 10 mL with the solvent last used. Record the final volume.

14.4.7 If further concentration is indicated, place the K-D concentrator tube under the blow down apparatus so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the airflow, as required, to complete the concentration in 5-10 min. Be careful that the airflow is not too high and extract is splattered out of the tube. When the apparent volume of liquid reaches 0.5 mL to 1.5 mL, remove the K-D concentrator tube from the water bath and allow to drain and cool for approximately 10 minutes. Adjust the final volume to 1.0 mL or 2.0 mL with methylene chloride. Record the final volume.

14.4.8 Using a 1.0 ml syringe transfer 1.0 mL of the concentrated extract to a clean crimp-top vial for analysis by SOP 4500 (8270C-SIM) and 4020 (8270C). If required, employ SOP 3330 Silica Gel Cleanup for SVOC prior to analysis by SOP 4500 (8270C-SIM). Employ appropriate clean-up SOPs and, using a 1.0 ml syringe, transfer 1.0 mL to a clean crimp-top vial for analysis by SOP 4050 Pesticides and PCB's by GC/ECD (8081A/8082).

14.5 PROCEDURE FOR HERBICIDES IF KUDERNA DANISH/WATER BATH METHOD IS TO BE USED FOR SAMPLE COLLECTION AND CONCENTRATION: (use this procedure only if all of the Labconco RapidVaps are not functional)

14.5.1 Assemble a Kuderna Danish concentrator by attaching a 10 or 15-mL concentrator tube to a 500-mL evaporator flask.

14.5.2 Starting with step 14.3.3, decant and dry the extract by passing it through a stemless funnel containing a plug of glass wool filled 2/3 with anhydrous sodium sulfate pre-rinsed with acetone. Collect the dried extract in the Kuderna Danish concentrator.

14.5.3 Add one or two clean boiling chips to the evaporative flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 mL diethyl ether to the top. Place the K-D apparatus on a hot water bath (80-90°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 10-15 minutes. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood with condensed solvent. If chambers flood, adjust the K-D apparatus so less is immersed. When the apparent volume of liquid reaches 4-6 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for about 10 minutes.

14.5.4 For the solvent exchange, momentarily remove the Snyder column, add 10 mL of the acetonitrile and a new boiling chip (it is important to add the new chip), and re-attach the Snyder column. Concentrate the extract as described in section 14.5.3, raising the temperature of the water bath, if necessary, to maintain proper distillation.

14.5.5 Remove the Snyder column and, using approximately 0.5-2 mL of diethyl ether, rinse the flask and its lower joints. Collect the rinse in the concentrator tube. The extract may be further concentrated by using the technique outlined in section 14.5.6 or adjusted to 10 mL with the solvent last used. Record the final volume.

14.5.6 If further concentration is indicated, place the K-D concentrator tube under the blow down apparatus so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the airflow, as required, to complete the concentration in 5-10 min. Be careful that the airflow is not too high and extract is splattered out of the tube. When the apparent volume of liquid reaches 0.5 mL to 1.5 mL, remove the K-D concentrator tube from the water bath and allow to drain and cool for approximately 10 minutes. Adjust the final volume to 1.0 mL or 2.0 mL with diethyl ether. Record the final volume.

14.5.7 Using a 1.0 ml syringe transfer 1.0 mL of the concentrated extract to a clean crimp-top vial for analysis by SOP 4080 (Herbicides). Employ appropriate clean-up SOPs and, using a 1.0 ml syringe, transfer 1.0 mL to a clean crimp-top vial for analysis by SOP 4080 (Herbicides).

14.6 AQUEOUS SAMPLES – CONTINUOUS LIQUID-LIQUID EXTRACTOR (Sections 14.4, see also sections 14.2 or 14.3)

14.6.1 Add boiling chips to the 500 mL round bottom flask. Attach the extraction apparatus without the condenser to the support frame.

14.6.2 Transfer approximately 500 mL of methylene chloride to the extractor. A pre-measured mark on the side of the extractor may be used for the approximation.

14.6.3 Shake the sample bottle to suspend any sediment in the sample. Pour the bottle contents into a 1 liter graduated cylinder, measure the volume and pour into the extractor. Record the sample ID and the volume (record two significant figures) of the sample used for extraction. Option: Mark the water meniscus on the side of the sample bottle for later determination of sample volume (see 14.1.7).

NOTE: If high concentrations are anticipated, a smaller volume may be used. Measure the desired sample volume using a 1 liter graduated cylinder and then dilute to a final volume of 1 liter using reagent water. Record the sample ID and the volume (record two significant figures) of the sample used for extraction.

14.6.4 Add the 1 mL of the surrogate standards (section 10.15) to all samples, spikes, and blanks. For each sample selected for matrix spiking, add 1 mL of the matrix spiking solution (section 10.16). Using a glass stirring rod, stir to mix the spiking solutions into the water. If necessary, add sufficient additional water to transfer the methylene chloride into the round bottom flask until the liquid is level with the top of the heater mantle. Record the surrogate and spiking solution IDs.

14.6.5 Check Table 1 for the extraction pH. If a pH adjustment is necessary prior to extraction, adjust the pH to that indicated for the determinative method that will be used to analyze the extract. Add 1 to 2 mL of either base or acid (sections 10.9 and 10.10) to the water and stir to mix. Check the pH to ensure that the proper extraction pH has been obtained. Record the base or acid solution ID.

14.6.6 Rinse the graduated cylinder (or sample bottle, if used) with 10 to 20 mL of methylene chloride and transfer to the extractor.

14.6.7 Connect the condenser, turn on the cold water to the condensers, turn on the heaters and extract for 18 to 24 hours. Make sure that all tubing connections for the water are secure. Record the start time.

14.6.8 At the end of the extraction period, turn off the heat, allow the extractor to cool, and detach the boiling flask. Record the stop time.

14.6.9 If extraction at a secondary pH is not required (see Table 1), the flask is removed from the extractor and the extract is quantitatively transferred, dried and concentrated using one of the techniques described in Sections 14.2 or 14.4. The water or dichloromethane remaining in the extractor must be placed in the appropriate waste container.

14.6.10 If a pH adjustment and second extraction is required (see Table 1), determine if the extracts are to be analyzed separately (step 14.6.11) or if they may be combined as a single extract (step 14.6.12).

14.6.11 If the extracts are to be analyzed separately (see Section 14.2.5), perform the following:

14.6.11.1 Carefully transfer the contents of the round bottom flask to a labeled Erlenmeyer flask. Rinse the round bottom flask with approximately 10 to 20 mL of methylene chloride to complete the transfer. Cover the Erlenmeyer flask with aluminum foil and refrigerate at 0.1 – 6.0 °C.

14.6.11.2 Attach a clean distilling flask containing 500 mL of methylene chloride to the continuous extractor.

14.6.11.3 Stir the sample after adding approximately 1 to 2 mL of acid or base to adjust the pH of the aqueous phase to the second pH indicated in Table 1. Follow the procedure as outlined in 14.6.5.

14.6.11.4 Extract for 18 to 24 hours following the procedure as outlined in 14.6.7 and 14.6.8

14.6.12 If the extracts are not to be analyzed separately, then the distilling flask and solvent need not be changed and may be used for the second pH extraction. Stir the sample after adding approximately 1 to 2 mL of acid or base to adjust the pH of the aqueous phase to the second pH indicated in Table 1. Follow the procedure as outlined in 14.6.5. Slowly add sufficient methylene chloride to the extractor such that the liquid level is even with the top of the heater mantle. Extract for 18 to 24 hours following the procedure as outlined in 14.6.7 and 14.6.8.

14.7 SOLID SAMPLES – SONICATION EXTRACTION (Sections 14.7, see also sections 14.2 or 14.4)

14.7.1 Sample Handling:

14.7.1.1 Sediment/soil samples: Mix sample thoroughly, especially composited samples. Record sample treatment in the logbook.

14.7.1.2 Waste samples: Samples consisting of multiphases must be either thoroughly mixed, representative aliquots taken, or analyze the phases separately. Confer with the Project Manager to determine how the client wants to extract multiphase samples.

14.7.2 Extraction for samples expected to contain low levels of organics:

14.7.2.1 The following steps are to be performed rapidly to avoid loss of the more volatile extractables. Weigh 30 – 35 g of sample into a 400-mL beaker. Record the sample ID and the sample weight used for extraction to the nearest 0.1 g. For herbicides analysis adjust the pH of the sample to < 2.0

with concentrated hydrochloric acid. Non-porous or wet samples (gummy or clay type) that do not have a free flowing sandy texture must be mixed with approximately 30 g of anhydrous sodium sulfate. Most, if not all samples, will require the addition of the sodium sulfate. The sample must be free-flowing at this point.

14.7.2.2 Add the 1 mL of the surrogate standards (section 10.15) to all samples, spikes, and blanks. The blank and LCS samples contain 60 g of sodium sulfate. For each sample selected for matrix spiking, add 1 mL of the matrix spiking solution (section 10.16). Record the surrogate and spiking solution IDs.

14.7.2.3 Immediately add approximately 100 mL of methylene chloride (add the solvent to the 150 mL mark on the beaker).

14.7.2.4 Place the bottom surface of the tip of the disruptor about 1/2 inch below the surface of the solvent, but above the sediment layer.

14.7.2.5 Sonicate for 3 minutes, with output control knob set at 10 (full power) and percent-duty cycle knob set at 50%. Do NOT use microtip probe.

14.7.2.6 Determine if the Labconco Rapid-Vap or the Kuderna Danish concentrator will be used to concentrate the extract.

14.7.2.7 Decant and dry the extract by passing it through a stemless funnel containing a glass wool plug or fluted filter paper filled 2/3 with anhydrous sodium sulfate. Collect the dried extract in the appropriate concentrator.

14.7.2.8 Repeat the extraction two more times with additional 100-mL portions of methylene chloride. Decant off the solvent after each sonication. After the final extraction, wash the sample into the drying funnel with approximately 10-25 mL of solvent. Rinse the sample with solvent to complete the quantitative transfer of the extract. For non-Herbicides, proceed to either section 14.2 or 14.4. For Herbicides proceed to 14.7.2.9.

14.7.2.9 For herbicide analysis collect the dried extract in a 500 mL Erlenmeyer flask equipped with a ground glass stopper. Add approximately 10 g of sodium sulfate to the flask. Periodically, vigorously shake the extract and drying agent and allow the drying agent to remain in contact with the extract for a minimum of 2 hours. Proceed to 14.3.6 or 14.5.

NOTE: The drying step is very critical. Any moisture remaining in the dichloromethane will result in low recoveries. The 2 hour drying time is minimum; however, the extracts may be held overnight in contact with the sodium sulfate.

14.7.2.10 If the sample does not filter or does not concentrate below 10 mL repeat the extraction process starting at 14.7.2.1 using approximately 3 g of sample instead of 30 grams.

14.8 NON-AQUEOUS SAMPLES and WIPE SAMPLES – WASTE DILUTION

14.8.1 Samples consisting of multiphases must be prepared before extraction. Choice of the procedure for separating multiphase samples is highly dependent on the objective of the analysis. With a sample in which some of the phases tend to separate rapidly, the percent weight or volume of each phase should be calculated and each phase should be individually analyzed for the required analytes. An alternate approach is to obtain a homogeneous sample and attempt a single analysis on the combination of phases. This approach will give no information on the abundance of the analytes in the individual phases other than what can be implied by solubility. A third alternative is to select phases of interest and to analyze only those selected phases. This tactic must be consistent with the sampling/analysis objectives or it will yield insufficient information for the time and resources expended.

14.8.2 The sample dilution may be performed in a 15 mL test tube. If disposable glassware is preferred, the 15 mL test tube may be calibrated for use. Pipet 10.0 mL of extraction solvent into the test tube and mark the bottom of the meniscus. Discard the solvent in the appropriate waste container.

14.8.3 Weigh approximately 1 g (1.5 g for solids) of each phase of the sample into separate 15 mL test tubes or 10 mL volumetric flasks. Wipe the mouth of the vial with a tissue to remove any sample material. Record the weight to the nearest 0.1g. Cap the vial before proceeding with the next sample to avoid any cross-contamination.

14.8.4 For TPH solid samples weigh approximately 5 g of the sample into a 15 mL test tube. Wipe the mouth of the vial with a tissue to remove any sample material. Record the weight to the nearest 0.1g. Cap the vial before proceeding with the next sample to avoid any cross-contamination.

14.8.5 Add 1.0 mL of the appropriate surrogate spiking solution to all samples and blanks. For the sample in each analytical batch selected for spiking, add 1.0 mL of the appropriate matrix spiking standard. Refer to the determinative method to be used for details on the surrogate standard and matrix spiking solutions.

14.8.6 For samples that are miscible in the extraction solvent (e.g., transformer oil in hexane) immediately dilute to the 10 mL mark with the appropriate solvent. For solid samples that are not miscible in the extraction solvent (e.g., soil in dichloromethane) add solvent to a final volume of 10 mL, including surrogate spike. For compounds to be analyzed by GC/ECD, e.g., organochlorine pesticides and PCBs, the dilution solvent should be hexane. For base/neutral and acid semivolatile priority pollutants, use methylene chloride. For TPH solid samples add 5.0 mL of dichloromethane.

14.8.7 Cap and vortex the sample for approximately 1 minute.

14.8.8 The extract is ready for cleanup or analysis, depending on the extent of interfering co-extractives.

14.8.9 For wipe samples, transfer the wipe to a 40-mL vial equipped with a Teflon lined cap. Add a known amount of the surrogate spike solution and a known amount of the appropriate extraction solvent to the vial. For PCB wipe samples, add 1 mL of surrogate spiking solution to all samples, LCSs, LCSDs and blanks. Use clean guaze pads for the LCS/LCSD and blank. Add sufficient hexane to the bottle to bring the final volume to 10 mL. Sonicate the vial for 10 minutes to ensure thorough interaction between the wipe and the solvent. Transfer approximately 5 mL of the extract into a 15 mL test tube. Perform the appropriate clean up procedures. Transfer 1.0 mL of cleaned extract into a 1.5 mL autosampler vial for analysis.

14.8.10 Alternate method for wipe samples: add a known amount of the surrogate spike solution and a known amount of the appropriate extraction solvent to the wipe sample bottle. Cap the bottle and swirl to ensure mixing of the solvent and the wipe. For PCB wipe samples, add 1 mL of surrogate spiking solution to all samples, LCSs, LCSDs and blanks. Add sufficient hexane to the bottle to bring the final volume to 10 mL. Vortex the bottle to ensure thorough interaction between the wipe and the solvent. Allow the solution to extract for at least fifteen minutes. Transfer approximately 5 mL of the extract into a 15 mL test tube. Perform the appropriate clean up procedures. Transfer 1.0 mL of cleaned extract into a 1.5 mL autosampler vial for analysis.

14.9 SOLID SAMPLES – PRESSURIZED FLUID EXTRACTION (ASE)

14.9.1 Sample Cartridge Prep

14.9.1.1 Ensure that the preparation area is clean. Cover the counter top with clean aluminum foil. Complete all of the sample preparation on the aluminum foil.

14.9.1.2 Clean the sample cell by thoroughly rinsing with acetone. Allow the cell to air dry. Replace the cell seals as needed. Hand tighten one cap to the sample cell. Place one 30mm filter (Dionex Part #056780) into the cell and seat with the cell plunger. Label the outside of the sample cell with the sample tracking number. Add approximately 5 g of sodium sulfate to the cell. Weigh 30 g of sample into a glass beaker. Record the weight in the prep logbook. Add 30 g of sodium sulfate to the sample and mix until the sample is free flowing. Add more sodium sulfate if necessary. Transfer the sample into the cell. Rinse the remaining sample out of the beaker with a small amount of dichloromethane. Fill any remaining void inside the cell with sodium sulfate and place one 30mm filter on top of the sample. Hand tighten the top cap on the cell.

14.9.1.3 Instrument Set up

14.9.1.4 Prepare Dionex ASE 300 for extraction. Start the instrument and load the appropriate extraction method. Press the "Menu" button until the "Menu of Screens" screen is shown. Press "1" to Load Method/Schedule. Select Schedule. Use the arrow keys to move to enter number 2. Press Menu to exit the screen. Press 4 to enter the Schedule Editor. Edit the schedule to reflect the number of samples in the batch. Use the following table as a guide.

BTTL#	CELL#	Method #	Rinse
1	1	4	OFF
2	2	4	OFF
3	3	4	OFF
4	4	4	OFF
5	5	4	OFF
6	6	4	OFF
7	7	4	OFF
8	8	4	OFF
9			
10			
11			
12			

14.9.1.5 Press the "Tray" button until the light is lit on the left side of the button. This unlocks the trays. Load the labeled extraction cells and collection bottles onto the instrument. Place an empty bottle in the R1 position for solvent rinsing. After the cells are loaded, press "Tray" again to lock and position the cells.

14.9.1.6 Method Parameters

Method 4

Method 2	Pressure	1500 psi
Heat 5 min	Temperature	100 C
Static 7 min	Sol A	MeCl2 100%
Flush% 120 vol	Sol B	Other
Purge 150 sec	Sol C	Other
Cycles 2	Sol D	Other

14.9.1.7 Fill the solvent bottle with Dichloromethane. Leave room at the top of the bottle for the gas inlet tube. Set the following pressures: Nitrogen pressure to the instrument: 150 psig; Solvent bottle pressure: 7 psig; System Air: 50 psig and Compression Oven: 130 psig. Press "Start" to start the extractions.

After the samples have finished extracting, transfer the contents of the collection bottle into a RapidVap concentrator tube. Rinse the collection bottle three times with dichloromethane to ensure complete transfer of the sample to the concentrator tube. Proceed to Section 14.2 or 14.4 to complete the concentration steps.

14.10 RECORDS

14.10.1 Record the sample condition: Sample ID, sample preservation, appropriate container, and holding time compliance.

14.10.2 Essential information and raw data includes: Sample ID, date (time of analysis if applicable), extraction procedure type, analyst's signature or initials; sample prep information to include sample weights/volumes, appropriate units, ID codes, any calculations, and reagents used (ID).

14.10.3 Any additional comments or observations that would aid in the future reconstruction of the data.

14.11 MAINTENANCE

14.11.1 Clean all glassware according to SOP 1020 Glassware Cleaning

14.11.2 Monitor the water level in the water bath if using the Kuderna Danish apparatus.

14.11.3 Tune the sonicator according to the manufacturer's instructions (if applicable).

14.11.4 Check that the exhaust fan in the RapidVap is operating correctly. Replace as needed.

15.0 CALCULATIONS

Not applicable to the SOP.

16.0 METHOD PERFORMANCE

Refer to the appropriate analytical SOP Section 16.0 for method performance criteria.

17.0 POLLUTION PREVENTION

The preparation of excessive volumes of laboratory reagents and standards shall be avoided so that waste and potential for pollution are minimized. Samples, reagents and standards shall be disposed in compliance with the lab waste disposal program, SOP 1130. With the consent of the client, the samples may be returned to their origin for treatment.

Uncontaminated paper waste, glass and cans should be separated for recycling. Laboratory staff are required to protect the laboratory's and our clients' business information when disposing of recycled paper or waste from the facility.

18.0 DATA ASSESSMENT AND CRITERIA FOR QUALITY CONTROL MEASURES

The review of the LCS result, surrogate recovery, and any other QC sample result for acceptable performance for each batch of samples is performed by the analyst performing the analytical

procedure and sample analyses. Refer to the appropriate analytical SOP Section 18.0 for data assessment and criteria for quality control measures.

19.0 CORRECTIVE ACTIONS FOR OUT-OF-CONTROL DATA

The process for handling unacceptable and out of control data is found in SOP 230 Corrective Action.

If the MB, LCS/LCSD, MS/MSD, lab duplicate, or surrogate recovery of any parameter falls outside the designated acceptance range, the laboratory performance for that parameter is judged to be out of control, and the problem must be immediately identified and corrected. The analytical result for that parameter in the samples is suspect and is only reported for regulatory compliance purposes with the appropriate corrective action form. Immediate corrective action includes reanalyzing all affected samples by using any retained sample before the expiration of the holding time. Final data results must be qualified in the client report for reported results not meeting the laboratory defined criteria.

1) Review standards preparation logbooks. Check all calculations and ensure dilution factors are properly recorded.
2) Re-prepare the suspected standard or QC sample to identify possible preparation errors of the standard or QC sample.
3) Re-Analyze the samples when the CCV or LCS is not within acceptable limits.

Perform routine preventative maintenance following manufacturer's specification. Record all maintenance in the instrument logbook.

20.0 CONTINGENCIES FOR HANDLING OUT-OF-CONTROL OR UNACCEPTABLE DATA

Every effort is made to prevent problems from occurring. When out of control or unacceptable data occurs the first option is to identify the problem and reanalyze the samples within the holding times. When this is not possible, the QA Manager and/or the Laboratory Director reviews data and discusses options with the client. Reanalysis or reporting the data with qualification are alternatives. Out of control or unacceptable data reported to the client must include the data qualifier, flag and discussion on the rationale for reporting.

Holding time exceedence and improper preservation are noted on the corrective action form and included on the final report.

Record any trends or unusual performance on a corrective action form. Final data results must be qualified in the client report for results not meeting the laboratory defined criteria.

The process for handling unacceptable and out of control data is found in the Laboratory QAM Section 11. The reporting of data that is out of control must be approved and documented by Quality Assurance Manager and either the Technical Manager or the Laboratory Director.

21.0 WASTE MANAGEMENT

The STAT Analysis Corporation Waste Disposal SOP 1130 identifies proper waste management practices for the chemicals and biological materials used in this procedure. Samples are stored and discarded in accordance with SOP 1130 Waste Disposal.

22.0 REFERENCES

22.1 Methods 3500, 3510C, 3520C, 3545, 3550B, 3580A, 8151a, Revision 3, December 1996; U.S. EPA SW-846 "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods" Update III, December 1996
22.2 STAT QA 001 Quality Assurance Manual
22.3 STAT SAP 003 Chemical Hygiene Plan
22.4 STAT SOP 230 Corrective Actions
22.5 STAT SOP 1000 Control and Use of Laboratory Notebooks
22.6 STAT SOP 1010 Analytical Standards and Reagents Receipt and Preparation
22.7 STAT SOP 1040 General Laboratory Practices
22.8 STAT SOP 1020 Glassware Cleaning
22.9 STAT SOP 1130 Waste Disposal
22.10 STAT SOP 1230 Training
22.11 STAT SOP 1250 Data Review
22.12 STAT SOP 1400 LIMS
22.13 STAT SOP 3060 Florisil Clean-up for PCB's and Pesticides (EPA Method 3620B)
22.14 STAT SOP 3070 Sulfur and Sulfuric Acid/Permanganate Cleanup for PCB's and Pesticides (EPA Methods 3660B & 3665A)
22.15 STAT SOP 3330 Silica Gel Clean-up for Semi-Volatile Organics (EPA Method 3630C)
22.16 STAT SOP 4020 Semi-Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS) (EPA Method 8270C)
22.17 STAT SOP 4050 Organochlorine Pesticides and Polychlorinated Biphenyls by Gas Chromatography/Electron Capture Detector (EPA Methods 8081A & 8082)
22.18 STAT SOP 4080 Chlorophenoxy Herbicides By HPLC (EPA Method 8321A)
22.19 STAT SOP 4500 Polynuclear Aromatic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS) with Selective Ion Monitoring (SIM) (EPA Method 8270C SIM)
22.20 STAT SOP 4550 Total Petroleum Hydrocarbons in Soils and Waters – (EPA Method 8015 modified)
22.21 Manufacturers' Equipment Instruction Manuals

23.0 TABLES, DIAGRAMS, FLOWCHARTS AND VALIDATION DATA

Attachment 1: Extraction Summary Tables
Attachment 2: Surrogate Spike Solutions
Attachment 3: Matrix Spike Solutions
Attachment 4: Internal Standard Solutions
Attachment 5: 3510 Extraction Quick Reference
Attachment 6: 3550 & 3580 Extraction Quick Reference

ATTACHMENT 1: Extraction Summary Table

Determinative Method	Initial Extraction pH	Secondary Extraction pH	Exchange solvent	Exchange solvent for cleanup	Vol. of extract required for cleanup (mL)	Final extract vol. for analysis (mL)
8081A/8082	as received	----	hexane	hexane	10.0	10.0
8270C (SVOC)	< 2	> 11	none	----	1.0	1.0
8270C (SIM)	as received	----	none	----	1.0	1.0
8321A (HERB)	<2	----	acetonitrile	acetonitrile	1.0	1.0
3545 (PNA)	as received	----	none	----	1.0	1.0
3545 (PCB)	as received	----	hexane	hexane	10.0	10.0
3580	as received	----	none	----	10.0	10.0

Attachment 2: Surrogate Spike Solutions

Analytical SOP	Surrogate Concentration	Surrogate Spike Stock *	Stock Amount (ml)	Solvent	Total Volume (ml)
SOP 4050 8081A/8082 (PCB/PEST)	1ug/ml	Supelco Pesticides Surrogate Spike	1.0 ml	Acetone	200 ml
SOP 4020 8270C (SVOC)	50 / 100 ug/ml	Supelco Semivolatiles Acid Surrogate HC / Semivolatile Base/Neutrals	2.0 ml each	Methanol	200 ml
SOP 4500 8270C-SIM (PNA)	5 ug/ml	Supelco Semivolatiles Acid Surrogate HC / Semivolatile Base/Neutrals	0.100 ml (acid) 0.200 ml (b/n)	Methanol	200 ml
SOP 4080 8151A (Herbicides)	1 ug/ml	AccuStandard M-8150B-SS	2.0 ml	Acetone	200 ml

* or equivalent

Attachment 3: Matrix Spike Solutions

Analytical SOP	Spike Concentration	Spike Stock *	Spike Amount (ml)	Solvent	Total Volume (ml)
SOP 4050 8081A (PEST)	50 µg/ml	Supelco CLP Pesticides Mix Hexachlorobenzene (solution #1)	0.250 ml	Acetone	10 ml
SOP 4050 8081A (PEST)	0.25 µg/ml	Solution #1 (from above)	0.250 ml	Acetone	50 ml
SOP 4050 8082 (PCB)	10 µg/ml	Supelco Aroclor 1016 Aroclor 1260	2.0 ml each	Acetone	200 ml
SOP 4020 8270C (SVOC)	50 / 100 µg/ml	Supelco Acid Composite Mix Base/Neutral Composite Mix Composite Mix #3 Benzidine & 3/3'-Dichlorobenzidine	10 ml Acid 5.0 ml each of others	Methanol	200 ml
SOP 4500 8270C-SIM (PNA)	5 µg/ml	Supelco TCL PNA Mix Custom PNA Additions Mix Custom Mix (TACO Additions)	0.5 ml each	Methanol	200 ml
SOP 4550 (TPH)	1000 µg/ml	AccuStandard #2 Diesel Fuel Unleaded Gasoline SAE 10W30 Motor Oil	2.5 ml	Methanol	50 ml
EPA 8015M (Glycols)	100 µg/ml	Supelco Custom Glycol Mix	1.0 ml	Methanol	20 ml
SOP 4080 (Herbicides)	1.0 – 10.0 µg/ml	Supelco Custom Mix	1.0 ml	Acetonitrile	100 ml
SOP 4020 8270C (Phthalates)	100 µg/ml	AccuStandard Phthalate Esters Restek Custom Bisphenol A Mix	0.5 mL (Accu) 0.25 mL (Restek)	N/A	N/A

* or equivalent

Attachment 4: Internal Standard Solutions

Analytical SOP	Spike Concentration	Spike Stock	Spike Amount (ml)	Solvent	Total Volume (ml)
SOP 4020 8270C (SVOC)	4000 ug/ml	Supelco HC Semivolatile Internal Standard Mix	1.0 ml	-	1.0 ml
SOP 4500 8270C-SIM (PNA)	400 ug/ml	Supelco HC Semivolatile Internal Standard Mix	1.0 ml	Dichloro-methane	10.0 ml

Attachment 5: 3510 Extraction Quick Reference

3510	Sample size	Stds	Solvent	Extraction	Concentration
QC for all samples	1000 ml DI H20 For TCLP use only 500 ml for the MS/MSD and the Blank TCLP	Surr 1 ml Spike 1ml (for LCS/ LCSD, MS/MSD)	QC's are the same as the samples	QC's are the same as the samples	QC's are the same as the samples
PNA	1000 ml (If sample doesn't have 1000 ml use 500 ml of sample and than complete the liter with DI H2O and concentrate to 0.5 ml)	Surr 1 ml Spike 1ml (for LCS/ LCSD, MS/MSD)	MeCl2	Shake samples three times 1st time adding 100 ml of MeCl2 and than 80 ml the next 2 times. Use Clean NaSO4 when filtering samples into collectors	Rapid Vap rinse twice condense to 1 ml or .5 if sample was initially 500 ml and spike with 10ul or 5ul with PNA Int Std
SVOC	1000 ml (If sample doesn't have 1000 ml use 500 ml and than complete the liter with DI H2O and concentrate to 0.5 ml) For TCLP use only 500 ml for the sample, the MS/MSD and the Blank TCLP	Surr 1 ml Spike 1ml (for LCS/ LCSD, MS/MSD)	MeCl2	Shake sample six times the first three times are done when the sample is acidic (add 2 ml of H2SO4 1:1) the second three times are in a basic solution (add 12 ml's of NaOH) Need to check samples to test the pH. Use Clean NaSO4 when filtering samples into collectors	Rapid Vap rinse twice condense to 1 ml or .5 if sample was initially 500 ml and spike with 10ul or 5ul with SVOC Int Std. For TCLP condense sample to 1 ml even though had an initial volume of 500 ml
3510	**Sample size**	**Stds**	**Solvent**	**Extraction**	**Concentration**

S/P (SVOC/PNA)	1000 ml (If sample doesn't have 1000 ml use 500 ml and than complete the liter with DI H2O and concentrate to 0.5 ml) Complete the SVOC procedure.	Use 1ml of SVOC surr for a S/P sample	MeCl2	Shake sample six times the first three times are done when the sample is acidic (add 2 ml of H2SO4 1:1) the second three times are in a basic solution (add 12 ml's of NaOH) Need to check samples to test the pH. Use Clean NaSO4 when filtering samples into collectors	Rapid Vap rinse twice and condense to 1 ml. Transfer .5 ml into the SVOC and PNA vials and spike with 5 ul of SVOC Int Std and 5 ul of PNA int Std. If the sample began with an initial volume of 500 ml only have an SVOC vial.
PCB	1000 ml (or whatever the amount of the collected sample and than complete the liter with DI H2O)	Surr 1 ml Spike 1ml (for LCS/ LCSD, MS/MSD)	MeCl2 and solvent exchange with Hexane and than acid wash	Shake samples three times 1st time adding 100 ml of MeCl2 and than 80 ml the next 2 times	Rapid Vap solvent exchange with Hexane bring final volume to 10 ml Pipet half of sample into second tube acid wash w/ 2 ml of H2SO4 conc. and transfer 1 pipet into copper vial.
Pest	1000 ml (or whatever the amount of the collected sample and than complete the liter with DI H2O) For TCLP use 500 ml's for the sample and the Blank TCLP	Surr 1 ml Spike 1ml (for LCS/ LCSD, MS/MSD)	MeCl2 and solvent exchange w/Hexane	Shake samples three times 1st time adding 100 ml of MeCl2 and than 80 ml the next 2 times	Rapid Vap solvent exchange with Hexane bring final volume to 10 ml and transfer 1 pipet into copper vial.
PCB/ Pest	1000 ml (or whatever the amount of the collected sample)	Surr 1 ml Spike 1ml (for LCS/ LCSD, MS/MSD)	Same as above	Shake samples three times 1st time adding 100 ml of MeCl2 and than 80 ml the next 2 times	Rapid Vap solvent exchange with Hexane bring final volume to 10 ml and transfer 1 pipet into copper vial.

3510	**Sample Size**	**Stds**	**Solvent**	**Extraction**	**Concentration**
HERB	1000 ml (or whatever the amount of the collected sample) For TCLP only use 100 ml for the sample and 500 for the Blank TCLP and than complete the liter with DI H2O. Rinse Shakers thoroughly with MeCL2 prior to starting extraction	Surr 1 ml Spike 1ml (for LCS/ LCSD, MS/MSD)	Ethyl Ether than solvent exchange with ACN	Add add 2 mls of H2SO4 1:1and then check the pH Shake samples three times 1st time adding 200 ml of Ethyl Ether and than 150 ml the next 2 times. After extraction add 200 grams of Clean NaSO4 and let sit for at 1.5 hours) Transfer into collectors rinsing the flask with approx 150ml of ether	Rapid Vap solvent exchange with 20 mls of ACN bring volume to 1 ml and transfer to vial.
TPH	1000 ml (or whatever the amount of the collected sample and than complete the liter with DI H2O)	No surr only spike (LCS/D)	MeCl2	Same as PNA Except rinse the clean NaSO4 with MeCl2 and expel waste from collector.	Rapid Vap rinse twice condense to 1 ml and transfer to vial.

Attachment 6: 3550 & 3580 Extraction Quick Reference

3550 (sonication: beaker)	Sample Size (MS/D must have at least 120 grams)	Standards	Solvent	Extraction	Concentration
PNA	30 g of sample with approx 30 g of NaSO4	1 ml PNA Surr (and 1 ml PNA Spike for LCS/D, MS/D)	MeCl2	Let sit overnight or ~2 hrs. Sonicate 2X for 3 minutes. First time with 200 ml of MeCl2 2nd time with 150 ml of MeCl2	Rapid Vap
SVOC	30 g of sample with approx 30 g of NaSO4	1 ml SVOC Surr (and 1 ml SVOC Spike for LCS/D, MS/D)	MeCl2	Let sit overnight or ~2 hrs. Sonicate 2X for 3 minutes. First time with 200 ml of MeCl2 2nd time with 150 ml of MeCl2	Rapid Vap
S/P (SVOC/PNA)	33 g of sample with approx 30 g of NaSO4	1 ml SVOC Surr	MeCl2	Let sit overnight or ~2 hrs. Sonicate 2X for 3 minutes. First time with 200 ml of MeCl2 2nd time with 150 ml of MeCl2	Rapid Vap
PCB	30 g of sample with approx 30 g of NaSO4	1 ml PCB Surr (and 1 ml PCB Spike for LCS/D,MS/D)	MeCl2	Let sit overnight or ~2 hrs. Sonicate 2X for 3 minutes. First time with 200 ml of MeCl2 2nd time with 150 ml of MeCl2	Rapid Vap Solvent exchange with Hexane
Pest or PP	30 g for PP need	1 ml PCB Surr (and 1	MeCl2	Let sit overnight or ~2	Rapid Vap

(PCB/PEST)	LCS, MS/D for both PCB and Pest	ml PCB or Pest Spike for LCS/D,MS/D)		hrs. Sonicate 2X for 3 minutes. First time with 200 ml of MeCl2 2nd time with 150 ml of MeCl2	
TPH	30 g of sample with approx 30 g of NaSO4	No Surr only 1 ml of Spike (LCS, MS/D	MeCl2	Let sit overnight or ~2 hrs. Sonicate 2X for 3 minutes. First time with 200 ml of MeCl2 2nd time with 150 ml of MeCl2	Rapid Vap
HERB	30 g of sample with approx 30 g of NaSO4, but use clean NaSO4	Surr/Spike 1 ml (LCS and MS/D) Then add 4 pipettes of HCL	MeCl2	Sonicate 3X for 3 minutes (filter into Erlenmeyer or 16/32 ounce glass jar) Let sit ~2 hrs.	Rapid Vap Solvent exchange with Acetonitrile
WIPE (PCB)	1 wipe	1 ml PCB Surr (and 1 ml PCB Spike for LCS/D)	Hexane	Jar	N/A

3550	**Final Vol.**	**Cleanup**	**Vial**	**Amt in Vial**	**Int Std**
PNA	1 ml	N/A	Empty	1 ml	PNA 10 ul
SVOC	1 ml	N/A	Empty	1 ml	SVOC 10 ul
S/P	1 ml = 0.5 ml for PNA and 0.5 ml for SVOC	N/A	Empty	0.5 ml for PNA and 0.5 ml for SVOC	5 ul of PNA and 5 ul of SVOC
PCB	10 ml (2 tubes and pipet 5 ml into 2nd tube)	Add 2 ml of conc. H2SO4 into 2nd tube	Copper (layer	1 pipet (Transfer top phase of the clean up	N/A

		and vortex 10 sec	bottom of vial)	tube)	
Pest or PP (PCB/PEST)	10 ml (1 tube)	N/A	Copper (layer bottom of vial)	1 pipet (FILTER IF NEEDED)	N/A
TPH	1 ml	N/A	Empty	1 ml	N/A
HERB	1 ml	Use filter vial if sample is cloudy	Empty	1 ml (FILTER IF NEEDED)	N/A
Wipe (PCB)	10 ml (1 tube)	Transfer 5 pipettes into tube from jar. Add 2 ml H2SO4 and vortex 10 sec.	Copper (layer bottom of vial)	1 pipet (Transfer top phase of the clean up tube)	N/A

3580 (waste dilution: tube)	**Sample Size**	**Standards**	**Solvent**	**Extraction**	**Conc.**
PCB	1 g for liquid sample 1.5 g for solid sample	1 ml of Surr and 1ml of Spike (Use MS/D)	Hexane (if solid, add 10 ml; if liquid, add up to 10 ml)	Vortex for 10 sec	N/A
TPH	5 grams	No Surr 1 ml of Spike (Use MS/D)	MeCl2 (add 5 ml)	Vortex for 10 sec	N/A
PNA/SVOC	1 gram	1 ml of Surr and 1ml of Spike (Use LCS/D)	MeCl2 (if solid, add 10 ml; if liquid, add up to 10 ml)	Vortex for 10 sec	N/A
PHTHALATES	1 gram	0.5 ml of Phthalate Ester Spike (AccuStd), 0.25 ml Bisphenol A Custom Mix (Restek) (Use LCS/D)	MeCl2 (if solid, add 10 ml; if liquid, add up to 10 ml)	Vortex for 10 sec	N/A

3580 (cont)	Final Volume	Cleanup	Vial	Amt in Vial	Int Std
PCB	10 ml (2 tubes and pipet 5 ml into 2nd tube)	2 ml of H2SO4 conc. Into 2nd tube and vortex 10 sec	Copper (layer bottom of vial)	1 pipet (Transfer top phase of the clean up tube)	N/A
TPH	5 ml	N/A	Empty	1 pipet	N/A
PNA/SVOC	10 ml	N/A	Empty	1 ml exactly	10 ul of PNA or SVOC Int Std
PHTHALATES	10 ml	N/A	Empty	1 ml exactly (filter extract)	10 ul SVOC Int Std

Appendix 1: Summary of Changes from Revision 03

Attachment 5: New.
Attachment 6: New.
Section 4.3, 5.3, 9.34-9.38, 14.9: Included from Addendum dated 7.20.07.

STAT Analysis Corporation

STANDARD OPERATING PROCEDURE 3610

TOTAL AND AMENABLE CYANIDE: DISTILLATION by EPA 9012A

Revision 01
Effective Date: June 10, 2005

Authors: Ian Graske/ Bruce Anderson

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1.0 Identification of Test Methods

SOP Title: Total and Amenable Cyanide: Distillation by EPA 9012A

2.0 Applicable Matrix or Matrices

This method is used to prepare samples for the determination of the concentration of inorganic cyanide in aqueous samples, wastes, leachate and soils. This method employs a distillation procedure that is used to prepare samples for both total cyanide and cyanide amenable to chlorination. This distillation method is not applicable to oil or multiphasic samples or samples not amenable to the distillation procedure.

3.0 Detection Limits

See SOP 4710 Automated Cyanide Analysis by EPA 9012A for applicable method detections limits and reporting ranges.

4.0 Scope and Application

This method is a reflux-distillation procedure used to extract soluble cyanide salts and many insoluble cyanide complexes from wastes and leachates. It is based on the decomposition of nearly all cyanides by a reflux distillation procedure using a strong acid and a magnesium catalyst. Cyanide, in the form of hydrocyanic acid (HCN) is purged from the sample and captured into an alkaline scrubber solution. For the determination of the concentration of cyanide in the scrubber solution refer to SOP 4710 Automated Cyanide Analysis by EPA 9012A. This method may be used as a reflux-distillation procedure for both total cyanide and cyanide amenable to chlorination. The "reactive" cyanide content of a waste, that is, the cyanide content that could generate toxic fumes when exposed to mild acidic conditions, is not determined by this method. Refer to STAT SOP 3615 Reactive Cyanide and Sulfide Distillation for the additional information on reactive cyanide.

5.0 Summary of Method

The cyanide, as hydrocyanic acid (HCN), is released from samples containing cyanide by means of a reflux-distillation operation under acidic conditions and absorbed in a scrubber containing sodium hydroxide solution. The cyanide concentration in the absorbing solution is then determined using automated colorimetry. The quantitative analysis of cyanide in these distillates is performed using the analytical procedure detailed in STAT SOP 4710 Automated Cyanide Analysis by EPA Method 9012A.

5.1 Method Modifications from Reference

5.1.1 STAT Analysis Corporation utilizes a Midi-Cyanide Distillation Apparatus. This involves using a smaller sample volume thus producing less waste. A volume of 50 mL is distilled (section 14.3 of this SOP). The reference method, EPA 9012A, recommends a 500 mL sample aliquot (section 7.2 of the reference method).

5.1.2 Test for cyanide amenable to chlorination: The laboratory performs this test in a fume hood (SOP section 14.1.1) not under an amber light as is required in the reference method (section 7.7.1 of the reference method).

6.0 Definitions

The STAT Analysis Corporation Quality Assurance Manual (QAM) contains the definitions of standard terms used in this SOP.

7.0 Interferences

7.1 Interferences are eliminated or reduced by using the distillation procedure. Chlorine and sulfide are interferences in this method.

7.2 Oxidizing agents such as chlorine decompose most cyanides. Chlorine interferences can be removed by adding an excess of sodium arsenite or ascorbic acid to the waste prior to preservation and storage of the sample to reduce the chlorine to chloride which does not interfere.

7.3 Sulfide interference can be removed by adding an excess of bismuth nitrate to the waste (to precipitate the sulfide) before distillation. Samples that contain hydrogen sulfide, metal sulfides, or other compounds that may produce hydrogen sulfide during the distillation should be treated by the addition of bismuth nitrate.

7.4 High results may be obtained for samples that contain nitrate and/or nitrite. During the distillation, nitrate and nitrite will form nitrous acid, which will react with some organic compounds to form oximes. These compounds once formed will decompose under test conditions to generate HCN. The possibility of interference of nitrate and nitrite is eliminated by pretreatment with sulfamic acid just before distillation. Nitrate and nitrite are interferences when present at levels higher than 10 mg/L and in conjunction with certain organic compounds.

7.5 Thiocyanate is reported to be an interference when present at very high levels. Levels of 10 mg/L were not found to interfere.

8.0 Safety

8.1 All samples must be assumed as hazardous and appropriate precautions taken during handling.

8.2 Safety glasses, gloves, lab coats and closed toe shoes are to be worn.

8.3 Care must be taken to ensure that the distillation apparatus is a closed system prior to the addition of acid.

8.4 Other safety precautions must be conducted in accordance with the Chemical Hygiene Plan. Other actions can also be applied if deemed necessary. A reference file of material safety data sheets (MSDS) is available in each room for personnel involved in an analysis using chemicals.

8.5 The following chemicals have the potential to be highly toxic or hazardous, for detailed explanation consult the MSDS.
- 8.5.1 Potassium Cyanide is poisonous. Use extreme caution when handling this material.
- 8.5.2 Strong acids and bases, sulfuric acid and sodium hydroxide, are strong oxidizers. Use extreme caution when handling these materials. Avoid eye and skin contact. Wash exposed areas immediately with copious amounts of water.

9.0 Equipment and Supplies

9.1 Reliance Midi-Still™ Midi-Cyanide Distillation System (or equivalent)
- 9.1.1 MIDI-STILL Cyanide Distillation System – 10 place
- 9.1.2 Distilling Head – Set of 10
- 9.1.3 Condenser, Cold Finger –Set of 10
- 9.1.4 Dispersion/Absorber Tube, Fritted – Set of 10
- 9.1.5 Purge Tube. Reaction Flask – Set of 20
- 9.1.6 Tygon Tubing Set

9.2 Vacuum source

9.3 Water source for condensers

9.4 Top loading balance capable of weighing to 0.01 g

9.5 Calibrated pH Meter

9.6 Centrifuge Tubes, 50 mL graduated

9.7 Volumetric Flasks, Class A: 1000mL, 250mL, 100mL, 50mL, 25mL with stoppers

9.8 Autopipetter: 0.010 to 0.10 mL, 0.10 to 1.0 mL, 1.0 to 5.0 mL

9.9 Glass Beakers, 500mL, 250mL

9.10 pH paper or strips, wide range and narrow range

9.11 Potassium iodide starch paper

9.12 Lead acetate paper

9.13 Test Tubes, 15 mL and Tube Racks

9.14 Plastic and glass bottles for solution storage

9.15 PTFE Thread sealant tape

9.16 Parafilm

10.0 Reagents and Standards

The following reagents and standards are required to perform this procedure. When instructions are given on how to prepare a specific volume of a reagent or standard, larger or smaller volumes can be prepares as needed so long as the final concentrations remain the same. Any other deviations from the reagents or standards listed in this SOP could be detrimental to the quality of the data produced. Such deviations would have to be approved and documented (see SOP 230 Corrective Action).

10.1 Instructions for labeling and record keeping of reagents and standards are contained in SOP 1010 Analytical Standards and Reagents Receipt and Preparation.

10.2 Reagents – In methods where the purity of reagents is not specified, analytical reagent grade shall be used. Reagents of lesser purity than those specified by the test method shall not be used. Unless otherwise indicated, all reagents are stored at room temperature for up to 1 year after preparation. Store in a glass or plastic bottles.

10.3 Sodium hydroxide solution, 10N, Commercially purchased, or dissolve 40 g NaOH in 100 mL of water. Used for sample preservation.

10.4 Sodium hydroxide solution, 1.25N NaOH: Dissolve 50 g of NaOH in 1 liter of water.

10.5 Sodium hydroxide solution, 0.25N NaOH: Dissolve 100g of NaOH in 10 L of reagent water. Degass with helium, if necessary to prevent bubble formation. Store in a carboy.

10.6 1:1 Sulfuric Acid (50% H_2SO_4): In the hood, **slowly** add 500 mL concentrated sulfuric acid to 500 mL of reagent water. This solution will generate heat.

10.7 Magnesium chloride solution (2.5M): Dissolve 255 g of MgCl2·6H2O in 500 mL of reagent water.

10.8 Sulfamic Acid solution (0.4N): Dissolve 20g sulfamic acid (H_2NSO_3H) in 500 mL of reagent water.

10.9 Calcium hypochlorite solution (0.35M), $Ca(OCl)_2$. Combine 5 g of calcium hypochlorite and 100 mL of water. Shake before using.

10.10 Sodium arsenite solution, 0.1 N: Dissolve 1.28 g sodium arsenite in 100 mL of reagent water. Shake until dissolved.

10.11 Ascorbic acid, granular or powder

10.12 Bismuth nitrate solution, 0.062M: $Bi(NO_3)\cdot 5H_2O$: Dissolve 3.0 g of $Bi(NO_3)\cdot 5H_2O$ in 10 mL reagent water. While stirring, add 25 mL of glacial acetic acid. Stir until dissolved and dilute to 100 mL with water.

10.13 Ottawa Sand

10.14 Standards

10.14.1 At least one of the standards must be traceable to a NIST traceable source when available. The manufacturer should include a certificate of analysis for each standard. If one is not provided, contact the manufacturer. Retain all certificates in the designated binder. (See SOP 1010 Analytical Standards and Reagents Receipt and Preparation.)

10.14.2 Standards must be prepared volumetrically using Class A volumetric glassware, calibrated micropipettes, or gas tight syringes.

10.14.3 Stock ICV/CCV Cyanide Standard (2nd Source) 1000 mg CN/L: Commercially purchased. Store per manufacturer's recommendations and shelf life. If shelf life not stated, then this solution may be used for twelve months if stored in the original container at 0.1 to 6 °C and shows no sign of deterioration.

10.14.4 Intermediate Cyanide Spiking Solution: (10 mg CN/L): Dilute 0.50 mL of Cyanide ICV/CCV Stock Standard to 50 mL with 0.25N NaOH. Prepare this solution fresh monthly and store in a 50 mL centrifuge tube at 0.1 to 6 °C.

10.14.5 LCS and MS solutions: The LCS and Matrix Spike solutions use the 2nd Source Cyanide standard. NOTE: These LCS solutions are used in place of calibration standards for the distillation check procedure. Prepare the following solutions fresh daily and store in 50 mL centrifuge tubes.

10.14.5.1. LCS 0.40 mg/L or 20 mg/Kg, high level: Spike with 2.0 mL Intermediate Cyanide Standard (10 mg/L) into 50 mL of water or 1 gram of Ottawa sand.

10.14.5.2. LCS 0.20 mg/L or 10 mg/Kg, low level: Spiked with 1.0 mL Intermediate Cyanide Standard (10 mg/L) into 50 mL of water or 1 gram of Ottawa sand.

10.14.5.3. Matrix Spike – Water at 0.20 mg/L: Spiked with 1.0 mL Intermediate Cyanide Standard (10 mg/L) into 50 ml of sample.

10.14.5.4. Matrix Spike – Soil at 10 mg/Kg: Spike 1.0 mL Intermediate Cyanide Standard (10 mg/L) into 1 gram of sample.

11.0 Sample Collection, Shipment, Preservation and Storage

11.1 Sample Collection

500 mL plastic bottles may be used for sampling and storage of samples. The sample is collected with a minimum of headspace in the container.

11.2 Sample Preservation

The samples must be preserved to a pH > 12, using approximately 1 mL of 10N NaOH per 500 mL sample, and may be held for 14 days between 0.1 and 6 °C.

Note: If residual chlorine is present, add 0.6 g of ascorbic acid or a few drops of 0.1N sodium arsenite solution. Test sample using KI starch paper to confirm absence of residual chlorine (a blue color indicates a need for additional treatment). Record the addition (amount and chemical ID) in the logbook.

Maximum holding time is 24 hours when sulfide is present. Optionally, all samples may be tested with lead acetate paper in the field before pH adjustments in order to determine if sulfide is present (black spot on the test paper). If sulfide is present, it can be removed by the addition of cadmium nitrate powder until a negative spot test is obtained. The sample is filtered and then NaOH is added to pH > 12.

11.3 Sample Shipment, Handling, and Storage

Samples shall be placed on ice immediately after collection. The holding time is 14 days for a refrigerated sample (0.1 to 6 C°C) with proper chemical preservation (pH > 12). Distillation and analysis must occur within the 14 day period to be compliant.

If sample is not properly preserved, analysis not performed, client notified

12.0 Quality Control.

The following details the QC requirements that apply to this analysis. Each Quality Control Indicator (QCI) provides information pertaining to either method or individual sample performance. Our goal is to produce defensible data of known and documented quality.

The results of these QCI samples are used to assess the acceptability of data.

12.1 Blanks

Method Blank analysis is performed to determine if any contamination is present in the analytical process and is used to evaluate acceptance of the batch of samples. A method blank shall be prepared once per preparation batch of 20 or less samples per matrix type. If more than 20 samples are prepared a second blank shall be prepared after the twentieth sample. The method blank shall be processed through all preparatory steps used for the samples, including

cleanup procedures. The blank shall be analyzed using the same instrument and conditions as the samples.

12.2 Laboratory Control Sample (LCS)

The LCS is used to evaluate the performance of the total analytical system, including all preparation and analysis steps. The LCS shall be prepared once per preparation batch of 20 or less samples per matrix type. If more than 20 samples are prepared a second LCS shall be prepared after the twentieth sample. The LCS shall be processed through all preparatory steps used for the samples, including cleanup procedures. The LCS shall be analyzed using the same instrument and conditions as the samples. Refer to section 10.14.5 for preparation and concentration instructions. OPTION: Two LCSs (a high and a low concentration) may be distilled with each batch to ensure that the distillation process is effective and in control.

12.3 Duplicates

Duplicates of field samples or of the LCS must be prepared in compliance with the method requirements and client directives. Note: the analysis of the Matrix Spike Duplicate (MSD) is used as a substitute for the laboratory duplicate. In those cases when there is insufficient sample to perform either a duplicate analysis or MSD analysis, the duplicate analysis of the LCS (LCS/LCSD) is used to judge the precision of the analytical results.

12.4 Matrix Spike and Matrix Spike Duplicate (MS/MSD)

MS/MSDs indicate the effect of the sample matrix on the precision and accuracy of the results generated using the selected method. This information does not determine the validity of the entire batch. MS/MSDs must be analyzed at a minimum of 1 per 20 samples per matrix per preparation procedure, or as specified by the required test method. For cases where the sample cannot be divided (e.g., wipes, air samples, not enough sample provided by customer) and thus a MS/MSD pair cannot be prepared in the preparation batch, an LCS/LCSD pair is analyzed.

Samples chosen for matrix spiking are rotated among different clients and/or different client projects. This is accomplished through communication between the Department Manager and the analyst. In addition, designated samples, as indicated by client request or contract requirement, are matrix spiked.

The MS/MSD pair shall be processed through all preparatory steps used for the samples. They shall be analyzed using the same instrument and conditions as the samples. Refer to section 10.14.5 for preparation and concentration instructions. Some clients may require different spiking levels; these specific needs are documented on the request for analysis forms.

13.0 Calibration and Standardization

Autopipettes - Check autopipette to ensure standardization is within control limits. (See SOP 1040 General Laboratory Practices for Pipette Calibration.)

Balances - Be sure the balance is checked prior to use and performance criteria are met. (See SOP 1040 General Laboratory Practices for Calibration of Balances.)

14.0 Procedure

All sample containers must be labeled with sample ID number. This includes the Reaction Flask, Absorber Tube, and the LACHAT Autosampler 14 ml sample tube. The 50 ml disposable sample tube (and cap) should be labeled with the batch number as well as the sample ID number.

14.1 Pretreatment for cyanides amenable to chlorination – aqueous samples

14.1.1 NOTE: This test is performed in the fume hood. The laboratory does not use an amber light.

14.1.2 Two identical sample aliquots are required to determine cyanides amenable to chlorination. One sample is chlorinated and the other sample is not. The difference of total cyanide in the chlorinated and unchlorinated samples is the cyanide amenable to chlorination.

14.1.3 To one 50 mL sample or to a sample diluted to 50 mL, add calcium hypochlorite solution dropwise while agitating and maintaining the pH between 11 and 12 with 1.25N sodium hydroxide until an excess of chlorine is present as indicated by KI-starch paper turning blue. The sample will be subjected to alkaline chlorination by this step. Monitor with pH paper (narrow range).

CAUTION: The initial reaction product of alkaline chlorination is the very toxic gas cyanogen chloride; therefore, it is necessary that this reaction be performed in a hood.

14.1.4 Test for excess chlorine with KI-starch paper and maintain this excess for one hour with continuous agitation. A distinct blue color on the test paper indicates a sufficient chlorine level. If necessary, add additional calcium hypochlorite solution.

14.1.5 After one hour, add several drops of the sodium arsenite solution until KI-starch paper shows no residual chlorine. Add a few additional drops to ensure the presence of excess reducing agent.

14.1.6 Distill both samples (Section 14.3) and then test for total cyanide (SOP 4710 Automated Cyanide Analysis by EPA 9012A) in both the chlorinated and the unchlorinated samples. The difference of total cyanide in the chlorinated and unchlorinated samples is the cyanide amenable to chlorination.

14.2 Sample Pretreatment – Aqueous Samples

14.2.1 Check samples for presence of oxidization agents such as chlorine using KI starch paper. A distinct blue color on the test paper indicates the presents of chlorine. If chlorine is present remove as in 11.2.

14.2.2 Check Samples for presence of sulfide by using lead acetate paper. A positive test is indicated by a black color on the paper.

14.2.3 If samples are known or suspected to contain sulfide, add 5 mL of 0.062M bismuth nitrate solution through the air inlet tube. Mix for three minutes.

14.2.4 NOTE: For samples containing sulfides, all calibration standards and check standards must also be distilled under the same conditions, i.e., the addition of the bismuth nitrate solution. A calibration curve is then generated using the distilled standards. Few if any samples received at the laboratory are positive for the sulfide test.

14.3 Distillation Procedure

14.3.1 Prepare all blanks, LCSs, MS/MSDs and samples in the same manner. All preparations must contain a final volume of 50 mL.

14.3.2 Aqueous samples: Using a 50 mL centrifuge tube, measure 50 mL of aqueous sample and add to the reflux tubes (Back). For samples that require dilution, measure the appropriate volume of sample using a pipette. Add additional reagent water to achieve a 50 mL final volume in the reflux tube. Record the sample ID and volume used for distillation.

14.3.3 Sediment/soil samples: Mix sample thoroughly, especially composited samples. Discard any foreign objects such as sticks, leaves, and rocks. Record sample treatment in the logbook if the sample was not homogeneous. Weigh a minimum of 1.0 g sample and add to the reflux tube (Back). Add 50 mL reagent water into the reflux tube. Record the Sample ID and the weight to the nearest 0.01g.

14.3.4 Add 50 mL 0.25N NaOH solution in Absorber tube. (Front)

14.3.5 Assemble the remaining glassware apparatus.

14.3.6 Place the Reflux Impinger (non-fritted) with the gas inlet tube facing the rear of the MIDI-STIL into the Reflux sample tube (Back).

14.3.7 Place the Absorber Impinger (Fritted) with the gas inlet tube facing the rear of the MIDI-STIL into the Absorber tube (Front)

14.3.8 Connect the Absorber Impinger vacuum tube and hose barb coupler.

14.3.9 Place the cold finger condenser into the reflux Impinger tube with the hose barbs facing to the rear. Wrap the PTFE sealant around the glass joint to the sample tube and wrap parafilm around the joint to the cold finger to ensure a good seals.

14.3.10 IF not already connected, connect the cold finger water tubes to the water manifold Quick Disconnect adapters to the rear of the unit. The lower tube connects to the forward manifold (water outlet) and the upper tube connects to the rear manifold (water inlet).

14.3.11 Turn on cooling water to condensers, approximately 6 GPH/ sample. [For 10 samples set at approximately 60 GPH]

NOTE: **DO NOT** operate the cooling water unless the cold finger condensers are connected to the water manifold. Improper use may damage the cold finger condensers and/ or rupture tubing.

14.3.12 Turn on main vacuum. Adjust each vacuum valve until 3 bubbles per second are observed.

14.3.13 Allow vacuum to draw for 5 minutes.

14.3.14 Inject 5mL sulfamic acid into each sample access tube. (Air inlet of each Reflux Impinger Tube)

14.3.15 Inject 5 mL of 50% H_2SO_4 through the air inlet of each reflux impinge.

14.3.16 Allow vacuum to draw for 5 minutes.

14.3.17 Inject 2 mL magnesium chloride solution through the air inlet of each reflux Impinger. Inject another 2 mL if excessive foaming occurs.

14.3.18 Turn on the red rocker switch for main power, the light will glow.

14.3.19 Verify that the operating temperature is set at 125°C. (Check temperature every 3 months using a calibrated thermometer)

14.3.20 Verify that the timer is set to 1-¾ hours (105 minutes). This time setting allows for 15 minutes heat up time and 90 minutes of refluxing time. Record the start time in the logbook. At the end of the time period, check the block to ensure that the timer has worked properly and that the heat is off. Record the stop time. This ensures that the timer is working properly.

14.3.21 Depress the timer start switch. (Black).

14.3.22 The timer will automatically turn off heat block after selected time has expired. Vacuum draw and cooling water are unaffected.

14.3.23 Allow the sample to cool approximately 15 minutes before turning off cooling water and vacuum.

14.3.24 Disconnect the tubing couplers and shut off the main vacuum

14.3.25 Remove the Absorber Impinger (Fritted) from the sample and pour the sample into a prelabeled 50 mL centrifuge tube.

14.3.26 Cap the 50 mL tube. If the distillates are not immediately analyzed, refrigerate the distillates at 4^0C.

14.3.27 Dispose of the used sample from the back tubes and wash all the glassware.

14.3.28 Enter Prep Batch with initial volumes (or weights) and final volumes into LIMS (see SOP 1400 LIMS).

14.4 Documentation requirements.

Record the following information in the appropriate logbook or data file: Analyst initials, date [and time if required by the specific project or QAPP] of analysis, sample number or ID, initial sample volume or weight processed, final digestate volume, QC sample or solution identifier, reagent solutions identifiers, any dilution information, [beginning and ending times of analytical steps if required by the specific project or QAPP], visual observations, and any other information as deemed necessary. Include any deviations from this procedure.

14.5 Routine Maintenance

Record all maintenance. Daily required maintenance includes the following: check all tubing connections, check all glassware for chips or cracks, and clean the area around the distillation apparatus.

15.0 Data Reduction, Calculations and Loading

Not applicable to the SOP

16.0 Method Performance

Demonstration of Capability (DOC)

All parameters of interest must meet the method acceptance criteria before actual sample analysis begins. See SOP 1230 Training for the procedure to perform and document the DOC. The DOCs for the analysts performing this method are located in the analysts' training form folders located in the QA office files.

A quality control (QC) reference concentrate is required containing cyanide at a concentration of 0.05 mg/L for aqueous samples and 2.5 mg/Kg for soil samples using the ICV/LCS solution. The QC reference sample is made using stock standards prepared independently from those used for calibration.
Other lower concentrations may be used.

For each analyte calculate the mean recovery (X) and standard deviation (s) and the average % Recovery (%R). Compare X and s and %R with the corresponding acceptance criteria for accuracy and precision, respectively. Note: For aqueous samples, X must be within 0.05 ± 0.005 mg/L and s must be less than 0.005 mg/L and %R must be within 100 ± 10%. Note: For soil samples, X must be within 2.5 ± 0.5 mg/Kg and s must be less than 0.5 mg/Kg and %R must be within 100 ± 20%. These limits are taken from established in-house criteria If X and s and %R for all analytes meet the acceptance criteria, the system performance is acceptable and analysis of actual samples can begin. If X or %R falls outside the range for accuracy, or s exceeds the precision limit, then the system performance is unacceptable for that analyte and corrective action must be taken.

Comparison to Reference Method Data

See SOP 4710 Automated Cyanide Analysis by EPA 9012A.

In-House Control Limits

See SOP 4710 Automated Cyanide Analysis by EPA 9012A.

17.0 Pollution Prevention

The preparation of excessive volumes of laboratory reagents and standards shall be avoided so that waste and potential for pollution are minimized. Samples, reagents and standards shall be disposed in compliance with the laboratory waste disposal program and applicable waste disposal regulations. With the consent of the client, the samples may be returned to their origin for treatment.

Uncontaminated paper waste, glass and cans should be separated for recycling. Laboratory staff are required to protect the laboratory's and our clients' business information when disposing of recycling or waste from the facility.

18.0 Data Assessment and Criteria for Quality Control Measures

The review of the LCS result, MS/MSD recovery, and any other QC sample result for acceptable performance for each batch of samples is performed by the analyst performing the analytical procedure and sample analyses. Refer to SOP 4710 Automated Cyanide Analysis by EPA 9012A, Section 18.0 for data assessment and criteria for quality control measures.

19.0 Corrective Action for Out-of-Control Data

The process for handling corrective actions is found in SOP 230 Corrective Action.

If the CCV, MB, LCS/LCSD, MS/MSD, or lab duplicate recovery of any parameter falls outside the designated acceptance range, the laboratory performance for that parameter is judged to be out of control, and the problem must be immediately identified and corrected. The analytical result for that parameter in the samples is suspect and is only reported for regulatory compliance

purposes with the appropriate corrective action form. Immediate corrective action includes reanalyzing all affected samples by using any retained sample before the expiration of the holding time. Final data results must be qualified in the client report for reported results not meeting the laboratory-defined criteria.

1) Review standards preparation logbooks. Check all calculations and ensure dilution factors are properly recorded.

2) Re-prepare the suspected standard or QC sample to identify possible preparation errors of the standard or QC sample.

3) Re-Analyze the samples when the CCV or LCS is not within acceptable limits.

4) Perform routine preventative maintenance following manufacturer's specification. Record all maintenance in the instrument logbook.

20.0 Contingencies for Handling Out-of-Control or Unacceptable Data

See SOP 4710 Automated Cyanide Analysis by EPA 9012A..

21.0 Waste Management

The STAT Analysis Corporation SOP 1130 Waste Disposal identifies proper waste management practices for the chemicals and biological materials used in this procedure. Samples are stored and discarded accordance with SOP 1130 Waste Disposal.

22.0 References

22.1 Method 9012A, U.S. EPA SW-846 “Test Methods for Evaluating Solid Waste, Physical/Chemical Methods” Update III, December 1996
22.2 National Environmental Laboratory Accreditation Conference (NELAC), Current version at date of signing, USEPA Office of Research and Development, Washington, DC EPA600/R-99-068
22.3 Instruction Manual for MIDI-STIL Midi-Cyanide Distillation Systems
22.4 STAT Analysis Corporation Quality Assurance Manual
22.5 STAT SOP 003 Chemical Hygiene Plan
22.6 STAT SOP 230 Corrective Action
22.7 STAT SOP 1000 Control and Use of Laboratory Notebooks
22.8 STAT SOP 1010 Analytical Standards and Reagents Receipt and Preparation
22.9 STAT SOP 1020 Laboratory Glassware Cleaning
22.10 STAT SOP 1040 General Laboratory Practices
22.11 STAT SOP 1130 Waste Disposal
22.12 STAT SOP 1210 Method Detection Limits
22.13 STAT SOP 1230 Training
22.14 STAT SOP 1250 Data Review
22.15 STAT SOP 1400 LIMS

22.16 STAT SOP 3615 Reactive Cyanide and Sulfide: Distillation by SW846 Chapter 7
22.17 STAT SOP 4210 pH of Aqueous, Soil, and Waste Samples (EPA 9040B, 9045C, 150.1)
22.18 STAT SOP 4710 Automated Cyanide Analysis by EPA 9012A

23.0 Forms, Figures, Tables, Diagrams, Flowcharts, Attachments or Validation Data

FORM 1. Cyanide Distillation Logbook Page

FORM 1. Cyanide Distillation Logbook Page

Cyanide Preparation Logbook (9010B)

Date	Analyst	Start/Stop Time	Sample ID	Bottle #	KI	Oxidizers	Matrix	Sample Vol/Wt	Final Vol	Comments

LCS/LCSD/MS/MSD = 1.0 mL 10.0 mg/L CN STD

Reviewed By:_____

Page 1 of 100 Logbook 35-0001

STA Analysis Corporation:

STANDARD OPERATING PROCEDURE 4000

VOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS) (EPA Methods 5030B/5035/8260B)

Draft
Revision 05
Effective Date: xxxx, 2009

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This Standard Operating Procedure has been prepared for the sole use of STAT Analysis Corporation.

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1.0 IDENTIFICATION OF TEST METHOD

SOP Title: Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS) is abbreviated as VOC in laboratory records.

2.0 APPLICABLE MATRICES

This method is also applicable to nearly all types of samples, regardless of water content, including, but not limited to, ground and surface water, mobility extracts, aqueous sludges, caustic liquors, acid liquors, waste solvents, oily wastes, mousses, tars, fibrous wastes, polymeric emulsions, filter cakes, spent carbons, spent catalysts, soils, and sediments. Purge-and-trap by Methods SW-846 5030 (aqueous samples) and SW-846 5035 (solid and waste oil samples) are the preparation techniques used in this SOP.

In addition, other preparation techniques are also appropriate and necessary for some additional compounds not routinely analyzed using this SOP (see Method SW-846 8260B). These additional preparation techniques and non-routine compounds are not addressed in this SOP.

3.0 DETECTION LIMITS

The lab follows the procedure found in 40CFR Part 136B to determine the MDL for each matrix type on an annual basis. See the STAT Analysis SOP 1210 for the MDL procedure, frequency and acceptance criteria. The MDLs measured by the lab and all supporting documentation are in the laboratory QA files for review.

The laboratory determined MDL must always be less than the reporting limit (RL), which is determined by the lowest calibration standard. The RLs will usually range from three to ten times the laboratory measured MDLs but this relationship may vary dependent on dilution of sample aliquots, matrix interferences, moisture adjustments (in solid samples), or method-specified requirements. Attachment 1 contains the current MDLs and reporting limits (RLs) for this SOP.

4.0 SCOPE AND APPLICATION

4.1 This standard operating procedure describes in detail the precise methods used at STAT Analysis Corporation for the analysis of environmental samples for Volatile Organic Compounds (VOCs) by GC-MS. This SOP as written is to be applied when Method SW-846 8260B is requested. This SOP is used to determine the concentration of VOC's in all types of solid waste matrices, soils, and various types of water.

4.2 SOP 4000 can be used to quantify most VOCs that have both boiling points below 200°C and are either insoluble or slightly soluble in water. Volatile water-soluble compounds can be included in this analytical technique; however, for more soluble compounds, quantitation limits are approximately ten times higher due to poor extraction efficiencies from water. The SOP is also limited to compounds that elute as sharp peaks from a GC non-polar capillary column. Such compounds include low-molecular weight halogenated hydrocarbons, aromatics, ketones, nitriles, acetates, acrylates, ethers, and sulfides. See Attachment 2 for a list of compounds and their characteristic ions that have been evaluated on the specified GC/MS system.

4.3 The reporting limits (RLs) for this SOP are shown in Attachment 1 for soils and water. RLs will be proportionately higher for sample extracts and samples that require dilution or reduced sample size to avoid saturation of the detector.

4.4 This method is restricted to use by or under the supervision of analysts experienced in the use of a Gas Chromatograph/Mass Spectrometer (GC/MS) and skilled in the interpretation of mass spectra. Each analyst must demonstrate the ability to generate acceptable results with this method.

5.0 SUMMARY OF TEST METHOD

5.1 Prior to using this method, the samples must be prepared for the GC/MS using the appropriate sample preparation technique (see Section 14.1). Volatile compounds (VOCs) are introduced into a Gas Chromatograph (GC) by the purge-and-trap method or by direct injection. Purge and Trap: An inert gas (Helium) is bubbled through the water at ambient temperature (Method SW-846 5030) and at 40°C for soils (Method SW-846 5035). The volatile components are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through an adsorbent column where the volatile components are trapped. After purging is completed, the adsorbent column is heated and back flushed with Helium desorbing the components into a GC column. If the above sample introduction techniques are not applicable, a portion of sample is dispersed in methanol to dissolve the volatile organic constituents. A portion of the methanol solution is combined with water in the purging chamber. It is then analyzed by purge-and-trap GC/MS following the normal soil method.

5.2 This method describes chromatographic conditions that will allow for the separation of the compounds and for their qualitative and quantitative analysis by Gas Chromatography/Mass Spectrometry (GC/MS). Identification of target compounds is accomplished by comparing component retention times to those of authentic standards and by comparing their mass spectra with the electron impact (or electron impact-like) spectra of authentic standards. Quantitation is accomplished by comparing the response of a major (quantitation) ion relative to an internal standard using a five-point calibration curve.

5.3 **Method Modifications from Reference** – This SOP is based on Methods SW-846 8260B, 5030B, and 5035. The 4-Bromofluorobenzene (BFB) mass spectrometer tuning criteria used in this SOP is referenced in the CLP Statement of Work (SOW) for Organic Analyses Revision OLM04.2 May 1999. This is an option in Method SW-846 8260B. Soil samples received in Encore (or equivalent) are prepped according to CLP Statement of Work (SOW) for Organic Analyses Revision OLM04.2 May 1999. Medium level dilutions are prepared from an aliquot of the methanol preserved sample that is transferred into 5 ml of reagent water and analyzed using the soil Archon procedure.

6.0 DEFINITIONS

The STAT Analysis Quality Manual Section 19.0 contains all the definitions of standard terms used in SOPs.

7.0 INTERFERENCES

7.1 GC/MS data from all blanks, samples, and spikes must be evaluated for interferences. Interferences purged or co-extracted with methanol from the samples, will vary from source to source depending upon the particular sample or extract being tested. Determine if the source of interference is laboratory induced. If the source of the interference is laboratory induced, take corrective action to eliminate the problem.

7.2 Contamination by carryover can occur whenever high-concentration and low-concentration samples are sequentially analyzed. Reagent blanks must be analyzed to demonstrate that carryover has been eliminated. Reanalysis must be performed on all affected samples to demonstrate that the compound concentration is from the sample and not due to carryover. The purge-and-trap system may require extensive bake out and cleaning after a high-level sample. Cleaning may include trap replacement, purge gas filter replacement, frit cleaning/replacement and/or transfer line cleaning/replacement.

7.3 Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride, acetone, and fluorocarbons) through the septum seal into the sample during shipment and storage. A refrigerator blank, consisting of preserved reagent water, is stored under the same conditions as the samples. It is analyzed weekly to ensure that samples are not cross-contaminated during the storage process. Clients may specify trip blanks and field blanks for additional contamination checks to monitor for cross contamination during the shipping and sample collection processes.

7.4 The laboratory where volatile analysis is performed must be kept completely free of solvents (except P&T Grade Methanol). Storage of sprays, neat standards, and white out (for capillary column marking only) is forbidden.

7.5 Impurities in the purge gas and from organic compounds out-gassing from the plumbing ahead of the trap account for the majority of contamination problems. The analytical system must be demonstrated to be free of contamination under the conditions of analysis by running calibration and reagent blanks. The use of non-PTFE plastic coating, non-PTFE thread sealants, or flow controllers with rubber components in the purging device should be avoided.

7.6 Laboratory clothing worn by the analyst should be kept only in the VOA laboratory since the clothing exposed to solvents can cross contaminate samples. Lab coats used in other areas the lab, i.e. liquid/liquid extractions, soil extractions, dishwashing and PCM prep, etc., are forbidden.

8.0 SAFETY

Numerous compounds analyzed by this method are known or suspected carcinogens. Proper personal protective equipment including safety glasses, nitrile gloves and a lab coat are required during different parts of this method. Other safety precautions must be conducted in accordance with the Chemical Hygiene Plan. Other actions can also be applied if deemed necessary. A reference file of Material Safety Data Sheets (MSDS) is available to all personnel involved in this method.

9.0 EQUIPMENT AND SUPPLIES

The following apparatus is recommended for performing this procedure. Equivalent items can be used, if with their use, the analytical and QA/QC requirements in this SOP can be met. All catalog numbers in this SOP are current as of the effective date and thereafter subject to change.

9.1 Gas Chromatograph/Mass Spectrometer system (GC/MS)

9.1.1 Gas chromatograph(GC) – Agilent 6890 or 5890/ HP 5890 with electronic flow control gas chromatograph with a split flow injection port used to reduce Helium flow. The column is directly coupled to the source.

9.1.2 Column – 20 m X 0.180 mm ID J&W DB-624 column with 1 µm film thickness.

9.1.3 Mass spectrometer(MS) - Agilent 5971 and 5973

9.1.4 Data system – A computer system using Agilent 3365 Chemstation Software (G1701AA Version C.03.00, G1701BA Version B.00.01, and G1701CA Version C.01.08) is used to collect and process data.

9.1.5 NIST Library of Reference Spectra, Edition NIST98.L

9.2 Purge-and-Trap device: Tekmar Model 3000/3100 (or equivalent) equipped with a 5 mL (or 25 mL) glass frit sampler and an VOC trap, Vocarb 3000.

9.3 Archon Auto Sampler

9.4 Microliter syringes - 10 µL, 25 µL, 100 µL, 250 µL, 500 µL and 1,000 µL. These syringes should be equipped with a 20-gauge needle having a length sufficient to extend into a volumetric flask

9.5 Glass Vials – 40 mL VOA vials with Teflon faced septum and screw cap

9.6 EnCore (or equivalent) samplers for soil samples

9.7 Gas tight glass syringes - 5mL and 10 mL

9.8 Syringe valve: two way, Luer ends

9.9 Volumetric flasks, Class A - 10 mL, 50 mL, 250 mL with ground glass stoppers

9.10 Balance: Analytical, capable of accurately weighing 0.0001g and a top loading balance capable 0.001g

9.11 Spatula - Stainless steel

9.12 Disposable pipettes: Pasteur

9.13 Amber glass vials - 10 mL with Teflon-lined mininert screw caps

9.14 pH strips, wide range

9.15 Magnetic Stirring bars – Teflon coated

9.16 EnCore extrusion tool.

9.17 Adjustable autopipette dispenser – 10 mL

10.0 REAGENTS AND STANDARDS

The following reagents and standards are required to perform this procedure. When instructions are given on how to prepare a specific volume of a reagent or standard, larger or smaller volumes can be prepared as needed so long as the final concentrations remain the same. Any other deviations from the reagents or standards listed in this SOP could be detrimental to the quality of the data produced. Such deviations would have to be approved and documented (see 230 Corrective Action SOP).

Instructions for labeling and record keeping of reagents and standards are contained in SOP 1010 Standard and Reagent Preparation.

10.1 Analytical reagent grade chemicals shall be used in all tests. Unless otherwise indicated, all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.

10.2 Organic-free reagent water - All references to water in this SOP refers to Type II reagent water (in-house system). Note: Reagent water may be de-gassed with High Purity Helium to remove trace impurities.

10.3 Stock Standard solutions - Standard solutions can be prepared from pure standard materials or purchased as certified solutions (e.g. Supelco). The routine laboratory practice is to purchase these standards from approved vendors. The standards used are purchased from: Protocol, Aldrich, Supelco, Restek, and AccuStandard. All purchased standards are stored at manufacturer's recommended conditions. Stock solutions prepared from neat compounds expire six months from preparation date. Working Standard solutions and Working Quality Control (QC) solutions are stored at < -10°C and must be replaced monthly or sooner if comparison with quality control check samples indicates a problem. Quality Control Standards must be from different source (lot numbers) than Calibration Standards.

Working Standard Solutions – These solutions are made using the Stock Standard solutions and Primary Stock Standards solutions. Using microliter syringes, the following amounts of each Stock Standard solution are injected into 10 mL volumetric flasks. Each solution is brought to volume with Methanol, capped and mixed. The final concentration of each component is listed in Table 1. These are the Working Standard solutions used to prepare the calibration standards in Section 10.4. These standards are stored at < -10°C in 10 mL amber vials equipped with Teflon lined mininert screw caps. Note: the 1,4-dioxane is stored in an 1ml vial with no dilution. Working Standard Solutions are freshly prepared every month, or sooner if check standards indicate a problem. The Working standard for gases, M-502B-GASES, has been found to be stable for one month when stored at the listed concentration and final volume (Table 1). This solution is replaced if Continuing Calibration Verification (CCV) or Laboratory Control Sample (LCS) outliers exist.

Table 1 Working Standard Solutions

Solution ID	Stock Solution	Vendor/Catalog No.[a]	Conc. Stock [b] (µg/ml)	Vol. Stock (µl)	Final Conc. (µg/ml)
VOC-MOR	Custom VOA Mix	Restek / 553515	2000 - 40000	1250	250 - 5000
	1, 1, 2 – Trichlorotriflouroethane	Restek / 30462	2000	1250	250
VOC-EH	M-8260-ADD-10X	AccuStandard/ M-8260-ADD-10X	2000	1250	250
	1,3-Butadiene	AccuStandard/ S-406A-10X	2000	1250	250
VOC-VCX	M-502A-R-10X	AccuStandard/ M-502A-R-10X	2000	1250	250
VOC-GAS	GASES/M-502B-10X	AccuStandard/ M-502B-10X	2000	1250	250
VOC-F.LIST	2-Nitropropane	Restek/30403-510	2000	1250	250
	Ethyl Acetate	Supelco/4-7947	2000	1250	250
	Ethyl Ether	Supelco/4-7948	2000	1250	250
1,4-Dioxane	1,4-Dioxane	Supelco/4-8367	2000	No dilution	2000
Gasoline	Gasoline	Supelco/ 47516-U	20000	No dilution	20000
Mineral Spirits	Mineral Spirits	AccuStandard/ HS-002S-40x	20000	No dilution	20000

Note: a: or equivalent
b: Preparations of calibration standards and QC check solutions using source materials of < 96% purity must be corrected using the stated purity of the material.

10.4 Calibration Standards - A minimum of five calibration standards are prepared. The low standard is the RL and above the MDL. The others define the working range of the GC/MS system. Calibration standards in current use: VOC Soil: 2, 5, 10, 50, 100, 200 and 300 µg/L, VOC Water: 1, 5, 10, 50, 100, 200, and 300 µg/L, Gasoline/ Mineral Spirits Soil and Water: 100, 200, 500, 1000, 2000, 5000, 10000. See Table 2 for Soil and Table 3 for Water standards.

10.4.1 Using microliter syringes, the following amounts of the Working solutions are injected into a volumetric flask. The flask contains water within 1 mL of the mark. After all Working solutions are injected into the water, the solution is brought to volume with water and capped. The flask is gently inverted three times to mix the solution. The contents of the neck portion of the flask are discarded prior to taking an aliquot. The final concentration of each component is listed in Table 2 and Table 3. The solution may be stored in a 40 mL VOA vial at 4°C for up to 24 hours. The continuing calibration verification standards (CCVs) are prepared daily. Levels 4 and 5 (50, and 100 µg/L) are used for the CCVs.

10.4.2 For soil calibration: A 5 mL gas tight syringe is used, the plunger from the syringe is removed. The calibration standard solution from the volumetric flask is gently decanted into the syringe until the syringe is filled to almost overflowing. The plunger is carefully placed into the syringe barrel; no air bubbles are trapped in solution. The solution volume is adjusted to 5 mL. The 5 mL aliquot of each calibration solution is then transferred to an individual 40 mL VOA vial containing a stir bar. The vial is sealed with a screw cap with Teflon faced septum.

Table 2 Soil Calibration Standards

Level VOC	Volume (µL) Secondary Stock	Volumetric Flask (mL)	Final Concentration (µg/L)
1	5.0/4.0*	500	2
2	1.0/1.25*	50	5
3	2.0/2.5*	50	10
4	2.0/2.5*	10	50
5	4.0/5.0*	10	100
6	8.0/10.0*	10	200
7	12.0/15.0*	10	300
Level Gasoline	Volume (µL) Secondary Stock	Volumetric Flask (mL)	Final Concentration (µg/L)
1	2.5	500	100
2	12.5	500	500
3	2.5	50	1000
4	5	50	2000
5	12.5	50	5000
6	25	50	10000
Level Mineral Spirits	Volume (µL) Secondary Stock	Volumetric Flask (mL)	Final Concentration (µg/L)
1	2.5	500	100
2	12.5	500	500
3	2.5	50	1000
4	5	50	2000
5	12.5	50	5000
6	25	50	10000

* Second Volume is for 1,4-Dioxane only.

10.4.3 For water calibration: The calibration standard solution from the volumetric flask is gently decanted into an individual 40 mL VOA vial until the vial is filled to almost overflowing. The screw cap with Teflon faced septum is carefully placed on the vial; no air bubbles are trapped in solution.

10.4.4 A 200 ppb Gas Only (GASES/M-502B-10X) Calibration Standard may be prepared if bromomethane and/or chloroethane response is suppressed due to an excessive volume of P&T methanol needed to prepare the 200 ppb standard. Methanol will co-elute with bromomethane and/or chloroethane causing their signal to be suppressed if excessive methanol is present.

Table 3 Water Calibration Standards

Level VOC (5mLpurge)	Volume (µL) Secondary Stock	Volumetric Flask (mL)	Final Concentration (µg/L)
1	2.5/2.0*	500	1
2	1.00/1.250*	50	5
3	2.0/25*	50	10
4	10.0/12.5*	50	50
5	20.0/25.0*	50	100
6	40.0/50.0*	50	200
7	60.0/75.0*	50	300
Level VOC (25mL purge)	Volume (µL) Secondary Stock	Volumetric Flask (mL)	Final Concentration (µg/L)
1	0.40	500	0.2
2	2.0	500	1
3	1.00	50	5
4	2.0	50	10
5	4.0	50	20
6	8.0	50	40
7	12.0	50	60
Level Gasoline	Volume (µL) Secondary Stock	Volumetric Flask (mL)	Final Concentration (µg/L)
1	2.5	500	100
2	12.5	500	500
3	2.5	50	1000
4	5	50	2000
5	12.5	50	5000
6	25	50	10000
Level Mineral Spirits	Volume (µL) Secondary Stock	Volumetric Flask (mL)	Final Concentration (µg/L)
1	2.5	500	100
2	12.5	500	500
3	2.5	50	1000
4	5	50	2000
5	12.5	50	5000
6	25	50	10000

* Second Volume is for 1,4-Dioxane only.

10.5 Internal Standards/Surrogate Standards Solution: The internal standards used are Chlorobenzene-d_5, Pentafluorobenzene, 1,4-Dichlorobenzene-d_4, and 1,4-Difluorobenzene. The surrogates are Toluene-d_8, 4-Bromofluorobenzene, Dibromofluoromethane, and 1,2-Dichloroethane-d_4. A commercially prepared stock solution, 2000 µg/ml, is purchased from Supelco (Cat. No. 4-8958/4-7778). The Working Standard solution is prepared by injecting 6.25 ml of stock standard into a 50 mL volumetric flask and diluting to mark with Methanol. The concentration of the Spiking solution is 250 µg/mL. This Working Standard solution is added to the standard reservoir of the Archon Autosampler. One microliter (1.0 µL) is added to each sample aliquot that is analyzed by the system. The concentration in the sample is 50 µg/L for all Internal Standard and Surrogate compounds. This solution expires after one month. The internal standards permit most of the compounds of interest in a chromatogram to have retention times of 0.80-1.20 relative to one of the internal standards. Use the base peak ion from the specific internal standard as the primary ion for quantitation (see Attachment 2, i.e. for 1,4-dichlorobenzene-d_4, use 152 m/z for quantitation). If interferences are noted, use the next most intense ion as the quantitation ion.

10.6 GC/MS tuning standard - A methanol solution containing 25 ng/µL of 4-Bromofluorobezene (BFB) is used to tune the mass spec. The VOC tuning standard is purchased from Supelco (Cat. No. 47077) Store at < -10°C when not being used. Use a syringe to inject 2 µL of this standard at the start of every 12 hours of operation. Prepare the purge solution by adding 2µL of the BFB standard to 5ml water in a gastight syringe. Add the water solution to the sparge tube and step the purge and trap to purge the solution. Analyze the solution using the same conditions outlined in Section 14.1.3.

10.7 The Laboratory Control Sample (LCS) is also used as an Initial Calibration Verification Standard (ICV). Spiking solutions are prepared from certified analytical stock standard solutions purchased independently from the Calibration Standards. The LCS stock standards are purchased from Supelco and Restek.

10.7.1 The LCS Spiking Solutions are prepared according to Table 4. These solutions are made using the LCS stock standard solutions. Using a microliter syringe, the following amounts of each solution are injected into a single 10 mL volumetric flask. The solution is brought to volume with Methanol, capped and mixed. The final concentration of each component is listed in Table 4. These are the source solutions used to prepare the LCS for both soil and water samples. These solutions are stored at < -10°C in a 10 mL amber vial equipped with a Teflon lined mininert screw cap. It is freshly prepared every month, or sooner if check standards indicate a problem. Note: The 2000 µg/mL Acrolein Stock solution is made from pure solution by diluting 25µL in a 10.0mL Volumetric Flask with methanol.

Table 4 LCS Spiking Solutions

Solution ID	Stock Solution	Vendor/Catalog No.*	Conc. Stock (µg/ml)	Vol. Stock (µL)	Final Conc. (µg/ml)
LCS-MIX 1	8260 VC Mix	Supelco/5-00607	2000	250	50
	VOC Mix #6	Supelco/48799-U	2000	250	50
	8240B Mix #2	Supelco/4-7364	2000	250	50
	Acrolein	Supelco/4-8501	1000	500	50
	Custom Mix	Supelco/20283002	2000 - 40000	250	50 -- 1000
	Vinyl Acetate	Restek/30216	2000	250	50
LCS-MIX 2	Ethyl Acetate	Restek/556319	2000	250	50
	2-Chloroethyl vinyl ether	Restek/30265	2000	500	100
Mineral Spirits	Mineral Spirits	AccuStandard/ HS-002S	500	No dilution	500
Gasoline	Unleaded Gasoline Composite Standard	Restek/ 30205	50000	No dilution	50000

* or equivalent

10.7.2 Soil LCS preparation: Using a 10 µL microliter syringe, inject 10 µL of each LCS Spiking Solutions into a 10 ml volumetric flask filled to the mark with water. The flask is capped and is gently inverted three times to mix the solution. The contents of the neck portion of the flask are discarded prior to taking an aliquot. A 5 mL gas tight syringe is used, the plunger from the syringe is removed and the LCS working solution from the volumetric flask is gently decanted into the syringe until the syringe is filled to almost overflowing. The plunger is carefully placed into the syringe barrel; ensure that no air bubbles are trapped in solution. The solution volume is adjusted to 5 mL. The 5 mL aliquot of the LCS solution is then transferred to an individual 40 mL VOA vial containing a stir bar and standard Ottawa sand. The vial is sealed with a screw cap with Teflon faced septum.

10.7.3 Water LCS preparation: Using a 100 µL syringe, inject 50 µL of each LCS Spiking Solution into a 50 ml volumetric flask filled to the mark with water. The flask is capped and is gently inverted three times to mix the solution. The contents of the neck portion of the flask are discarded prior to taking an aliquot. The LCS solution from the volumetric flask is gently decanted into an individual 40 mL VOA vial until the vial is filled to almost overflowing. The screw cap with Teflon faced septum is carefully placed on the vial. Ensure that no air bubbles are trapped in the vial.

10.8 Matrix Spike standards - The LCS Spiking solutions are also used for the Matrix Spiking solution. For soil samples, prepare the LCS Spiking solution (50µg/L) as in Section 10.7.3. The LCS solution from the volumetric flask is gently decanted into a 10 mL gas tight syringe with removable needle, and injected into each vial already containing the soil sample. For water samples, transfer the water sample into a 50 ml volumetric flask and follow the procedure in Section 10.7.3

10.9 Methanol - Purge & Trap (P&T) Grade quality. Due to possible cross contamination, store in VOA room only.

10.10 Helium – UHP grade for purge gas and carrier gas.

10.11 Helium –HP grade for optional reagent water degassing .

10.12 Ottawa Sand.

11.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

11.1 Containers used to collect samples for the determination of volatile organic compounds: For water samples, use 40 mL VOA glass vials equipped with Teflon faced septum and screw cap, no headspace and preserved with concentrated HCl to pH <2. Water samples containing residual chlorine should be field treated to remove the chlorine prior to collection. Soil samples may be collected in either a 40 mL VOA vial, a 40 mL VOA vial preserved with sodium bisulfate, a 40 mL VOA vial with 5.0 ml methanol, or EnCore (or equivalent) samplers. Plastic containers or lids must NOT be used for the storage of samples due to the possibility of sample loss. A separate 4 oz jar should be supplied for percent moisture determination for soil and sediment analysis. Soils analyzed from a glass jar will NOT be reported by Method 5035 .

11.2 Water samples, soil samples preserved with sodium bisulfate, and soil samples preserved with 5.0 ml methanol must be stored under refrigeration at between 0.1°C and 6.0°C. Analysis must be within 14 days from sampling date for water preserved with HCl (7 days for unpreserved water samples) and 14 days for soils. Soil samples collected in 40 mL VOA vial or ENCORE (or equivalent) samples are transferred to empty vial and frozen at <-7°C until thawed for analysis. It may be advisable to place the vials on their side during the freezing process to prevent breakage. Freezing has been found effective to preserve both aromatic and chlorinated hydrocarbon VOCs in soil for two weeks at all VOC concentrations studied. Sample vials should not be frozen below -20°C due to potential problems with vial seals and loss of constituents upon sample thawing.

11.3 All samples are stored away from all standards, reagents, food, and other potentially contaminating sources in order to prevent cross contamination.

12.0 QUALITY CONTROL

The following details the QC requirements that apply to this analysis. Each Quality Control Indicator (QCI) provides information pertaining to either method or individual sample performance. Our goal is to produce defensible data of known and documented quality. The results of these Quality Control Indicator (QCI) samples are used to assess the acceptability of data.

12.1 Calibration Verification

An Initial Calibration Verification (ICV) standard containing all of the target compounds reported in this method (refer to section 10.7) shall be analyzed immediately after the completion of the initial calibration. The ICV shall be purchased from a second source to verify compound concentrations.

12.2 Blanks

Method Blank analysis is performed to determine if any contamination is present in the analytical process and is used to evaluate acceptance of the batch of samples. A method blank shall be prepared once per preparation batch of 20 or less samples per matrix type. If more than 20 samples are prepared a second blank shall be prepared after the twentieth sample. The method blank shall be processed through all preparatory steps used for the samples. The blank shall be analyzed using the same instrument and conditions as the samples.

12.3 Laboratory Control Sample (LCS)

The LCS is used to evaluate the performance of the total analytical system, including all preparation and analysis steps. The LCS shall be prepared once per preparation batch of 20 or less samples per matrix type. If more than 20 samples are prepared a second LCS shall be prepared after the twentieth sample. The LCS shall be processed through all preparatory steps used for the samples, including cleanup procedures. The LCS shall be analyzed using the same instrument and conditions as the samples. Refer to section 10.7 for LCS compounds and concentrations.

12.4 Surrogates

The surrogates used for this method are added to all samples, standards, and blanks. Refer to section 10.5 for preparation and concentration instructions.

12.5 Duplicates

Duplicates of field samples or of the LCS must be prepared in compliance with the method requirements and client directives. Duplicate LCSs are prepared for cases in which there is insufficient sample to perform a matrix spike and matrix spike duplicate. Reproducibility performance would be the same as for a matrix spike/matrix spike duplicate.

12.6 Matrix Spike and Matrix Spike Duplicate (MS/MSD)

MS/MSDs indicate the effect of the sample matrix on the precision and accuracy of the results generated using the selected method. This information does not determine the validity of the entire batch. MS/MSDs must be analyzed at a minimum of 1 per 20 samples per matrix per preparation procedure, or as specified by the required test method. If an MS/MSD pair is not analyzed in the preparation batch, an LCS/LCSD pair is analyzed. Samples chosen for matrix spiking are rotated among different clients and/or different client projects. This is accomplished through communication between the Department Manager and the analyst. In addition, designated samples, as indicated by client request or contract requirement, are matrix spiked. The MS/MSD pair shall be processed through all preparatory steps used for the samples. They shall be analyzed using the same instrument and conditions as the samples. The LCS solutions in Section 10.7 are used for matrix spiking (see also Section 10.8). Some clients may require different spiking levels and/or target compounds, these specific needs are documented on the request for analysis forms.

12.7 Internal Standards

The internal standards used for this method are added to all samples, standards, and blanks. Refer to section 10.5 for preparation and concentration instructions.

13.0 CALIBRATION AND STANDARDIZATION

13.1 Mass Spectrometer Tuning Verification

Mass Spec is software-tuned with the BFB tuning macro using PFTBA. Each GC/MS system must be hardware-tuned to meet the criteria in Table 5 for a 50 ng injection of BFB. Analyses must not begin until all these criteria are met. Using a 10 µL syringe, inject 2 µL of BFB tuning standard solution directly on to the column. Analyze the solution using the following BFB method conditions:

BFB method operating conditions	
EMV	1300-2500
Mass Range	35-300
Scan Sampling Rate	2^2
Initial Column Temp.	70°C
Initial Temp Holding Time	2 minutes
Ramp 1 Temp Program	20°C/minute
Ramp 1 Final Column Temp.	230°C
Ramp 1 Holding Time	3 minutes
Injector Temp.	220°C
Source Temp.	250°C
Transfer Line Temp.	250°C
Split Ratio	50:1
Carrier Gas	UHP Helium

Background subtraction must be straightforward and designed only to eliminate column bleed or instrument background ions. Obtain a mass spectral analysis, using the method listed above, of BFB and confirm that all the key m/z criteria in Table 5 are achieved. The mass spectra of BFB are acquired using the following methods: three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged, the peak apex only is evaluated, or the entire BFB peak is averaged. If background subtraction is required, this must be accomplished using a single scan no more than 20 scans prior to the elution of BFB. Do not background subtract part of the BFB peak. Note: the instrument-tuning file used to acquire the BFB criteria must be also used to acquire QC and sample data. If the criteria are not passed, the analyst must perform needed maintenance, retune the mass spectrometer and repeat the test until all criteria are achieved.

Note: the 12-hour tune period begins at the start of the BFB analysis, which is recorded as the data acquisition start time on the data file. The last valid calibration standard in the ICAL must have a data acquisition start time less than 12 hours from the start of the tune period.

Table 5 Acceptance Criteria for BFB

Target Mass	Relative to Mass	Lower Limit%	Upper Limit%
50	95	8	40
75	95	30	66
95	95	100	100
96	95	5	9
173	174	0	<2
174	95	50	120
175	174	4	9
176	174	93	101
177	176	5	9

13.2 **Initial Calibration (ICAL)**

13.2.1 Analyze each calibration standard according to the procedure listed in Section 14 (standards are analyzed under the same conditions as samples) and tabulate the target ion area of the compound against concentration for each compound relative to the appropriate relative internal standard. See Attachment 5 for the list of internal standard assigned to each compound. Calculate response factors (RFs) for each compound in each calibration standard as follows:

$$RF = \frac{A_x * C_{is}}{A_{is} * C_x}$$

where:

A_x = Area of the characteristic ion for the compound being measured.
A_{is} = Area of the characteristic ion for the specific internal standard.
C_{is} = Concentration of the specific internal standard (50 µg/L for this method)
C_x = Concentration of the compound being measured (µg/L).

13.2.2 Calculate the average response factor ($\overline{RF}$) for each compound as follows:

$$\overline{RF} = (S\ RF_1 \text{ to } RF_n)/n$$

where:

RF = RF for each of the calibration levels (i.e., 5)
n = Number of RF values (i.e., 5)

13.2.3 A system performance check must be performed to ensure that minimum average RFs are met before the calibration curve is used. If it is determined that one calibration level has an unacceptable response, that level may be reanalyzed once. If the minimum average RF is still not met, corrective action must be taken and the calibration sequence repeated. If any major changes are made to the system (e.g. column changed or detector cleaned), recalibration of the system must take place. For Volatiles, the System Performance Check Compounds (SPCCs) and the the minimum average RFs are as follows:

Chloromethane	0.100
1,1-Dichloroethane	0.100
Bromoform	0.100
Chlorobenzene	0.300
1,1,2,2-Tetrachloroethane	0.300

13.2.4 Calibration Check Compound (CCC) responses are monitored to check the integrity of the system. The CCCs are as follows:

Vinyl chloride	1,2-Dichloropropane
1,1-Dichloroethene	Toluene
Chloroform	Ethylbenzene

Using the RFs from the initial calibration, calculate the percent relative standard deviation (%RSD) for the Calibration Check Compounds (CCC).

To calculate %RSD: $\%RSD = 100\% \times SD/\overline{RF}$

where:

%RSD = % Relative Standard Deviation

$\overline{RF}$ = average of initial RFs for a compound
SD = standard deviation (n-1) of average RFs for a compound

To calculate Standard Deviation (n-1 degrees of freedom)

$$SD = \sqrt{\sum_{i=1}^{N} \frac{(RF_i - \overline{RF})^2}{N-1}}$$

where: RF_i = RF for each of the 5 calibration levels
N = Number of RF values (i.e., 5)

13.2.5 If the %RSD of any CCC compound is > 30%, then the chromatographic system is too reactive for analysis to begin. Check stability of the trap, replace if necessary. Perform the initial calibration procedure beginning with section 13.2.1.

13.2.6 Linearity : If the %RSD of any compound is 15% or less, then the relative response factor is assumed to be constant over the calibration range, and the average relative response factor is used for quantitation. If the %RSD is greater than 15%, first order linear regression is used. The calibration curve must meet the requirements for curve fitting listed in SW-846 8000B and the correlation coefficient is = 0.99. The equation is not forced through the origin.

13.2.7 Retention Times: The Relative Retention Times (RRT) of each compound in each calibration standard should be within ± 0.06 RT units.

13.2.8 Before sample analysis can begin, a Initial Calibration Verification (ICV) (see Sec. 10.7) must be performed. The ICV results must be within the acceptance criteria as established for the CCV compounds (Section 13.3). Other components should be be recovered within 85 to 115% of the true value.

13.2.9

1. All calibration curves must have a unique identifier. The calibration date is incorporated into the method identifier for easy reference.
2. All initial calibration standards must be analyzed within the 12-hour BFB tune verification window.
3. Calibration must be completed (all standard levels analyzed) within 36 hours or the entire calibration sequence must be repeated. If the calibration was not completed in the first tune window it may continue into a second tune window. Standard calibration levels from either tune window can be used. An exception follows: If BFB criteria does not pass criteria for the second tune window and major maintenance was done to the instrument or the Mass Spec tuning parameters were adjusted in order to obtain an acceptable tune for BFB, the entire calibration sequence must be repeated.
4. All initial calibration standards must be analyzed and verified prior to field sample analyses.
5. Do not add calibration standards and update the curve after the original calibration date.
6. Multiple analyses of the same calibration level are not allowed to be included in the calibration curve.
7. Compound responses cannot be selected from different analyses of the same calibration level (i.e. all compound responses for level 1 must come from the same data file), except for bromomethane and/or chloroethane, see Section 10.4.4.
8. If more than five calibration levels are analyzed, it is permissible to either drop the low compound concentration (poor response) or the high compound concentration (detector saturation). Do not drop a point in the middle of the curve, unless as discussed in Item 9.
9. If more than five calibration levels are analyzed, it is permissible to drop an entire level if the analyst can document a specific reason or reasons why that level should be excluded. Mechanical failures, significant loss of all compound responses possibly due to poor technique in standard preparation, or software malfunction during data acquisition (system did not acquire all compound data) are plausible reasons. The reason must be justified and documented. The supervisor should review this situation and approve the analyst's decision.
10. The need to analyze more than two analyses of the same calibration level indicates a potential problem with the Working Standard solution. Prepare a fresh Working Standard solution and repeat all five-calibration levels. All calibration standard levels must come from the same Working Standard solution.
11. Manual integration must only be used if the software fails to properly integrate the peak (See SOP 1255 Manual Integration). If manual integration is used for a particular compound, all levels of that compound do not have to be manually integrated. Example: the computer generated integration of a compound in the low level standard is not technically sound. A manual integration of the compound is performed (due to baseline noise, etc) in order to achieve a technically sound integration. Other levels of the compound are integrated correctly by the computer. The manual integration of the low level must match, as best as possible, the computer generated integrations for all other levels.
12. If any compound in the mid-point level is manually integrated, the integration of this compound must be reviewed for every continuing calibration standard and QC check solution (i.e. LCS, and Matrix Spike) to ensure that the integration is the same as the manual integration performed in the initial calibration (ICAL) mid-point. A consistent manner of integration must be achieved.

13. All manual integrations must be reviewed and approved according to SOP 1255 Manual Integration.

13.3 Continuing Calibration Verification (CCV)

13.3.1 The mass spec must pass tune criteria (see Section 13.1) every 12 hours during analysis of samples.

13.3.2 A continuing calibration verification (CCV) sample is analyzed every 12 hours during analysis of samples. Different standards are analyzed for the CCV such that a wider range of the calibration curve is verified. For example: on successive days analyze the 50 µg/L and the next day the 100 µg/L standard solution. Compare the response factors, of the SPCCs and the CCCs, and the internal standards from the CCV with the following criteria.

13.3.3 The SPCC compounds must meet the minimum criteria as stated in Section 13.2.3.

13.3.4 Control limits for the CCC compounds are ± 20% difference from the ICAL Response Factor (RF) if the average RF is used for quantitation, or ± 20% drift from the true concentration of the CCV compound if linear regression is used.

13.3.5 The areas of the internal standards in the CCV must be between –50% and +100% of the respective areas of the internal standards in the ICAL mid-point calibration standard.

13.3.6 The retention times of the internal standards in the CCV must be within ± 30 seconds of the respective retention times of the internal standards in the ICAL mid-point calibration standard.

13.3.7 If the CCV results obtained are outside the acceptance criteria, corrective actions must be performed. If routine corrective actions fail to produce an acceptable *second consecutive (immediate)* CCV, then either the lab has to demonstrate performance after corrective action with two consecutive successful CCVs, or a new ICAL must be performed. If the instrument has not demonstrated acceptable performance, sample analyses cannot continue until a new ICAL is established and verified with an ICV. However, sample data associated with an unacceptable CCV may be reported as qualified data under the following special conditions:

13.3.7.1 When the acceptance criteria for CCV are exceeded high, i.e., high bias, and there are associated samples that are non-detects, then those non-detects may be reported. Otherwise the samples affected by the unacceptable calibration verification must be reanalyzed after a new ICAL has been established, evaluated and accepted.

13.3.7.2 When the acceptance criteria for the CCV are exceeded low, i.e., low bias, those sample results may be reported if they exceed a maximum regulatory limit/decision level. Otherwise the samples affected by the unacceptable verification must be reanalyzed after a new ICAL is established and verified with an ICV.

13.3.7.3 When the acceptance criteria for the CCV are exceeded and it is not possible to reanalyze the sample due to limited sample quantity AND a new sample cannot be obtained by the laboratory, the data may be reported with the appropriate data qualifiers if the client has been contacted and agrees, in writing, to accept the qualified data.

13.4 Records: Initial and Continuing Calibration Records will contain, at a minimum, the following:

1) Calibration date
2) Test method
3) Instrument
4) Analysis date
5) Each compound name
6) Analyst's initials or signature
7) Standard Concentration (appropriate units) and number of standards
8) Response (appropriate units)
9) Calibration curve or response factor
10) Evaluation of and Statistics for ICAL curve fit in order to judge calibration curve acceptance
11) Evaluation of and Acceptance Limits for ICV analysis in order to judge calibration curve acceptance
12) Evaluation of and Acceptance Limits for CCV analysis in order to judge continuing calibration acceptance

13.5 Thermometers - The thermometers in the sample refrigerators and the standards freezer must be checked daily. They must meet performance criteria. Check the thermometer to ensure the calibration is not expired (see SOP 1040 General Laboratory Practices).

13.6 Balances - Be sure the balance is checked prior to use and performance criteria are met (see SOP 1040 General Laboratory Practices).

14. PROCEDURE

14.1 Sample Preparation

14.1.1 Samples are removed from the refrigerator and placed in the Archon autosampler. The samples are allowed to warm to ambient temperature prior to analysis. All standards, method blanks, and QC solutions (made from the same reagent water) are prepared in 40 mL VOA vials and put in the Archon.

14.1.2 Samples are prepared for analysis by using a Purge and Trap. If the trap is new, condition it by purging it with Helium at 40ml/min for 30 minutes at room temperature followed by a bake at 270°C in the bake mode with Helium flow of 40 mL/min.

14.1.3 Purge and Trap Conditions:

Purge and Trap operating conditions	
Purge Ready Temp	30°C
Sample Size	5 mL
Purge Time	11 minutes
Purge Flow	40 mL/min
Dry Purge Time	5 minutes
Pre-heat Temp	245°C
Desorb Temp	250°C
Desorb Time	2 minutes
Bake Temp	260°C
Bake Time	7 minutes
Transfer Line Temp.	250°C
Purge Gas	UHP Helium

14.1.4 Check the Internal Standards/Surrogate Solution reservoir to ensure that enough solution is present. One (1) microliter of this solution is added automatically to the 5 mL (or 25mL) water sample aliquot as it transfers to the 5 ml (or 25 ml) purging vessel. Soils samples are treated similarly except they are purged directly in the 40 ml VOA vial without opening. Five (5) ml of reagent water is added to transfer the one (1) microliter of internal standard/surrogate solution to the sample vial.

14.2 GC/MS Analysis

14.2.1 GC/MS Conditions:

GC/MS operating conditions	
EMV	1300-2500
Mass Range	35-300
Scan Sampling Rate	2^2
Initial Column Temp.	40°C
Initial Temp Holding Time	4 minutes
Ramp 1 Temp Program	10°C/minute
Ramp 1 Final Column Temp.	230°C
Ramp 1 Holding Time	5 minutes
Injector Temp.	220°C
Source Temp.	250°C
Transfer Line Temp.	250°C
Split Ratio	50:1
Carrier Gas	UHP Helium

14.2.2 Access the computer and create a batch sequence file by following Section 14.3.

14.2.3 Using a 10µL syringe, inject 2 µL of BFB tuning standard solution directly on to the column (50 ng on column). Analyze using the BFB method. Evaluate using the tune acceptance criteria (See Section 13.1).

14.2.4 Analyze the Continuing Calibration Verification Standard (CCV) and evaluate using CCV acceptance criteria (See Section 13.3).

14.2.5 Analyze the Method Blank. The method blank must contain less than the reporting level for all target compounds. If target parameters achieve these limits, recovery and retention times of the surrogate compounds are within acceptance limits, and the chromatography (baseline noise and compound tailing) is acceptable, continue the analysis. If any one of these criteria is not met, take appropriate corrective action to identify and correct the problem.

14.2.6 Analyze the Laboratory Control Sample (in duplicate if a Matrix Spike/Matrix Spike Duplicate is not analyzed). Recovery (and RPD) must meet criteria specified in section 18.2.

14.2.7 If all criteria are met, continue with sample analysis as outlined below.

14.2.8 Water samples – a 5 mL (or 25mL) water sample aliquot is transferred to the 5 ml (or 25ml) purging vessel. One (1) microliter of Internal Standards/Surrogate Solution is added automatically to the 5 mL (or 25ml) water sample aliquot as it transfers to the 5 ml (or 25ml) purging vessel.

14.2.9 Soil samples: - VOA soil samples are prepared for analysis in the field with pre-preserved and pre-weighed 40 ml VOA Vial (5035 Kit). These vials are post-weighed and the sample amount is determined by the difference between post-weight and pre-weight. The weight is recorded in the VOA Soil Sample Prep Logbook and in the Prep Batch in LIMS (sees SOP 1400 LIMS). Each VOC sub-sample is assigned its own unique Prep Batch. Three (3) EnCore samples (or equivalent) are usually collected for each sampling point and are placed in a tared 40 ml Vial with stir bar. The entire EnCore (or equivalent) soil sample is placed in the 40 ml VOA vial with the use of the extrusion tool (in cases where the sample collector has provided one 5 gm EnCore and one 25 gm Encore, the initial analysis is performed using the 5 gm EnCore and re-analysis and/or dilutions are performed using the 25 gm EnCore). The vial is weighed and recorded in the VOA Soil Sample Prep Logbook and the Prep Batch in LIMS (see SOP 1400 LIMS). Soil samples received in jars are also prepared into tared 40 ml VOA vials in a similar manner with care taken to minimize exposure of the sample to the environment (these samples are always reported without mention of Method 5035). The type of VOC collection device is recorded with the sample weights (5035 Kit, EnCore, or Jars). The sample of known weight is placed in the Archon autosampler and five (5) ml of reagent water is added to transfer the one (1) microliter of internal standard/surrogate solution to the sample vial. Medium level analysis is performed upon samples preserved in 5 ml or 10 ml (P&T) methanol. The volume of P&T methanol is noted. Aliquots of methanol are removed as appropriate; a 100 µL aliquot of methanol extract is the largest aliquot that can be analyzed as methanol may affect the system chemistry.

14.2.10 If the response for any quantitation ion exceeds the initial calibration curve range of the GC/MS system, sample dilution and reanalysis is an option. If sample dilution is required for water samples, the sample is diluted using the following procedure: A 50 mL volumetric flask is filled with reagent water close to the mark. A 5 mL syringe is filled with sample from a second (intact) 40 mL VOA vial. An appropriate amount of sample (minimum 1 mL) is injected into the flask, the solution is brought to volume with water and capped. The flask is gently inverted three times to mix the diluted sample. The contents of the neck portion of the flask are discarded prior to taking an aliquot. The diluted solution from the volumetric flask is gently decanted into an individual 40 mL VOA vial until the vial is filled to almost overflowing. The screw cap with Teflon faced septum is carefully placed on the vial; no air bubbles are trapped in solution. The VOA vial is placed in the Archon for analysis. If sample dilution is required for soil samples, the sample is diluted using the following procedure: Using microliter syringes, an appropriate amount of methanol extract (minimum 5.0 uL) is removed from sample preserved with methanol, and is injected into a 40ml VOA vial containing a stir bar and 5ml of reagent water. The VOA vial is placed in the Archon autosampler for analysis. Note: Some soil samples will be reported with an "E" (exceeded the calibration range on the undiluted analysis and reported with a "J" value on the diluted analysis. The "E" value is reported and a Quality Control Exception Report is generated and delivered to the project manager.

14.2.11 Perform all qualitative and quantitative measurements as described in Sections 14.4 and 14.5. After water (5030) analysis, check the sample pH using the pH strips and record the result. Used vials are kept for 14 days in VOC room and then disposed according to SOP 1330 Waste Disposal.

14.3 Analytical Sequence

START CHEMSTATION SOFTWARE:

From NT Desktop: Start/Programs/MSD ChemStation/Instrument #1/Instrument #1

The software will locate the instrument and all peripheral equipment. Once the software is fully loaded there will be two windows visible. Window one is the instrument control window. Instrument parameters are readily viewed from this window. The second window is the sequence control window. No instrument parameters are viewable from this window.

SEQUENCE SETUP

From menu: Sequence/Load

1. Load the method you want to use for analysis (soil/water)
2. OK (to save changes)

From menu: Sequence/Run

3. Set current date in Data File Directory space (ie., C:\MSDCHEM\1\DATA\060702\)
4. OK (to save changes)

From menu: Sequence/Edit Sample Log Table

1. Set data file name using current date using the following format MMDDYY## (ie., 06070201)
2. Set up sequence order using the following format: (**NOTE:** Tune and CCV must always run first)

LINE	TYPE	VIAL	DATA FILE	METHOD	SAMPLE NAME-INSTRUMENT
1	Sample	100	11240201	BFBS	TUNE VBFB112402-1
2	Sample	1	11240202	S1121002	CCV VSTD050
3	Sample	2	11240203	S1121002	MBLK VBLK112402-1
4	Sample	3	11240204	S1121002	LCS VLCS112402-1
5	Sample	4	11240205	S1121002	SAMP ##########
6	Sample	5	11240206	S1121002	SAMP ##########
7	Sample	6	11240207	S1121002	SAMP ##########

NOTE: The number of samples, including tune and CCV that can be analyzed within the 12 hour window varies with each analysis. Use this list as a guide but always check that the samples were analyzed within 12 hours of the BFB injection.

3. OK (to save changes)

From menu: Method/Set New Default Paths

1. Update the method and data file paths using the current date (ie., C:\MSDCHEM\1\DATA\060702\)
2. OK (to save changes)

Using Windows Explorer copy all of the method files from the previous day's folder into the current day's folder. Note: After each ICAL, the water/soil method is saved using the following format: matrixinstrumentMMDDYYof last ICAL (ie., S1121002).

TO START SEQUENCE:

From menu: Sequence/Run/Run Sequence

Start of the 12 hour sequence (as documented as the date/time stamp on the data file for the Tune Standard):

The analytical sequence for Initial Calibration is:

BFB (Tune Standard)
Calibration standard (S1)
Calibration standard (S2)
Calibration standard (S3)

Calibration standard (S4)
Calibration standard (S5)
Calibration standard (S6) optional
Calibration standard (S7) optional
Initial Calibration Verification Standard (ICV)
Method Blank (MBLK)

The analytical sequence for Sample Analysis is:

BFB
Continuing Calibration Verification Standard (CCV)
Method Blank (MBLK)
LCS
(LCS Duplicate optional)
Sample #1
Sample #1 Matrix Spike (MS)
Sample #1 Matrix Spike Duplicate (MSD)
Sample #1 Laboratory Duplicate (optional)
Samples #2, #3, etc. until the end of 12 hour tune period

14.4 Data Interpretation - Qualitative Analysis

14.4.1 An compound is identified based upon Relative Retention Time (RRT) and by comparison of the sample mass ions with the mass ions of a standard of the suspected compound (standard reference ions). The reference mass ion ratio must be generated by the laboratory using the conditions of this method. The characteristic ions from the reference mass ion are defined to be the two or three ions of greatest relative intensity. See Attachment 2 for the ions to be monitored. Two criteria must be satisfied to verify identification: (1) elution of sample component at the same GC relative retention time (RRT) as those of the standard component; and (2) correspondence of the sample component and the standard component mass ions. Intensities of the characteristic ions must maximize in the same scan or within one scan of each other.

14.4.2 The RRT of the sample component is within ± 0.06 RRT units of the RRT of the standard component.

14.4.3 The relative intensities of the characteristic ions must agree within 20% of the relative intensities of these ions in the reference spectrum. (example: For an ion abundance of 50% in the reference, the corresponding abundance in a sample spectrum can range between 30% and 70%.)

14.4.4 Structural isomers that produce very similar mass spectra must be identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs. The Manual Integration SOP 1255 is used for guidance in the integration of these two peaks and for other situations that may require analyst efforts to correct computer generated integrations that are not technically sound.

14.4.5 Identification is hampered when sample components are not resolved chromatographically or co-elute and produce mass spectra containing ions contributed by more than one compound. When gas chromatographic peaks obviously represent more than one sample component (i.e., a broadened peak with shoulder(s) or a valley between two or more maxima), appropriate selection of compound spectra and background spectra is important. Examination of extracted ion current profiles of appropriate ions can aid in the selection of spectra, and in qualitative identification of compounds, but each compound spectrum will contain extraneous ions contributed by the coeluting compound.

14.4.6 For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the purpose of the analyses being conducted. Computer generated library search routines must not use normalization routines that would misrepresent the library or unknown spectra when compared to each other. Only after visual comparison of sample spectra with the nearest library searches will the mass spectral interpretation specialist assign a tentative identification. Guidelines for making tentative identification are:

14.4.6.1 Relative intensities of major ions in the reference spectrum (ions >10% of the most abundant ion) must be present in the sample spectrum.

14.4.6.2 The relative intensities of the major ions must agree within ± 20%. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30 and 70%).

14.4.6.3 Molecular ions present in the reference spectrum must be present in the sample spectrum.

14.4.6.4 Ions present in the sample spectrum but not in the reference spectrum must be reviewed for possible background contamination or presence of coeluting compounds.

14.4.6.5 Ions present in the reference spectrum but not in the sample spectrum must be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks. Data system library reduction programs can sometimes create these discrepancies.

14.5 Data Interpretation - Quantitative Analysis

14.5.1 Once a compound has been identified, the quantitation of that compound must be based on the integrated abundance from the EICP of the primary characteristic ion. The internal standard used shall be the one nearest the retention time of that of a given compound.

14.5.2 If the RSD of a compound's response factors is 15% or less, then the concentration in the sample is determined using the average response factor (RF) from initial calibration data (13.2). See Method 8000, Sec. 7.0, for the equations describing internal standard calibration and either linear or non-linear calibrations.

14.5.3 Where applicable or required, the concentration of any non-target compounds (TICs) identified in the sample are estimated. The same formulae must be used with the following modifications: The areas A_x and A_{is} must be from the total ion chromatograms, and the RF for the compound must be assumed to be 1. The resulting concentration must be reported indicating: (1) that the value is an estimate, and (2) which internal standard was used to determine concentration. Use the nearest internal standard free of interferences.

14.6 Record the following information in the appropriate logbook or data file. Include any deviations from this procedure. Analyst initials, date of analysis, sample number or ID, initial sample volume or weight processed, calibration standard sample or solution identifier, QC sample or solution identifier, surrogate solution identifier, internal standard solution identifier, any dilution information, readings from support equipment, data file name, instrument method name, visual observations, and any other information as deemed necessary.

14.7 Troubleshooting - The experience of the analyst performing GC/MS analyses is invaluable to the success of the methods. Each day that the analysis is performed, the daily calibration standard (CCV) must be evaluated to determine if the chromatographic system is operating properly. Questions that must be asked: Do the peaks look normal? Is the response obtained comparable to the response from previous calibrations? Careful examination of the standard chromatogram can indicate whether the column is still good, the injector is leaking, the injector septum needs replacing, etc. If any major changes are made to the system (e.g. column changed or detector cleaned), recalibration of the system must take place.

14.8 Routine Maintenance - Record all maintenance, including the problem encountered, steps taken to correct the problem, and verification that the problem has been corrected (i.e. tune passed).

14.8.1 Change the septum and or the injection port liner as needed according to sample throughput. Trim a short section from the analytical column as necessary.

14.8.2 Clean the source on an as needed basis (loss of sensitivity).

14.8.3 Inspect the Archon autosampler, perform routine maintenance as necessary. Refill the standard reservoir of the autosampler with Internal Standards/Surrogate solution as needed according to sample throughput. Check Helium purge flow, clean the vial gripper, clean soil purge needle, and recalibrate as necessary.

14.8.4 Check the carrier gas supply; replace as necessary, record carrier gas change in the maintenance log book.

15. DATA REDUCTIONS, CALCULATIONS, AND LOADING

15.1 The data system performs the calculations.

15.1.1 If the %RSD of a compound's relative response factor is 15% or less, then the concentration in the sample may be determined using the average response factor (RF) from the initial calibration data (13.2) and the following equation. The equation is based upon all sample sizes equivalent to either 5 ml or 5 gram.

$$\text{Concentration } (\mu g/L \text{ or } \mu g/Kg) = \frac{A_x * C_{is} * D}{A_{is} * RF}$$

where:

A_x = Area of the characteristic ion for the compound being measured
C_{is} = Concentration of the specific internal standard (50 µg/L for this method)
A_{is}= Area of the characteristic ion for the specific internal standard
RF= average response factor for compound being measured
D = Dilution factor if dilutions are made

If another sample weight is analyzed, adjust the concentration using the factor: 5g / initial weight g

15.1.2 Alternatively, linear regression (Sec. 13.2) is used for determination of the sample concentration.

In calculating sample concentrations (C_s) by the internal standard method, the equation to be used is as follows:

$$Cs = [\{A_s \times C_{is}/A_{is}\}-b]/ a$$

Where:

A_s = Area (or height) of the peak for the target analyte in the sample

A_{is} = Area (or height) of the peak for the internal standard

C_{is} = Concentration of the internal standard

a = Slope of the linear regression

b = The intercept

15.2 If appropriate, recalculate the concentration of the compound in the sample using the equations in Secs. 15.2.1, 15.2.2, and 15.2.3.

15.2.1 The concentration of the compound in the sample is reported as µg/L or µg/Kg. If conversion to mg/L or mg/Kg is required, calculate as follows:

$$\text{Concentration (mg/L or mg/Kg)} = \frac{\text{Conc (µg/L or µg/Kg)} * D}{1000}$$

15.2.2 For soil samples reported on dry weight basis, divide the concentration by the decimal equivalent of the Percent Solids. For example: a sample contains 90% solids, thus

$$\text{Concentration (µg/Kg or mg/Kg) dry weight} = \frac{\text{Conc (µg/Kg or mg/Kg)}}{0.90}$$

15.2.3 If an aliquot of a methanol extract was analyzed, calculate as follows:

$$\text{Concentration in sample (mg/Kg)} = \frac{\text{Conc (µg/L readout)} * 5 * V_{ex}}{W_i * V_a}$$

V_a = amount of methanol extract analyzed in µL
V_{ex} = total extract volume of methanol in mL
W_i = initial sample weight in g

15.3 The procedure for uploading data into the LIMS system is detailed in SOP 1400 LIMS.

16. METHOD PERFORMANCE

16.1 Demonstration of Capability (DOC)

All parameters of interest must meet the method acceptance criteria before actual sample analysis begins. See SOP 1230 Training for the procedure to perform and document the DOC. The DOCs for the analysts performing this method are located in the analysts' training form folders located in the QA office files.

A quality control (QC) reference concentrate in methanol is required containing each compound at a concentration of 10 µg/L to 200 µg/L. The QC reference sample used is the LCS solution (see Section 10.7). The QC reference sample is made using stock standards prepared independently from those used for calibration. This analysis is

performed in quadruplicate. For each analyte calculate the mean recovery (X), standard deviation (s) and average % Recovery (%R). Water and soil recovery must be between 70 to 130%.

Continuing Demonstration of Capability will be documented with the use of PT sample results and four consecutive Laboratory Control Samples (LCS). This must be documented annually.

16.2 Comparison to Reference Method Data

EPA Method 8000B provides guidance for the establishment of control limits for the LCS and MS QC samples. Recovery limits of 70% to 130% are provided as initial benchmarks for performance (8000B Section 8.5.4). These limits are designed for a wide variety of organic test methods. Individual compound performance may vary.

16.3 In-House Control Limits

Method performance data is on file in the laboratory QC department. Comparison of method performance data for the laboratory to the reference method criteria occurs when laboratory in-house acceptance limits are generated. In-house generated data is compared to the specifications of the reference method. If the in-house limits are within the specifications of the reference method, the control limits are updated in LIMS. If the in-house limits are not within specifications, an investigation is performed to determine the cause(s) of the problem and a corrective action is completed. The analysis may continue until enough data points are collected to regenerate new control limits. Any QC data generated outside of reference method limits during that time frame is flagged.

The laboratory maintains performance records to document the quality of data that is generated. Method accuracy for samples is assessed and records maintained. After the analysis of at least 20 laboratory control samples and surrogates, calculate the average percent recovery (R) and the standard deviation of the percent recovery (S).

Control limits for method parameters are generated by the QC staff generates the method parameters and distributed to the analysts via updates to the LIMS control charts. The control limits are calculated based on in-house performance data. At a minimum, these limits are reviewed annually.

17. POLLUTION PREVENTION

The preparation of excessive volumes of laboratory reagents and standards shall be avoided so that waste and potential for pollution are minimized. Samples, reagents and standards shall be disposed in compliance with the lab waste disposal program, SOP 1130. With the consent of the client, the samples may be returned to their origin for treatment.

Uncontaminated paper waste, glass and cans should be separated for recycling. Laboratory staff are required to protect the laboratory's and our clients' business information when disposing of recycled paper or waste from the facility.

18. DATA ASSESSMENT AND CRITERIA FOR QUALITY CONTROL MEASURES

Data assessment includes review of: proper sample condition, preservation, and storage; analysis within holding time limitations; deviations from the SOP, evaluation of performance based or in-house control limits, reference method limits or project specific limits.

The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When results of sample spikes indicate atypical method performance, a calibration verification standard is used to confirm the measurements were performed in an in-control mode of operation. The data review is conducted according to SOP 1250 Data Review.

18.1 Blanks

The method blank must contain less than reporting level for all target compounds. If the blank exceeds these limits, the source of contamination must be investigated and corrective actions taken. Re-analyze the method blank. If after re-analysis, the blank criteria is still exceeded, stop the analysis prior to sample analyses and correct the problem. Consult with the department manager for guidance. Refer to a client specific QAPP for additional guidance, if applicable.

If samples were analyzed with a contaminated method blank during unattended automated analysis, affected samples must be reanalyzed or data must be appropriately qualified if:

1) The concentration of a targeted compound in the blank is at or above the reporting limit as established by the SOP or by regulation, AND is greater than 1/10 of the amount measured in any sample.

2) The blank contamination otherwise affects the sample results as per the test method requirements or the individual project data quality objectives.

18.2 Laboratory Control Samples (LCS)

The results of the individual batch LCS are calculated in percent recovery (%R) and compared to established acceptance criteria. Current acceptance criteria used are 70 - 130% (SW-846 8000B Section 8.5.4) and 50-150% for water soluble compounds, until in-house LCS limits for both soils and waters are developed. If LCS Duplicate (LCSD) is performed, recovery limits must be met and the Relative Percent Difference (RPD) see the STAT QAM, Section 5.4 for the calculation for RPD, must be less than 20%. If the LCS is outside the acceptance criteria the analytical system is "out of control". Any affected samples associated with an out of control LCS must be reprocessed and reanalyzed or the results reported with appropriate data qualifiers. If after re-analysis the control criteria has not been met, the entire analysis batch must be re-analyzed. Always refer to a client specific QAPP for additional guidance.

18.3 Surrogates

18.3.1 The results of the individual Surrogate compounds are calculated in percent recovery (%R) and are compared to established acceptance criteria derived from in house generated control limits, see Attachment 3. Water Surrogate Recovery Limits are per Method 8260B. Soil Surrogate Recovery Limits are based on in house control limits due to the high clay content of Northeastern Illinois soils. Surrogates outside the acceptance criteria must be re-analyzed to determine matrix effect. Separate Soil Surrogate Recovery Limits are generated for samples preserved with sodium bisulfate as this acid has a destructive matrix effect (excessive CO_2 generation, reduction of metals to the elemental state, carbon dilsulfide and sulfur dioxide generation) using this preservative.

If surrogate recoveries are not within the established acceptance criteria, proceed as follows (SW-846 8000B):

1) Check to be sure that there are no errors in the calculations, surrogate solutions or internal standards. If errors are found, recalculate the data accordingly. Examine chromatograms for interfering peaks and integrated peak areas.

2) Check instrument performance. If an instrument performance problem is identified, correct the problem and re-analyze the sample.

3) If no instrument problem is found and if sufficient sample is available, the sample should be re-analyzed.

18.3.2 If, upon re-analysis (in either 2 or 3 above), the recovery is again not within limits, generate a Quality Exception Report (QER) as referenced in SOP 230 Corrective Action. If the recovery is within the limits in the re-analysis, provide the re-analysis data to the data user. If the holding time for the method has expired prior to the re-analysis, provide both the original and reanalysis results to the data user, and note the holding time problem.

18.4 Duplicates

The results from laboratory Duplicates are designed to assess the precision of analytical results in a given matrix and are expressed as relative percent difference (RPD). See the STAT QAM, Section 5.4 for the calculation for RPD. Results are compared to established acceptance criteria as listed in the MS/MSD Attachment 4. For duplicates results outside established criteria corrective action must be documented or the data reported with appropriate data qualifying codes.

For this test method, the analysis of the MS/MSD pair is used for determination of method precision. Duplicate LCS samples will be analyzed for all matrices where it would be impractical to perform a MS/MSD, such as wipe samples. Precision data from 18.2 will be used for RPD acceptance criteria for LCS/LCSD.

18.5 Matrix Spikes

18.5.1 The results from MS/MSD are primarily designed to assess the precision and accuracy of analytical results in a given matrix and are expressed as percent recovery (%R) and relative percent difference (RPD). See the STAT QAM, Section 5.4 for the calculation for RPD. Sixteen compounds are listed in Attachment 4 for in house generated recovery and RPD control limits. Results are compared to established acceptance criteria derived from in house generated control limits. Note: SW846 Method 8000B mandates that RPD's be calculated based on concentration rather than % recovery. VOC soils have widely varied samples weights due to EnCore/5035 preservations. This will lead to very broad RPD control limits. For matrix spike results outside established criteria corrective action must be documented or the data reported with appropriate data qualifying codes.

18.6 Internal Standards

The results of the individual Internal Standard compounds on all samples, blanks, and spikes are calculated in percent recovery (%R) and are compared to established acceptance criteria. If the Internal Standard recovery is outside the acceptance criteria, see Table 6, corrective action may be taken. Note: the recovery of internal standards in these samples within the stated limits is not mandatory per the reference method, 8260B. It can be a useful diagnostic tool. Client specific project criteria may require the adherence to these limits. If so, then corrective action must be documented or the data reported with appropriate data qualifying codes.

Table 6 Internal Standards

INTERNAL STD COMPOUND	CRITERIA (%)
Chlorobenzene-d_5	-50 to +200
Pentafluorobenzene	-50 to +200
1,4-Dichlorobenzene-d_4	-50 to +200
1,4-Difluorobenzene	-50 to +200

18.6 Other

The laboratory will analyze standard reference materials and/or participate in relevant performance evaluation studies quarterly.

19 CORRECTIVE ACTIONS FOR OUT-OF-CONTROL DATA

The process for handling unacceptable and out of control data is found in SOP 230 Corrective Action.

If the CCV, MB, LCS/LCSD, MS/MSD, lab duplicate, surrogate, or internal standard recovery of any parameter falls outside the designated acceptance range, the laboratory performance for that parameter is judged to be out of control, and the problem must be immediately identified and corrected. The analytical result for that parameter in the samples is suspect and is only reported for regulatory compliance purposes with the appropriate corrective action form. Immediate corrective action includes reanalyzing all affected samples by using any retained sample before the expiration of the holding time. Final data results must be qualified in the client report for reported results not meeting the laboratory defined criteria.

1) Review standards preparation logbooks. Check all calculations and ensure dilution factors are properly recorded.
2) Re-prepare the suspected standard or QC sample to identify possible preparation errors of the standard or QC sample.
3) Re-Analyze the samples when the CCV or LCS are not within acceptable limits.
4) Perform routine preventative maintenance following manufacturer's specification. Record all maintenance in the instrument logbook.

20 CONTINGENCIES FOR HANDLING OUT-OF-CONTROL OR UNACCEPTABLE DATA

Every effort is made to prevent problems from occurring. When out of control or unacceptable data occurs the first option is to identify the problem and reanalyze the samples within the holding times. When this is not possible, the QA Manager and/or the Laboratory Director reviews data and discusses options with the client. Reanalysis or reporting the data with qualification are alternatives. Out of control or unacceptable data reported to the client must include the data qualifier, flag and discussion on the rationale for reporting.

Holding time exceedence, improper preservation and improper sample condition or storage are noted on the corrective action form and included on the final report.

Review the CCV standard response, LCS result, surrogate recovery, and internal standard recovery for acceptable performance for each batch of samples. Record any trends or unusual performance on a corrective action form. Final data results must be qualified in the client report for results not meeting the laboratory defined criteria.

Manual integration must be minimized for standards, reagent blanks and surrogates. Routine manual integration of the same parameters indicates a system performance problem. Correct this problem or note in the instrument analysis logbook the suspected causes for routine manual integration. Sign and date all manually integrated chromatograms.

20.1 The process for handling unacceptable and out of control data is found in the Laboratory QAM Section 11. The reporting of data that is out of control must be approved and documented by Quality Assurance Manager and either the Technical Manager or the Laboratory Director.

20.2 Client Requested Modifications:

20.2.1 Clients must request modifications from the laboratory SOP in writing to the lab.

20.2.2 The lab director, technical manager and quality assurance manager will evaluate the requested client deviations, determine the feasibly of the deviation and the potential effects on the data.

20.2.3If it is determined that the lab will perform the requested deviations, lab director, technical manager and quality assurance manager will decide if a method validation study is required.

20.2.4The designated project manager will retain all documentation concerning the requested deviation, including all correspondence with the client, in the client folder.

20.2.5The final analytical report must include the statement "*This report has analyses performed using client requested modifications* ".

21 WASTE MANAGEMENT

The STAT Analysis Corporation Waste Disposal SOP 1130 identifies proper waste management practices for the chemicals and biological materials used in this procedure. Samples are stored and discarded accordance with SOP 1130 Waste Disposal.

22 REFERENCES

22.1 Method 8260B, Revision 2; Method 5030B, Revision 2; Method 5035 Revision 0, Method 5035A. U.S. EPA SW-846 "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods" Update III, December 1996 and July 2002.
22.2 STAT SOPs: 1210 [support equipment, recordkeeping, MDLs, etc]
22.3 SOP 230 Corrective Actions
22.4 SOP 1010 Standard and Reagent Preparation
22.5 SOP 1400 LIMS
22.6 SOP 1130 Waste Disposal
22.7 SOP 003 Chemical Hygiene Plan
22.8 SOP 1250 Data Review
22.9 Manufacturers' Equipment Instruction Manuals
22.10 SOP 1255 Manual Integration
22.11 SW-846 8000B Determinative Chromatographic Separations
22.12 SOP 1230 Training
22.13 "USEPA Contract Laboratory Program Statement of Work for Organic Analysis" Revision OLM04.2 May 1999, U. S. Environmental Protection Agency. Office of Solid Waste, Washington DC 20460.
22.14 NIST Library of Reference Spectra, 1998

23 FORMS, FIGURES, TABLES, DIAGRAMS, FLOWCHARTS, ATTACHMENTS OR VALIDATION DATA

Attachment 1
MDLs and REPORTING LIMITS FOR VOLATILE COMPOUNDS

CASN	Compound name	MDL (µg/L)	RL (µg/L)	RL (mg/L)	MDL (µg/Kg)	RL (µg/Kg)	RL (mg/Kg)
75-71-8	Dichlorodifluoromethane	0.2	10	0.01	0.1	10	0.01
75-01-4	Vinyl Chloride	0.2	5	0.005	0.1	5	0.005
74-87-3	Chloromethane	0.3	10	0.01	0.1	10	0.01
106-99-0	1,3-Butadiene	0.3	10	0.01	0.2	10	0.01
74-83-9	Bromomethane	0.6	10	0.01	0.3	10	0.01
75-00-3	Chloroethane	0.4	10	0.01	0.2	10	0.01
75-69-4	Trichlorofluoromethane	0.3	5	0.01	0.1	5	0.005
67-63-0	Isopropyl alcohol	39	400	0.4	55	400	0.4
67-64-1	Acetone	4.3	10	0.01	5.7	25	0.025
60297	Ethyl ether	0.4	50	0.05	0.2	50	0.05
76-13-1	Freon-TF	0.2	5	0.005	0.1	5	0.005
107925	Acrolein	1.6	50	0.05	2.9	50	0.05
75-35-4	1,1-Dichloroethene	0.2	5	0.005	0.1	5	0.005
75-15-0	Carbon Disulfide	0.3	5	0.005	0.1	5	0.005
75-09-2	Methylene Chloride	0.3	5	0.005	0.1	10	0.01
107131	Acrylonitrile	1.7	5	0.005	2.0	5	0.005
1634-04-4	MTBE	0.4	5	0.005	0.1	5	0.005
110-54-3	Hexane	0.3	5	0.005	0.1	5	0.005
156-60-5	trans-1,2-Dichloroethene	0.3	5	0.005	0.1	5	0.005
108-05-4	Vinyl acetate	0.4	10	0.01	1.5	10	0.01
75-34-3	1,1-Dichloroethane	0.2	5	0.005	0.1	5	0.005
78-93-3	2-Butanone	3.0	10	0.01	3.0	10	0.01
78-87-5	2,2-Dichloropropane	0.2	5	0.005	0.2	5	0.005
156-59-2	cis-1,2-Dichloroethene	0.3	5	0.005	0.1	5	0.005
67-66-3	Chloroform	0.3	5	0.005	0.1	5	0.005
78-83-1	Isobutyl alcohol	87	400	0.4	59	400	0.4
74-97-5	Bromochloromethane	0.2	5	0.005	0.2	5	0.005
141-78-6	Ethyl acetate	1.9	50	0.05	4.1	50	0.05
71-55-6	1,1,1-Trichloroethane	0.2	5	0.005	0.1	5	0.005
71-36-3	1-Butanol	55	400	0.400	69	400	0.4
563-58-6	1,1-Dichloropropene	0.3	5	0.005	0.1	5	0.005
56-23-5	Carbon Tetrachloride	0.3	5	0.005	0.1	5	0.005
107-06-2	1,2-Dichloroethane	0.2	5	0.005	0.1	5	0.005
71-43-2	Benzene	0.2	5	0.005	0.1	5	0.005
79-46-9	2-Nitropropane	1.6	50	0.05	2.9	50	0.05
74-95-3	Dibromomethane	0.1	5	0.005	0.3	5	0.005
79-01-6	Trichloroethene	0.2	5	0.005	0.1	5	0.005
78-87-5	1,2-Dichloropropane	0.3	5	0.005	0.1	5	0.005
107-06-2	1,4-Dioxane	50	200	0.2	33	200	0.2
75-27-4	Bromodichloromethane	0.3	5	0.005	0.2	5	0.005
110-75-8	2-Chloroethyl vinyl ether	4.8	50	0.05	1.2	50	0.05

Attachment 1
MDLs and REPORTING LIMITS FOR VOLATILE COMPOUNDS

CASN	Compound name	MDL (µg/L)	RL (µg/L)	RL (mg/L)	MDL (µg/Kg)	RL (µg/Kg)	RL (mg/Kg)
108-10-1	4-Methyl-2-Pentanone	0.4	10	0.01	0.2	10	0.01
10061-01-5	cis-1,3-Dichloropropene	0.3	5	0.005	0.1	5	0.005
108-88-3	Toluene	0.3	5	0.005	0.1	5	0.005
10061-02-6	trans-1,3-Dichloropropene	0.3	5	0.005	0.2	5	0.005
79-00-5	1,1,2-Trichloroethane	0.3	5	0.005	0.2	5	0.005
106-93-4	1,2-Dibromoethane	0.2	5	0.005	0.2	5	0.005
591-78-6	2-Hexanone	0.3	10	0.01	2.1	10	0.01
142-28-9	1,3-Dichloropropane	0.2	5	0.005	0.2	5	0.005
630-20-6	1,1,1,2-Tetrachloroethane	0.2	5	0.005	0.1	5	0.005
127-18-4	Tetrachloroethene	0.3	5	0.005	0.2	5	0.005
124-48-1	Dibromochloromethane	0.2	5	0.005	0.2	5	0.005
108-90-7	Chlorobenzene	0.2	5	0.005	0.2	5	0.005
100-41-4	Ethylbenzene	0.2	5	0.005	0.1	5	0.005
108-38-3	m&p-Xylene	0.5	10	0.01	0.3	10	0.01
95-47-6	o-Xylene	0.3	5	0.005	0.2	5	0.005
100-42-5	Styrene	0.2	5	0.005	0.2	5	0.005
75-25-2	Bromoform	0.2	5	0.005	0.9	5	0.005
108-94-1	Cyclohexanone	420	500	0.5	120	500	0.5
98-82-8	Isopropylbenzene	0.3	5	0.005	0.2	5	0.005
79-34-5	1,1,2,2-Tetrachloroethane	0.2	5	0.005	0.2	5	0.005
96-18-4	1,2,3-Trichloropropane	0.7	5	0.005	1.8	5	0.005
103-65-1	n-Propylbenzene	0.2	5	0.005	0.2	5	0.005
108-86-1	Bromobenzene	0.2	5	0.005	0.3	5	0.005
108-67-8	1,3,5-Trimethylbenzene	0.3	5	0.005	0.1	5	0.005
95-49-8	2-Chlorotoluene	0.2	5	0.005	0.7	5	0.005
106-43-4	4-Chlorotoluene	0.3	5	0.005	0.6	5	0.005
611-14-3	1-Ethyl-2-methylbenzene	0.3	5	0.005	0.2	5	0.005
98-06-6	tert-Butylbenzene	0.3	5	0.005	0.2	5	0.005
95-63-6	1,2,4-Trimethylbenzene	0.2	5	0.005	0.2	5	0.005
135-98-8	sec-Butylbenzene	0.3	5	0.005	0.2	5	0.005
98-82-8	p-Isopropyltoluene	0.3	5	0.005	0.2	5	0.005
541-73-1	1,3-Dichlorobenzene	0.3	5	0.005	0.4	5	0.005
106-46-7	1,4-Dichlorobenzene	0.2	5	0.005	0.4	5	0.005
104-51-8	n-Butylbenzene	0.3	5	0.005	0.3	5	0.005
95-50-1	1,2-Dichlorobenzene	0.3	5	0.005	0.3	5	0.005
96-12-8	1,2-Dibromo-3-chloropropane	1.4	10	0.010	2.1	10	0.010
87-61-6	1,2,3-Trichlorobenzene	0.5	5	0.005	0.9	5	0.005
120-82-1	1,2,4-Trichlorobenzene	0.4	5	0.005	0.9	5	0.005
87-68-3	Hexachlorobutadiene	0.8	5	0.005	0.6	5	0.005
91-20-3	Naphthalene	0.3	15	0.015	0.9	15	0.015

Attachment 2
CHARACTERISTIC IONS FOR VOLATILE COMPOUNDS

#	Compounds	Retention Time (min.)	Primary Ion	Secondary Ion(s)
1	Dichlorodifluoromethane	1.22	85	87
2	Vinyl Chloride	1.43	62	64
3	Chloromethane	1.35	50	52
4	1,3-Butadiene	1.45	39	54
5	Bromomethane	1.65	94	96
6	Chloroethane	1.73	64	66
7	Trichlorofluoromethane	1.93	101	103
8	Ethyl ether	2.17	59	45,74
9	Isopropyl Alcohol	2.54	45	43,59
10	Acrolein	2.27	56	55
11	Acetone	2.4	43	58
12	Freon-TF	2.36	151	101,152
13	1,1-Dichloroethene	2.36	96	61, 63
14	Carbon Disulfide	2.54	76	78
15	Methylene Chloride	2.77	84	49, 86
16	Acrylonitrile	2.99	53	52, 51
17	MTBE	3.02	73	57
18	Hexane	3.27	57	56, 41
19	trans-1,2-Dichloroethene	3.02	96	61, 98
20	Vinyl acetate	3.46	43	86
21	1,1-Dichloroethane	3.4	63	65, 83
22	2-Butanone	3.97	72	43, 57
23	Ethyl Acetate	4.04	45	43, 61
24	2,2-Dichloropropane	3.95	77	41,97
25	cis-1,2-Dichloroethene	3.95	96	61, 98
26	Chloroform	4.27	83	85, 47
27	Isobutyl Alcohol	4.79	43	74,41,42
28	Bromochloromethane	4.18	128	130, 49
29	1,1,1-Trichloroethane	4.44	97	61, 99
30	1-Butanol	5.5	56	41, 43
31	1,1-Dichloropropene	4.61	75	110, 77
32	Carbon Tetrachloride	4.61	117	119, 82
33	1,2-Dichloroethane	4.84	62	49, 98
34	Benzene	4.82	78	51
35	Dibromomethane	5.88	93	95, 174
36	Trichloroethene	5.51	95	97, 130, 132
37	1,2-Dichloropropane	5.75	63	112
38	2-Nitropropane	6.33	41	39, 43
39	1,4-Dioxane	5.92	88	58
40	Bromodichloromethane	6.07	83	85, 127
41	2-Chloroethylvinyl ether	6.44	63	65, 106
42	4-Methyl-2-Pentanone	6.78	43	58,85
43	cis-1,3-Dichloropropene	6.59	75	77, 39
44	Toluene	6.97	92	91

45	trans-1,3-Dichloropropene	7.26	75	77, 39
46	1,1,2-Trichloroethane	7.48	83	85, 97

Attachment 2
CHARACTERISTIC IONS FOR VOLATILE COMPOUNDS

#	Compounds	Retention Time (min.)	Primary Ion	Secondary Ion(s)
47	1,2-Dibromoethane	8.08	107	109, 188
48	2-Hexanone	7.81	43	58, 100
49	1,3-Dichloropropane	7.68	76	78
50	1,1,1,2-Tetrachloroethane	8.84	131	133, 119
51	Tetrachloroethene	7.63	164	129, 131, 166
52	Dibromochloromethane	7.95	129	127
53	Ethylbenzene	8.88	91	106
54	m&p-Xylene	9.04	106	91
55	o-Xylene	9.56	106	91
56	Styrene	9.59	104	78
57	Bromoform	9.81	173	175, 254
58	Chlorobenzene	8.72	112	77, 114
59	Isopropyl benzene	10.07	105	120
60	1,1,2,2-Tetrachloroethane	10.5	83	131, 85
61	Cyclohexanone	10.17	55	42, 69
62	1,2,3-Trichloropropane	10.90	75	77
63	n-Propyl benzene	10.64	91	120
64	Bromobenzene	10.44	156	77, 158
65	1,3,5-Trimethylbenzene	10.9	105	120
66	2-Chlorotoluene	10.73	91	126
67	4-Chlorotoluene	10.83	91	126
68	1-Ethyl-2-methylbenzene	11.17	105	120
69	tert-Butylbenzene	11.34	119	91, 134
70	1,2,4-Trimethylbenzene	11.41	105	120, 77
71	sec-Butylbenzene	11.65	105	134
72	p-Isopropyl Toluene	11.87	119	91, 134
73	1,3-Dichlorobenzene	11.77	146	111, 148
74	1,4-Dichlorobenzene	11.9	146	111, 148
75	n-Butylbenzene	12.46	91	92, 134
76	1,2-Dichlorobenzene	12.41	146	111, 148
77	1,2-Dibromo-3-chloropropane	13.54	75	155, 157
78	1,2,3-Trichlorobenzene	15.43	180	182, 145
79	1,2,4-Trichlorobenzene	14.74	180	182, 145
80	Hexachlorobutadiene	15.02	225	223, 227
81	Naphthalene	15.07	128	102
	Internal Standards:			
82	Pentafluorobenzene	4.49	168	99
83	1,4-Difluorobenzene	5.24	114	88
84	Chlorobenzene-d5	8.68	82	117, 119
85	1,4–Dichlorobenzene-d4	11.87	152	115, 150
	Surrogates:			

86	Dibromofluoromethane	4.43	113	111,192
87	1,2-Dichloroethane-d4	4.76	102	65
88	Toluene-d8	6.89	98	100
89	Bromoflurobenzene	10.27	174	95, 176

Attachment 3
SURROGATES RECOVERY LIMITS FOR VOC COMPOUNDS

Surrogate Compound	Soil % Recovery	Water% Recovery
1,2-Dichloroethane-d4	84 - 129	80 - 120
Toluene-d_8	85 - 110	88 - 110
4-Bromofluorobenzene	63 - 110	86 - 115
Dibromofluoromethane	83 - 119	86 - 118
$NaHSO_4$ Preserved		
1,2-Dichloroethane-d4	78 – 160	
Toluene-d_8	62 - 122	
4-Bromofluorobenzene	44 - 114	
Dibromofluoromethane	74 - 150	

Attachment 4
MS/MSD RECOVERY LIMITS FOR VOC COMPOUNDS

MATRIX SPIKE –WATER			
Compound	Amount added µg/L	RPD Limit	% Recovery
1,1-Dichloroethene	50	15	64 - 140
Methylene Chloride	50	11	71 - 134
trans-1,2-Dichloroethene	50	12	76 - 130
1,1-Dichloroethane	50	10	71 - 123
cis-1,2-Dichloroethene	50	8	71 - 133
Chloroform	50	9	74 - 127
1,1,1-Trichloroethane	50	9	87 - 118
Carbon tetrachloride	50	9	78 - 121
Benzene	50	8	78 - 123
Trichloroethene	50	11	74 - 124
cis-1,3-Dichloropropene	50	10	77 - 129
Toluene	50	10	80 - 123
trans-1,3-Dichloropropene	50	9	73 - 149
Tetrachloroethene	50	8	80 - 120
Chlorobenzene	50	8	88 - 115
Ethylbenzene	50	10	83 - 119
MATRIX SPIKE –SOIL			
Compound	Amount added µg/Kg	RPD Limit	% Recovery
1,1-Dichloroethene	50	54	61 - 137
Methylene Chloride	50	53	63 - 131
trans-1,2-Dichloroethene	50	53	61 - 134
1,1-Dichloroethane	50	54	60 - 123
cis-1,2-Dichloroethene	50	55	55 - 129
Chloroform	50	56	56 - 129
1,1,1-Trichloroethane	50	51	62 - 137
Carbon tetrachloride	50	55	59 - 131
Benzene	50	53	56. - 129
Trichloroethene	50	58	31 - 135
cis-1,3-Dichloropropene	50	58	45 - 120
Toluene	50	58	39 - 131
trans-1,3-Dichloropropene	50	65	45 - 133
Tetrachloroethene	50	62	39 - 132

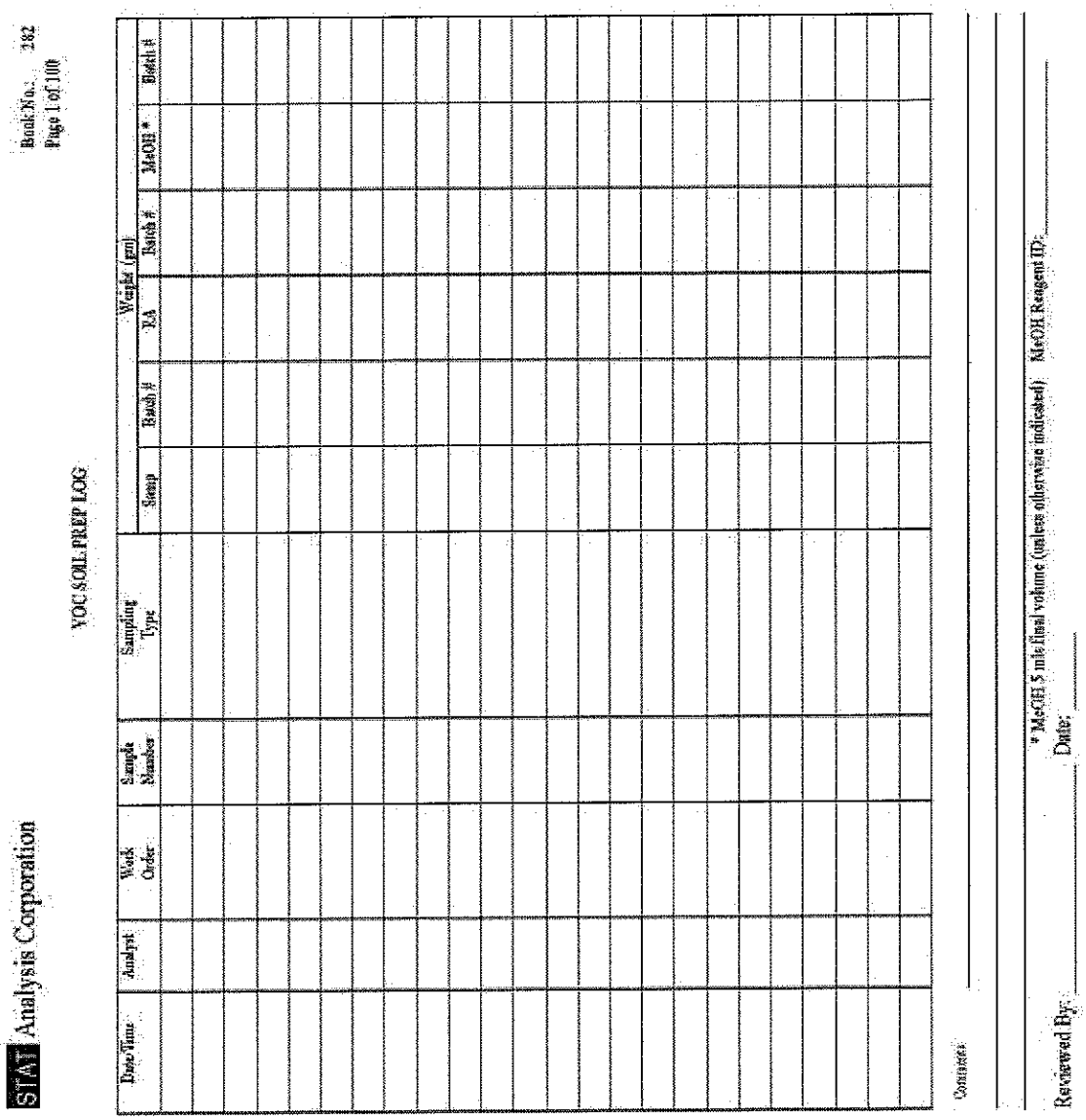
Chlorobenzene	50	64	35 - 121
Ethylbenzene	50	59	41 - 130

Attachment 5
Volatile Internal Standards with Corresponding Compounds Assigned for Quantitation

Pentafluorobenzene (I)	1,4-Difluorobenzene (I)	Chlorobenzene-d5 (I)	1,4-Dichlorobenzene-d4 (I)
Dichlorodifluoromethane	1,2-Dichloroethane-d4 (S)	Trans-1,3-Dichloropropene	1,2,3-Trichloropropane
Chloromethane (SPCC)	Isobutyl Alcohol	2-Hexanone	n-Propylbenzene
Vinyl Chloride (CCC)	Carbon Tetrachloride	1,1,2-Trichloroethane	Bromobenzene
1,3-Butadiene	1,2-Dichloroethane	1,3-Dichloropropane	1,3,5-Trimethylbenzene
Bromomethane	1,1,1-Trichloroethane	Tetrachloroethene	2-Chlorotoluene
Chloroethane	1,1-Dichloropropene	Dibromochloromethane	4-Chlorotoluene
Trichlorofluoromethane	1-Butanol	1,2-Dibromoethane	1-Ethyl-2-methylbenzene
Ethyl ether	Benzene	Chlorobenzene (SPCC)	tert-Butylbenzene
Isopropyl Alcohol	Trichloroethene	Ethylbenzene (CCC)	1,2,4-Trimethylbenzene
Acrolein	1,2-Dichloropropane (CCC)	1,1,1,2-Tetrachloroethane	sec-Butylbenzene
Acetone	1,4-Dioxane	m&p-Xylene	p-Isopropyl Toluene
Freon-TF	2-Nitropropane	o-Xylene	1,3-Dichlorobenzene
1,1-Dichloroethene (CCC)	Bromodichloromethane	Styrene	1,4-Dichlorobenzene
Methylene Chloride	Dibromomethane	Isopropyl benzene	n-Butylbenzene
Carbon Disulfide	2-Chloroethylvinyl ether	Cyclohexanone	1,2-Dichlorobenzene
Acrylonitrile	4-Methyl-2-Pentanone	Bromoform (SPCC)	1,2-Dibromo-3-hloropropane
MTBE	cis-1,3-Dichloropropene	1,1,2,2-Tetrachloroethane (SPCC)	1,2,4-Trichlorobenzene
Hexane	Toluene-d8 (S)	Bromofluorobenzene (S)	Hexachlorobutadiene
trans-1,2-Dichloroethene	Toluene (CCC)		Naphthalene
Vinyl acetate			1,2,3-Trichlorobenzene
1,1-Dichloroethane (SPCC)			
2-Butanone			
Ethyl Acetate			
2,2-Dichloropropane			
cis-1,2-Dichloroethene			
Chloroform (CCC)			
Bromochloromethane			
Dibromofluoromethane (S)			

(I) = Internal Standard
(S) = Surrogate
(CCC) = Calibration Check Compounds
(SPCC) = System Performance Check Compounds

Attachment 6



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VOC SOIL PREP LOG

Date/Time	Analyst	Work Order	Sample Number	Sampling Type	Weight (gm)					
					Samp	Batch #	RA	Batch #	MeOH *	Batch #

Comments: _____

* MeOH 5 mls final volume (unless otherwise indicated) MeOH Reagent ID: _____

Reviewed By: _____ Date: _____

STAT Analysis Corporation:

STANDARD OPERATING PROCEDURE 4010

VOLATILE ORGANIC COMPOUNDS IN AMBIENT AIR BY /GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS) (EPA Method TO-14A/TO-15)

Revision 02
Effective Date: February 2, 2006

Author: Peter A. Brodek

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1.0 IDENTIFICATION OF TEST METHOD

SOP Title: Volatile Organic Compounds in Ambient Air by 2-Stage Thermal Desorbtion/Gas Chromatography/Mass Spectrometry (GC/MS) (EPA Method TO-14A/TO-15) is abbreviated as TO-14A/TO-15 in laboratory records.

2.0 APPLICABLE MATRICES

This method is applicable to air samples (source monitoring, ambient outdoor/indoor, etc.) collected in Tedlar™ bags, stainless steel or Silcosteel™ sampling canisters at sub-ambient (passively sampled) or positive pressure (actively sampled).

3.0 DETECTION LIMITS

The lab follows the procedure found in 40CFR Part 136B to determine the MDL for each matrix type on an annual basis. See the STAT Analysis SOP 1210 for the MDL procedure, frequency and acceptance criteria. The MDLs measured by the lab and all supporting documentation are in the laboratory QA files for review.

The laboratory determined MDL must always be less than the reporting limit (RL), which may be determined by the lowest standard. The RLs will usually range from three to ten times the laboratory measured MDLs. Attachment 1 contains the current MDLs and reporting limits (RLs) for this SOP for TO-14A compounds and TO-15 compounds.

4.0 SCOPE AND APPLICATION

4.1 This SOP describes in detail the precise methods used at STAT Analysis Corporation for the analysis of environmental samples for Volatile Organic Compounds (VOCs) in air by GC-MS. This SOP as written is to be applied when TO-14A or TO-15 analysis is requested. This SOP is used to determine the concentration of VOCs in all types of air matrices.

4.2 SOP 4010 can be used to quantify most VOCs that have both boiling points below 200°C and are either insoluble or very slightly soluble in water. The SOP is also limited to compounds that elute as sharp peaks from a GC non-polar capillary column. Such compounds include low-molecular weight hydrocarbons, low molecular weight halogenated hydrocarbons, and aromatics. See Attachment 2 for a list of compounds and their characteristic ions that have been evaluated on the specified GC/MS system.

4.3 The reporting limits (RLs) for this SOP are shown in Attachment 1. RLs will be proportionately higher for samples that require dilution or reduced sample size to avoid saturation of the detector.

4.4 This method is restricted to use by or under the supervision of analysts experienced in the use of a Gas Chromatograph/Mass Spectrometer (GC/MS) and skilled in the interpretation of mass spectra. Each analyst must demonstrate the ability to generate acceptable results with this method.

5.0 SUMMARY OF TEST METHOD

5.1 Prior to using this method, the samples must be prepared for the GC/MS using the appropriate sample preparation technique (see Section 14.1). VOCs are introduced into a Gas Chromatograph (GC) by the Tekmar Autocan Canister Autosampler. A known volume of air sample (usually 500cc) is trapped on a multi-bed adsorbent trap at ambient temperature (25 °C). This trap is then back-purged with inert gas (He) while being balistically heated from 25 °C to 300 °C to quantitatively transfer the analytes of interest to the cryofocuser. The cryofocuser is cooled to – 175 °C in order to focus the analytes of interest into a small injection volume. The cryofocuser is then heated rapidly to 300 °C to transfer the sample to the chromatographic column.

5.2 This method describes chromatographic conditions that will allow for the separation of the compounds and for their qualitative and quantitative analysis by GC/MS. Identification of target compounds is accomplished by comparing component retention times to those of authentic standards and by comparing their mass spectra with the electron impact (or electron impact-like) spectra of authentic standards. Quantitation is accomplished by comparing the response of a major (quantitation) ion relative to an internal standard using a calibration curve containing a minimum of 5 points for each target compound.

5.3 **Method Modifications from Reference** – This SOP is based on EPA Methods TO-14A and TO-15 with the following modifications:

1) Calibration standards are prepared using a static dilution system. EPA Method TO-15 recommends a dynamic dilution system. Static dilution is used to minimize the cost of standards preparation. Static dilution has been demonstrated to be as accurate as dynamic dilution through the periodic testing of performance evaluation samples.
2) Because we do not have the capacity to wait 24 hours for the leak test, the leak test was modified to a canister pressure drops < 1.0 psi over 12 hours, instead of < 2.0 psi over a 24-hr. period.
3) All blanks, QC samples (LCS, LCSD) and samples must have internal standard responses within ± 40% of the daily CCV internal standard responses. (Method states ± 40% of the internal standard responses from the most recent valid calibration.) ICAL internal standard response for each calibration standard must be within ± 40% of the mean internal standard response of the ICAL.
4) EPA Method TO-14A specifies the use of a 3-point calibration curve with the addition of a humidified zero air reference point. We will be using a minimum of 5 points for the calibration curve; however, the zero point will not be included because we will be using internal standard (rather than external standard) calibration- see modification 5 (following).
5) EPA Method TO-14A does not require the use of internal standards. The three internal standards specified by EPA Method TO-15 will be used.
6) In cases where QA/QC criteria differ between EPA Methods TO-14A and TO-15, the more stringent QA/QC criteria will be employed.
7) In cases where a compound is listed only on EPA Method TO-15, the quality control specifications from TO-15 will be applied to only those compounds.

6.0 DEFINITIONS

The STAT Analysis Quality Manual Section 19.0 contains all of the definitions of standard terms used in SOPs.

7.0 INTERFERENCES

7.1 GC/MS data from all blanks, samples, and spikes must be evaluated for interferences. Interferences will vary from source to source depending upon the particular sample being tested. Determine if the source of interference is laboratory induced. If the source of the interference is laboratory induced, take corrective action to eliminate the problem.

7.2 Contamination by carryover can occur whenever high-concentration and low-concentration samples are sequentially analyzed. A Method blank (zero air) must be analyzed to demonstrate that carryover has been eliminated. Reanalysis must be performed on all affected samples to demonstrate that the compound concentration is from the sample and not due to carryover. The sampling system may require extensive bake out and cleaning after a high-level sample. Cleaning may include trap replacement, purge gas filter replacement, and/or transfer line cleaning/replacement.

7.3 The sampling system can be contaminated by diffusion of volatile organics (particularly methylene chloride and fluorocarbons) into the sampling system. The system is leak-tested daily to ensure that compounds potentially present in the laboratory environment do not contaminate the system. A zero-air blank, consisting of humidified zero air is prepared in a previously cleaned and certified sampling canister. It is analyzed daily to ensure that system is not contaminated. Because of the design of air sampling canisters, it is extremely rare for canisters to become contaminated during shipment/transport to the lab.

7.4 All sampling canisters are cleaned in batches on a manifold. They are cleaned using repeated cycles of pressurization with humidified zero air followed by evacuation. All canisters in the batch are pressurized to 30psia (15.3 psig) with humidified zero air and the canister valves are closed. The canisters are allowed to stand overnight, and then the pressure in each canister is individually checked. A pressure-drop of >1.0psi in any canister over a 12-hour period is indicative of a leak. Any leaking canister should be taken out of service and tagged for a leak test. If the canister can be repaired and subsequently demonstrated to pass the leak test, it can again be cleaned and certified and placed back in service. At least one canister per batch is certified by final pressurization to 30psia (15.3 psig) with humidified zero air, followed by analysis on the GC/MS system. The canister must contain less than the reporting limit of each target compound in order to be considered clean. Cleaning cycles are repeated for ALL canisters in the batch if the selected canister fails certification criteria. (Alternatively, the clean canister can be certified using a GC/FID system designed to measure total Non-Methane Organic Compounds [TNMOC]. The canister is certified if the concentration of TNMOC is <10.0ppbv in this analysis.) Following certification of at least one canister from each cleaning batch, all canisters are evacuated to –14 psig. The canisters are then ready for field sampling. However, if a canister fails a leak test, the sample that was in that canister is considered suspect and a note is added to the case narrative stating so and the sample report is reissued.

7.5 Any apparatus used for sample collection must be certified as clean on a periodic basis. The sampling apparatus is used to sample a stream of humidified zero air into a clean, certified sample canister or directly into the sample concentrator to verify that the sample collection device is free from contamination. If the sampling device is contaminated, it must be cleaned and re-tested.

7.6 Impurities in the purge gas and from organic compounds out-gassing from the plumbing ahead of the trap account for the majority of contamination problems. The analytical system must be demonstrated to be free of contamination under the conditions of analysis by running calibration and reagent blanks. The use of non-PTFE plastic coating, non-PTFE thread sealants, or flow controllers with rubber components in the purging device should be avoided. Pressure regulators with stainless steel diaphragms should be used for all cylinder gasses. Carrier gas for the GC/MS system should be passed through moisture, hydrocarbon, and oxygen traps.

8.0 SAFETY

The concentrations of hazardous chemicals in most air samples are minimal and the analyst should not be exposed to the sample due to the closed nature of the sample canisters and analytical system; however, numerous compounds analyzed by this method are known or suspected carcinogens. Proper personal protective equipment including safety glasses and a lab coat are suggested. Other safety precautions must be conducted in accordance with the SAP 003 Chemical Hygiene Plan. Other actions can also be applied if deemed necessary. A reference file of Material Safety Data Sheets (MSDS) is available to all personnel involved in this method. This method requires the safe handling and use of pressurized cylinders.

9.0 EQUIPMENT AND SUPPLIES

The following apparatus is recommended for performing this procedure. Equivalent items can be used, if with their use, the analytical and QA/QC requirements in this SOP can be met. All catalog numbers in this SOP are current as of the effective date and thereafter subject to change.

9.1 Gas Chromatograph/Mass Spectrometer system (GC/MS)

9.1.1 Gas chromatograph(GC) – Agilent 6890 electronic flow control gas chromatograph with the column directly coupled from the transfer line to the source.

9.1.2 Column – 60 m X 0.320 mm ID J&W DB-1 column with 1 µm film thickness.

9.1.3 Mass spectrometer(MS) - Agilent 5973N.

9.1.4 Data system – A computer system using Agilent 3365 Chemstation Software (G1701AA Version C.00.00 or more current) is used to collect and process data.

9.1.5 Tekmar #64 Air Toxics trap.

9.1.6 NIST Library of Reference Spectra, Edition NIST98.L

9.2 Tekmar Autocan canister autosampler.

9.3 Microliter syringes - 10 µL, 100µL and 500 µL

9.4 Sample canisters - Restek TO-Can

9.5 Cleaning manifold – in-house design capable of automated cleaning of canisters in batches of at least 8.

9.6 Pressure gauge – Wallace & Tiernan 0 – 100psi test pressure gauge, 0.1% accuracy, 0.2psi graduations

9.7 Pressure gauge- Glycerin filled vacuum compound gauge (± 1% accuracy, -14 psig (30" Hg)/ 0-30 psi)

9.8 Air sampling apparatus – Restek non-Silco Air Kit

9.9 Gas Supplies
- 9.9.1 Ultra-High Purity Helium (99.999%)
- 9.9.2 Reagent Grade Zero air or ultra grade air
- 9.9.3 Liquid Nitrogen

9.10 Hydrocarbon filters, Agilent model HT-200-2 or equivalent

10.0 REAGENTS AND STANDARDS

The following reagents and standards are required to perform this procedure. When instructions are given on how to prepare a specific volume of a reagent or standard, larger or smaller volumes can be prepared as needed so long as the final concentrations remain the same—this is especially applicable if standards are being prepared in 1L or 33L canisters as opposed to the usual 6L canisters. Any other deviations from the reagents or standards listed in this SOP could be detrimental to the quality of the data produced. Such deviations would have to be approved and documented (see 230 Corrective Action SOP).

Instructions for labeling and record keeping of reagents and standards are contained in SOP 1010 Analytical Standards and Reagents Receipt and Preparation.

NOTE: All concentration listed below are nominal concentrations. Any stock standard where an individual compound differs from the listed nominal concentration by greater than 10% will be rejected or the spike value in LIMS must be corrected to match the reported concentration on the COA.

NOTE: Zero Grade air or ultra grade air must be logged in and tracked as a reagent

10.1 Analytical reagent grade chemicals shall be used in all tests. Unless otherwise indicated, all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.

10.2 Organic-free reagent water - All references to water in this SOP refers to Type II reagent water (in-house system). Note: Reagent water may be de-gassed with High Purity Helium to remove trace impurities.

10.3 Stock Standard mixtures - Standard mixtures are purchased in cylinders from certified vendors traceable to NIST, where possible. The primary standard mixture used is the TO-15 Calibration Mix (100ppbv, Restek Catalog # 34437). Secondary source standard mixture is Scott Specialty Gases 04-AZP0002-110 TO-15 Standard Air. Calibration standards and Quality Control Standards (see section 10.4) are prepared directly from the Stock Standard mixtures in clean, certified 6L canisters, diluted to appropriate concentration with zero grade air, and humidified with reagent water. The prepared standards must be replaced monthly or sooner if comparison with quality control check samples indicates a problem. Quality Control Standards must be from different source (lot numbers) than Calibration Standards.

10.3.1 The primary stock solution that is not available in cylinders which is needed for this method is BFB. BFB is purchased in vials containing 5000µg/ml of BFB in methanol (Restek Catalog 30003). See section 10.6 for preparation.

10.3.2 The internal standard stock is Restek TO-14A Internal Standard Mix (Restek Catalog # 34427), 100 ppbv each of bromochloromethane, 1,4-difluorobenzene, and Chlorobenzene-d5.

10.4 Calibration Standards – A minimum of five calibration standards are required. Two canisters containing calibration standards are prepared at concentrations of 5ppbv and 50ppbv. Eight levels of calibration standard concentrations are run: 0.2ppbv, 0.5ppbv, 1.0ppbv, 2.0ppbv. 5.0ppbv, 10ppbv, 25ppbv and 50ppbv (see Table 1).

10.4.1 A static dilution system is used to prepare the calibration standards. The system incorporates a very accurate (0.1% gauge) test pressure gauge and uses pressure differential to calculate dilutions. This method of standard preparation is documented to be equivalent to dynamic dilution. Working standards are prepared by pressurizing a clean, certified, evacuated canister to just above 0psi on the test pressure gauge.The pressure differential on the gauge for standard preparation is 1.5psi for the 5ppbv calibration standard, and 15psi for the 50ppbv calibration standard. Finally, the canister is pressurized to 30psia (15.3 psig) final pressure using zero grade air. The prep factor is equal to the gauge pressure differential of Stock Standard mixture (or internal standard mixture) divided by the final canister pressure. The trapping volume required for each calibration level is given in Table 1. Calibration standards and quality control standards in canisters can be used for one month from the date of preparation, or
until the pressure in the canister falls below 0 psig. The pressure in the canister should be checked periodically in order to prevent the system from appearing to be out of control due to low standard pressure. The 2, 5 and 10ppbv level standards are rotated on a subsequent day for CCVs.

Table 1 Calibration Standards

Desired conc. (ppbv)	Trapping volume of standard mix	Trapping volume of ISTD	Calibration Canister Used
50	500	50	50ppbv
25	250	50	50ppbv
10	100	50	50ppbv
5	500	50	5ppbv
2	200	50	5ppbv
1	100	50	5ppbv
0.5	50	50	5ppbv
0.2	20	50	5ppbv

10.5 Internal Standards: The internal standards used are bromochloromethane, 1,4-difluorobenzene, and chlorobenzene-d_5. The internal standard Working calibration and QC standards expire after one month. The internal standards permit most of the compounds of interest in a chromatogram to have retention times of 0.80-1.20 relative to one of the internal standards. Use the base peak ion from the specific internal standard as the primary ion for quantitation (see Attachment 2, e.g. for 1,4-difluorobenzene, use 114 m/z for quantitation). If interferences are noted, use the next most intense ion as the quantitation ion.

10.6 GC/MS tuning standard - This mixture is made using the Primary stock solution BFB (5000 µg/mL in methanol). A 6-L canister is prepared containing enough BFB to quantitatively transfer 50ng of BFB in a known air volume to the analytical system. The BFB-containing canister is prepared by injecting 1.0µl of the stock BFB solution into a 6-liter air canister and pressurizing the canister to 30 psia with zero air. Each 125cc sample from this canister contains 50ng of BFB. At this concentration, BFB is very stable in the canister and can be used up to 6 months. The absolute pressure in the BFB canister should be checked each time it is used. When the pressure falls below 0 psig in the canister, the response of BFB will start to drop and the spectrum may not pass tune requirements. Prepare a new canister of BFB when the pressure in the current canister falls to 0 psig. Failure to check the pressure in the BFB canister could lead to unnecessary instrument maintenance and downtime.

10.7 The Laboratory Control Sample/Laboratory Control Sample Duplicates (LCS/LCSD): An LCS/LCSD must be analyzed with every sample batch. Spiking solutions are prepared from certified analytical stock standard solutions purchased independently from the Calibration Standards. The LCS stock standards are purchased fromScott Specialty Gases, TO-15 62 component mix at 100ppbv/compound. The LCS Spiking mixtures are prepared in the same manner as the calibration mixtures (See section 10.4, 10.4.1, and Table 1). The LCS is also used for initial calibration verification (ICV). The concentration of the LCS and LCSD is 5ppbv.

10.8 Method Blank- A canister containing zero air will be analyzed during each series of analytical runs. Each sequence will have an evaluation of the BFB tuning solution , followed by a continuing calibration check, and then the blank canister. The blank must contain less than the reporting limit of each target analyte for analysis to continue.

10.9 Matrix Spike/Matrix Spike Duplicates – Matrix spikes are not applicable for this method.

10.10 Reagent Grade Zero Air.

11.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

11.1 Containers used to collect samples for the determination of volatile organic compounds: clean, certified air sampling canisters, Tedlar bags, adsorbent tubes. Adsorbent tube analysis will not be covered in this SOP. Tedlar bags and air sampling canisters are available from a variety of vendors.

11.1.1 The lab may provide clean, evacuated canisters to the client(s) for sampling. If the client(s) choose to use their own sampling containers, the client will be issued a statement of potentially inaccurate results in the case narrative.

11.1.2 The lab may provide sample collection devices (passive or active samplers) to the client(s) or provide for initial and periodic certification (see sections 7.4 and 7.5) of sampling equipment belonging to clients. Samples may not be deemed of known quality for analysis if either the sampler or canister used for sample collection is not properly documented as clean and/or certified.

11.2 All samples are generally kept free of contamination because the sample containers must be leak-free. See section 14.9 for details of how to perform the leak-test procedure. As a precaution, samples should be stored away from standards, reagents, or other laboratory chemicals that could cause cross-contamination.

11.3 Sample analysis must be within 30 days from the date of sample collection. After client approval or 30 days have elapsed, the sample will be disposed.

12.0 QUALITY CONTROL

The following details the QC requirements that apply to this analysis. Each Quality Control Indicator (QCI) provides information pertaining to either method or individual sample performance. Our goal is to produce defensible data of known and documented quality. The results of these QCI samples are used to assess the acceptability of data.

12.1 Calibration Verification

An Initial Calibration Verification (ICV) standard containing all of the target compounds reported in this method (refer to section 10.7) shall be analyzed immediately after the completion of the initial calibration. The ICV shall be purchased from a second source to verify compound concentrations. Continuing calibration verification is performed daily by rotating the 2ppbv, 5 ppbv, and 10 ppbv .primary calibration standards.

12.2 Blanks

Method Blank analysis is performed to determine if any contamination is present in the analytical process and is used to evaluate acceptance of the batch of samples. A method blank shall be analyzed once per 24-hour period per matrix type. The method blank shall be processed through all preparatory steps used for the samples. The blank shall be analyzed using the same instrument and conditions as the samples.

12.3 Laboratory Control Sample (LCS)

The LCS is used to evaluate the performance of the total analytical system, including all preparation and analysis steps. The LCS shall be analyzed once per batch of samples not to exceed the 24-tuning clock. The LCS shall be processed through all preparatory steps used for the samples. The LCS shall be analyzed using the same instrument and conditions as the samples. Refer to section 10.7 for LCS compounds and concentrations. All target compounds are evaluated in the LCS.

12.4 Surrogates

Not applicable to this method.

12.5 Duplicates

Duplicates of field samples or of the LCS must be prepared in compliance with the method requirements and client directives. Replicate samples will be analyzed whenever the client provides them. However, when they are not, then the LCS/LCSD pair must be analyzed per batch of 20 incoming samples. In both cases, reproducibility performance is defined as ± 25% RPD.

Note: It is an option to analyze the same can as a duplicate. The same acceptance criteria would apply.

12.6 Matrix Spike and Matrix Spike Duplicate (MS/MSD)

Not applicable to this method.

12.7 Internal Standards

The internal standards used for this method are added to all samples, standards, and blanks. Refer to section 10.5 for preparation and concentration instructions. The internal standard responses for all samples including QA/QC samples (blank, LCS, LCSD, etc.) must be within +/-40% (60 to 140%) of the daily calibration check internal standard responses. If any sample is run in which the internal standard responses fall outside of these criteria, the sample will be re-analyzed. If, upon re-analysis, the internal standard response(s) still fall outside of these criteria, the sample will be re-prepared if possible (blank, LCS, or LCSD) or if the criteria are not met for a client submitted sample, a note will be made in the case narrative of unacceptable internal standard response(s).

13.0 CALIBRATION AND STANDARDIZATION

13.1 Mass Spectrometer Tuning Verification

The Mass Spectrometer is software-tuned with the BFB tuning macro using perfluorotributylamine (PFTBA). Each GC/MS system must be hardware-tuned to meet the criteria in Table 2 for a 50 ng injection of BFB. Analyses must not begin until all these criteria are met. From the BFB canister, 125cc of air volume are trapped that contains 50ng BFB/125cc. Analyze the solution using the GC/MS instrument conditions for sample anaysis shown in section 14.2.1.

Background subtraction must be straightforward and designed only to eliminate column bleed or instrument background ions. Obtain a mass spectral analysis, using the method listed above, of BFB and confirm that all the key m/z criteria in Table 2 are achieved. The mass spectra of BFB are acquired using the following methods: three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged, the peak apex only is evaluated, or the entire BFB peak is averaged. If background subtraction is required, this must be accomplished using a single scan no more than 20 scans prior to the elution of BFB. Do not background subtract part of the BFB peak. Note: the instrument-tuning file used to acquire the BFB criteria must be also used to acquire QC and sample data. If the criteria are not passed, the analyst must perform needed maintenance, retune the mass spectrometer and repeat the test until all criteria are achieved.

Note 1: The 24-hour tune period begins at the start of the BFB analysis, which is recorded as the data acquisition start time on the data file. The last valid calibration standard in the ICAL must have a data acquisition start time less than 24 hours from the start of the tune period.

Table 2 Acceptance Criteria for BFB

Target Mass	Relative to Mass	Lower Limit%	Upper Limit%
50	95	8	40
75	95	30	66
95	95	100	100
96	95	5	9
173	174	0	< 2
174	95	50	120
175	174	4	9
176	174	93	101
177	176	5	9

13.2 **Initial Calibration (ICAL)**

13.2.1 Analyze each calibration standard according to the procedure listed in Section 14 (standards are analyzed under the same conditions as samples) and tabulate the target ion area of the compound against concentration for each compound relative to the appropriate relative internal standard. See Attachment 3 for the list of internal standard assigned to each compound. Calculate response factors (RFs) for each compound in each calibration standard as follows:

$$RF = \frac{A_x * C_{is}}{A_{is} * C_x}$$

where:
A_x = Area of the characteristic ion for the compound being measured.
A_{is} = Area of the characteristic ion for the specific internal standard.
C_{is} = Concentration of the specific internal standard (10ppbv for this method)
C_x = Concentration of the compound being measured (ppbv).

13.2.2 Calculate the average response factor ($\overline{RF}$) for each compound as follows:

$\overline{RF} = (\Sigma RF_1 \text{ to } RF_n)/n$

where:
RF = RF for each of the calibration levels (minimum 5)
n = Number of RF values (minimum 5)

13.2.3 Calibration Check Compound (CCC) responses are monitored to check the integrity of the system. All compounds are considered calibration check compounds.

Using the RFs from the initial calibration, calculate the percent relative standard deviation (%RSD) for the CCCs.

To calculate %RSD: $\%RSD = 100\% \times SD/\overline{RF}$

where:
%RSD = % Relative Standard Deviation

$\overline{RF}$ = average of initial RFs for a compound
SD = standard deviation (n-1) of average RFs for a compound

To calculate Standard Deviation (n-1 degrees of freedom)

$$SD = \sqrt{\sum_{i=1}^{N} \frac{(RF_i - \overline{RF})^2}{N-1}}$$

where: RF_i = RF for each of the calibration levels
N = Number of RF values (minimum 5)

13.2.4 The %RSD of all CCC compound should be < 30%. If the response of any CCC compound varies by more than 30%, the system is considered too reactive for analysis to continue. Perform the initial calibration procedure beginning with section 13.2.1.

13.2.5 Linearity : If the %RSD of any compound is 30% or less, then the relative response factor is assumed to be constant over the calibration range, and the average relative response factor is used for quantitation. Two exceptions of up to 40% are permitted. This exception will be applied only to analysis by EPA Method TO-15.

13.2.6 Retention Times: The Relative Retention Times (RRT) of each compound in each calibration standard should be within ± 0.06 RT units.

13.2.7 Internal Standards: For the Initial Calibration, the response for each internal standard must be within ± 40% of the mean internal standard response for all calibration standards.

13.2.8 Before sample analysis can begin, a Initial Calibration Verification (ICV) (see Sec. 10.7) must be performed. The ICV results must be within the acceptance criteria as established for the CCV compounds (Section 13.3).

13.2.9 NOTES:

1. All calibration curves must have a unique identifier. The calibration date is incorporated into the method identifier for easy reference.
2. All initial calibration standards must be analyzed within the 24-hour BFB tune verification window.
3. Calibration must be completed (all standard levels analyzed) within 24 hours or the entire calibration sequence must be repeated. All initial calibration standards must be analyzed and verified prior to field sample analyses.
4. Do not add calibration standards and update the curve after the original calibration date.
5. Multiple analyses of the same calibration level are not allowed to be included in the calibration curve.
6. Compound responses cannot be selected from different analyses of the same calibration level (i.e. all compound responses for level 1 must come from the same data file). If more than five calibration levels are analyzed, it is permissible to either drop the low compound concentration (poor response) or the high compound concentration (detector saturation). Do not drop a point in the middle of the curve.
7. If more than five calibration levels are analyzed, it is permissible to drop an entire level if the analyst can document a specific reason or reasons why that level should be excluded. Mechanical failures, significant loss of all compound responses possibly due to poor technique in standard preparation, or software malfunction during data acquisition (system did not acquire all compound data) are plausible reasons. The reason must be justified and documented. The supervisor should review this situation and approve the analyst's decision.
8. The need to reanalyze the same calibration level more than once indicates a potential problem with the Working Standard mixture. Prepare a fresh Working Standard and repeat all calibration levels. All calibration standard levels must come from the same Working Standard.
9. Manual integration must only be used if the software fails to properly integrate the peak (See SOP 1255 Manual Integration). If manual integration is used for a particular compound, all levels of that compound do not have to be manually integrated. Example: the computer generated integration of a

compound in the low level standard is not technically sound. A manual integration of the compound is performed (due to baseline noise, etc) in order to achieve a technically sound integration. The computer integrates other levels of the compound correctly. The manual integration of the low level must match, as best as possible, the computer generated integrations for all other levels.

10. If any compound in the mid-point level is manually integrated, the integration of this compound must be reviewed for every continuing calibration standard and QC check solution (e.g. LCS) to ensure that the integration is the same as the manual integration performed in the initial calibration (ICAL) mid-point. A consistent manner of integration must be achieved.
11. All manual integrations must be reviewed and approved according to SOP 1255 Manual Integration.

13.3 Continuing Calibration Verification (CCV)

13.3.1 The mass spec must pass tune criteria (see Section 13.1) every 24 hours during analysis of samples.

13.3.2 A continuing calibration verification (CCV) sample is analyzed every 24 hours during analysis of samples. Different standards are analyzed for the CCV such that a wider range of the calibration curve is verified. For example: on successive days analyze the 2ppbv, the next day the 5ppbv standard solution is analyzed, and the following day, the 10ppbv standard solution is verified. Compare the response factors and the CCCs, and the internal standards from the CCV with the following criteria.

13.3.3 Control limits for the CCC compounds are ± 30% difference from the ICAL Response Factor (RF).

13.3.4 The areas of the internal standards in the CCV must be between 60% - 140% of the respective areas of the internal standards in the ICAL mean internal standard response

13.3.5 The retention times of the internal standards in the CCV must be within ± 20 seconds of the respective retention times of the internal standards in the ICAL mid-point calibration standard.

13.3.6 If the CCV results obtained are outside the acceptance criteria, corrective actions must be performed. If routine corrective actions fail to produce an acceptable *second consecutive (immediate)* CCV, then either the lab has to demonstrate performance after corrective action with two consecutive successful CCVs, or a new ICAL must be performed. If the instrument has not demonstrated acceptable performance, sample analyses cannot continue until a new ICAL is established and verified with an ICV. However, sample data associated with an unacceptable CCV may be reported as qualified data under the following special conditions:

13.3.6.1 When the acceptance criteria for CCV are exceeded high, i.e., high bias, and there are associated samples that are non-detects, then those non-detects may be reported. Otherwise the samples affected by the unacceptable calibration verification must be reanalyzed after a new ICAL has been established, evaluated and accepted.

13.3.6.2 When the acceptance criteria for the CCV are exceeded low, i.e., low bias, those sample results may be reported if they exceed a maximum regulatory limit/decision level. Otherwise the samples affected by the unacceptable verification must be reanalyzed after a new ICAL is established and verified with an ICV.

13.3.6.3 When the acceptance criteria for the CCV are exceeded and it is not possible to reanalyze the sample due to limited sample quantity and the laboratory cannot obtain a new sample, the data may be reported with the appropriate data qualifiers if the client has been contacted and agrees to accept the qualified data.

13.4 Records: Initial and Continuing Calibration Records will contain, at a minimum, the following:

1) Calibration date
2) Test method
3) Instrument
4) Analysis date

5) Each compound name
6) Analyst's initials or signature
7) Standard Concentration (appropriate units) and number of standards
8) Response (appropriate units)
9) Calibration curve or response factor
10) Evaluation of and Statistics for ICAL curve fit in order to judge calibration curve acceptance
11) Evaluation of and Acceptance Limits for ICV analysis in order to judge calibration curve acceptance.
12) Evaluation of and Acceptance Limits for CCV analysis in order to judge continuing calibration acceptance.

14.0 PROCEDURE

14.1 Sample Preparation

14.1.1 Incoming samples will have their pressure checked using the test pressure gauge. Samples collected using a passive sampler should have a pressure of 0.0 ± 3psig. Samples collected using an active (pump equipped) sampler should have a pressure of 7.0 ± 3psig. Samples can be accepted outside of this range, but note sample pressures that do not conform to these limits on the analytical report. If canister pressures are dramatically outside of the specified ranges, the sample can be invalidated and not analyzed, or, if the sample is analyzed, the data should be flagged as suspect.

14.1.1.1 Samples in Tedlar bags will be checked for sample pressure, but will not otherwise be prepared. The Tedlar bag can be connected directly to the Autocan for analysis. Alternatively, the contents of the Tedlar bag can be transferred to a clean, evacuated canister. The pressure in the canister is recorded, and the canister is pressurized to 30 psia to yield a final volume of 12500cc in the canister.

14.1.2 Zero air is added to each incoming canister sample so that the final pressure of every sample is 30.0psia (15.3 psig) The initial and final sample volumes are recorded in LIMS and used to calculate the sample prep factor. Each sample will have a final volume of 12500cc (the calculated volume of air in a 6L canister at 30psia).

14.2 GC/MS Analysis

14.2.1 GC/MS Conditions:

GC/MS operating conditions	
EMV	1100-2500
Mass Range	35-300
Scan Sampling Rate	2^2
Initial Column Temp.	30°C
Initial Temp Holding Time	6 minutes
Ramp 1 Temp Program	15°C/minute
Ramp 1 Final Column Temp.	120°C
Ramp 1 Holding Time	0 minutes
Ramp 2 Temp Program	4 °C/minute
Ramp 2 Final Column Temp	160 °C
Ramp 2 Holding Time	0 minutes
Ramp 3 Temp Program	20 °C/minute
Ramp 3 Final Column Temp	220 °C
Ramp 3 Holding Time	5 minutes
Injector Temp.	n/a
Source Temp.	230°C
GC/MS Interface Temp.	280°C
Split Ratio	n/a
Carrier Gas	UHP Helium

14.2.2 Tekmar Autocan operating conditions

GC Start Option	End of Desorb
GC Cycle Time	12 minutes
Cryo	On
Line Temp	150 °C
Valve Temp	150 °C
MCS Line Temp	40 °C
Trap Standby Temp	150 °C
Cryo Standby Temp	130 °C
MFC Standby Flow	20
Trap Cool Temp	20 °C
MFC Transfer Flow	25
Drypurge Time	7.5 minutes
Drypurge Temp	25 °C
Drypurge Flow	75
Desorb Preheat Temp	50 °C
Trap Desorb Time	5 minutes
Trap Desorb Temp	275 °C
Cryo Cool Temp	-175 °C
Cryo Inject Time	1 minute
Cryo Inject Temp	130 °C
Trap Bake Time	10 minutes
Trap Bake Temp	280 °C
MCS Bake Temp	60 °C
MCS Cool	20 °C

Note 3: All standards will have the trapping volume noted in section 10.4. Blanks and LCS/LCSDs will have trapping volumes of 500 cc. Undiluted samples will have trapping volumes of 500 cc. The volume trapped of diluted samples will be noted.

14.2.2 Perform Standard Spectra Auto-tune with the GC oven at 100 °C to check for air and water leaks in the GC/MS system.

14.2.3 Access the Teklink software to generate a sample analysis sequence.

14.2.4 Access the Chemstation software to generate a sample analysis sequence. (This must match the Teklink sequence.)

14.2.5 Analyze the BFB tuning standard and verify that the tuning requirements from section 13.1 Table 2 are met.

14.2.6 Analyze the Continuing Calibration Verification Standard (CCV) and evaluate using CCV acceptance criteria (See Section 13.3).

14.2.7 Analyze the Method Blank. The method blank must contain less than the reporting level for all target compounds. In addition the response of the internal standards must be within ± 40% of the internal standard response of the daily calibration check (CCV). If target parameters achieve these limits, recovery and retention times of the compounds are within acceptance limits, and the chromatography (baseline noise and compound tailing) is acceptable, continue the analysis. If any one of these criteria is not met, take appropriate corrective action to identify and correct the problem.

14.2.8 Analyze the LCS (and its duplicate, if applicable). The percent recovery must meet the criteria listed in section 18.2. If the LCSD is analyzed, it must meet the %RPD criteria listed in section 18.4.

14.2.9 If all criteria are met, continue with sample analysis.

14.2.10 Analyze the sample replicates, when provided by the client. The RPD must meet criteria specified in section 18.4.

14.2.11 If the response for any quantitation ion exceeds the initial calibration curve range of the GC/MS system, sample dilution and reanalysis is an option. Variable trapping volume on the Autocan can be used to accomplish sample dilutions of up to 1:100. Trapping 50cc of sample (rather than 500) while still trapping 50cc of the internal standard mixture will yield a 1:10 dilution.

14.2.12 Perform all qualitative and quantitative measurements as described in Sections 14.4 and 14.5. Samples may be retained for up to 30 days from the date of sample collection for repeat analysis should the sample fail data review for any reason. After client approval or 30 days has elapsed, the canister should be cleaned along with a batch of other canisters, and one canister from each batch should be certified as described in section 7.4.

14.3 Analytical Sequence

START CHEMSTATION SOFTWARE:
From NT Desktop: Start/Programs/MSD ChemStation/Instrument #2/Instrument #2

The software will locate the instrument and all peripheral equipment. Once the software is fully loaded there will be two windows visible. Window one is the instrument control window. Instrument parameters are readily viewed from this window. The second window is the sequence control window. No instrument parameters are viewable from this window.

SEQUENCE SETUP

From menu: Method/Load
1. Load the method you want to use for analysis (i.e., A112102.m)
2. OK (to save changes)

From menu: Sequence/Run
3. Set current date in Data File Directory space (i.e., C:\MSDCHEM\2\DATA\060702\)
4. OK (to save changes)

From menu: Sequence/Edit Sample Log Table
1. Set data file name using current date using the following format MMDDYY##.d (e.g., 06070202.d)
2. Set up sequence order using the following format: (**NOTE:** Tune and CCV must always run first, followed by analysis of the method blank. The only exception to this is the ICAL sequence.)

LINE	TYPE	VIAL	DATA FILE	METHOD	SAMPLE NAME-INSTRUMENT
1	Sample	1	11240201	A112102	TUNE TOBFB112402-1
2	Sample	1	11240202	A112102	CCV TOSTD050
3	Sample	2	11240203	A112102	MBLK TOBLK112402-1
4	Sample	3	11240204	A112102	LCS TOLCS112402-1
5	Sample	4	11240204	A112102	LCSD TOLCS112402-1
6	Sample	5	11240205	A112102	SAMP ###########
7	Sample	6	11240207	A112102	SAMP ###########

...	Sample	...	...	A112102	...
32	Sample	32	11240231	A112102	SAMP ##########

NOTE: The number of samples, including tune and CCV that can be analyzed within the 24-hour window varies with each analysis. Use this list as a guide but always check that the samples were analyzed within 24 hours of the BFB injection.

3. OK (to save changes)

From menu: Method/Set New Default Paths

1. Update the method and data file paths using the current date (i.e., C:\MSDCHEM\1\DATA\060702\)
2. OK (to save changes)

Using Windows Explorer copy all of the method files from the previous day's folder into the current day's folder. Note: After each ICAL, the water/soil method is saved using the following format: matrix instrument MMDDYY of last ICAL (e.g., A112102.m).

TO START SEQUENCE:

From menu: Sequence/Run/Run Sequence

Start of the 24 hour sequence (as documented as the date/time stamp on the data file for the Tune Standard):

The analytical sequence for Initial Calibration is:

BFB (Tune Standard)
Calibration standard (S1)
Calibration standard (S2)
Calibration standard (S3)
Calibration standard (S4)
Calibration standard (S5)
Calibration standard (S6)
Calibration standard (S7)
Calibration Standard (S8)
Initial Calibration Verification Standard (ICV)
Method Blank (MBLK)

The analytical sequence for Sample Analysis is:

BFB
Continuing Calibration Verification Standard (CCV)
Method Blank (MBLK)
LCS (ICV)
LCS Duplicate (2nd ICV, prepared in separate canister)
Sample #1
Sample #1 Laboratory Duplicate (optional)
Samples #2, #3, etc. until the end of 24 hour tune period

NOTE THAT THE GC/MS SEQUENCE CAN BE STARTED BEFORE CHOOSING INSTRUMENT/RUN SEQUENCE FROM THE TEKLINK MENU. THIS WILL SAVE ON LIQUID NITROGEN USEAGE IF THE GC/MS SEQUENCE IS STARTED APPROXIMATELY 10 MINUTES AFTER STARTING THE TEKLINK SEQUENCE.

14.4 Data Interpretation - Qualitative Analysis

14.4.1 A compound is identified based upon Relative Retention Time (RRT) and by comparison of the sample mass ions with the mass ions of a standard of the suspected compound (standard reference ions). The reference mass ion ratio must be generated by the laboratory using the conditions of this method. The characteristic ions from the reference mass ion are defined to be the two or three ions of greatest relative intensity. See Attachment 2 for the ions to be monitored. Two criteria must be satisfied to verify identification: (1) elution of sample component at the same GC relative retention time (RRT) as those of the standard component; and (2) correspondence of the sample component and the standard component mass ions. Intensities of the characteristic ions must maximize in the same scan or within one scan of each other.

14.4.2 The RRT of the sample component is within ± 0.06 RRT units of the RRT of the standard component.

14.4.3 The relative intensities of the characteristic ions must agree within 20% of the relative intensities of these ions in the reference spectrum. (Example: For an ion abundance of 50% in the reference, the corresponding abundance in a sample spectrum can range between 30% and 70%.)

14.4.4 Structural isomers that produce very similar mass spectra must be identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs. The Manual Integration SOP 1255 is used for guidance in the integration of these two peaks and for other situations that may require analyst efforts to correct computer generated integrations that are not technically sound.

14.4.5 Identification is hampered when sample components are not resolved chromatographically or co-elute and produce mass spectra containing ions contributed by more than one compound. When gas chromatographic peaks obviously represent more than one sample component (i.e., a broadened peak with shoulder(s) or a valley between two or more maxima), appropriate selection of compound spectra and background spectra is important. Examination of extracted ion current profiles of appropriate ions can aid in the selection of spectra, and in qualitative identification of compounds, but each compound spectrum will contain extraneous ions contributed by the coeluting compound.

14.4.6 For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the purpose of the analyses being conducted. Computer generated library search routines must not use normalization routines that would misrepresent the library or unknown spectra when compared to each other. Only after visual comparison of sample spectra with the nearest library searches will the mass spectral interpretation specialist assign a tentative identification. Guidelines for making tentative identification are:

14.4.6.1 Relative intensities of major ions in the reference spectrum (ions >10% of the most abundant ion) must be present in the sample spectrum.
14.4.6.2 The relative intensities of the major ions must agree within ± 20%. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30 and 70%).
14.4.6.3 Molecular ions present in the reference spectrum must be present in the sample spectrum.
14.4.6.4 Ions present in the sample spectrum but not in the reference spectrum must be reviewed for possible background contamination or presence of coeluting compounds.
14.4.6.5 Ions present in the reference spectrum but not in the sample spectrum must be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks. Data system library reduction programs can sometimes create these discrepancies.

14.5 Data Interpretation - Quantitative Analysis

14.5.1 Once a compound has been identified, the quantitation of that compound must be based on the integrated abundance from the EICP of the primary characteristic ion. The internal standard used shall be the one nearest the retention time of that of a given compound. The responses of the internal standards in the samples must be within ± 40% of the internal standard responses for the daily CCV sample.

14.5.2 The concentration in the sample is determined using the average response factor (RF) from initial calibration data (13.2). See Section 15.1.1 for the equations describing internal standard calibration.

14.5.3 Where applicable or required, the concentration of any non-target compounds (TICs) identified in the sample is estimated. The same formulae must be used with the following modifications: The areas A_x and A_{is} must be from the total ion chromatograms, and the RF for the compound must be assumed to be 1. The resulting concentration must be reported indicating: (1) that the value is an estimate, and (2) which internal standard was used to determine concentration. Use the nearest internal standard free of interferences.

14.6 Record the following information in the appropriate logbook or data file. Include any deviations from this procedure. Analyst initials, date of analysis, sample number or ID, initial sample volume or weight processed, calibration standard sample or solution identifier, QC sample or solution identifier, internal standard solution identifier, any dilution information, readings from support equipment, data file name, instrument method name, visual observations, and any other information as deemed necessary.

14.7 Troubleshooting - The experience of the analyst performing GC/MS analyses is invaluable to the success of the methods. Each day that the analysis is performed, the daily calibration standard (CCV) must be evaluated to determine if the chromatographic system is operating properly. Questions that must be asked: Do the peaks look normal? Is the response obtained comparable to the response from previous calibrations? Careful examination of the standard chromatogram can indicate whether the column is still good, the injector is leaking, the injector septum needs replacing, etc. If any major changes are made to the system (e.g. column changed or detector cleaned), recalibration of the system must take place.

14.8 Routine Maintenance - Record all maintenance, including the problem encountered, steps taken to correct the problem, and verification that the problem has been corrected (i.e. tune passed).

14.8.1 Realign the tube in the Unity instrument if it fails the leak test. Change o-rings, filters, and seals as needed.

14.8.2 Bake out (using trap heating method) or change the Autocan Trap as needed (loss of sensitivity)

14.8.3 Clean the source on an as needed basis (loss of sensitivity or EMVoltage required to pass BFB and perform analyses is approaching 2500).

14.8.4 Repair leaks in the GC/MS system. The daily standard spectra auto-tune is very useful for detecting the need for source cleaning and/or leak repair.

14.8.5 Check the carrier gas supply; replace as necessary.

14.8.6 Replace purifier traps on carrier gas supply as needed- the use of indicating traps is a big help in determining the need for purifier replacement.

14.9 Sample Container Leak Test

The sample containers are pressurized to 30psia (15.3 psig) with zero air and allowed to stand on the cleanup assembly for a 12-hour period with the valves closed. After 12 hours, the container pressures are checked individually. If the canister pressure drops < 1.0 psi over the 12 hour period, the container is free of leaks. This test is performed when the container is cleaned and certified. If the client provides the sample container, a leak test will be performed when the container is cleaned and certified for return to the client.

15.0 DATA REDUCTIONS, CALCULATIONS, AND LOADING

15.1 The LIMS data system performs the calculations. Since each sample will have a preparation factor, this must be accounted for in the calculations.

15.1.1 The concentration in the sample is determined using the average response factor (RF) from the initial calibration data (13.2) and the following equation. The equation is based upon equivalent sample sizes of 500cc air volume trapped.

$$\text{Concentration (ppb)} = \frac{A_x * C_{is} * PF}{A_{is} * RF}$$

where:
A_x = Area of the characteristic ion for the compound being measured
C_{is} = Concentration of the specific internal standard (10ppbv for this method)
A_{is}= Area of the characteristic ion for the specific internal standard
RF= average response factor for compound being measured
PF = Preparation factor as defined in 14.1.2.

If another sample volume is analyzed, adjust the concentration using the factor: 500cc / volume sampled cc.

15.2 If appropriate, recalculate the concentration of the compound in the sample using the equations in Secs. 15.2.1, 15.2.2, and 15.2.3.

15.2.1 The concentration of the compound in the sample is reported ppbv. If conversion to $\mu g/m^3$ is required, calculate as follows:

$$\text{Concentration } (\mu g/m^3) = \frac{\text{Conc. (ppbv)} * MW}{24.45}$$

Where:
24.45 is the volume in L of 1 mole of an ideal gas at 25 °C and standard pressure.
Conversion of L to m^3 is cancelled out by conversion of mg to μg.
MW is the molecular weight

15.3 The procedure for uploading data into the LIMS system is detailed in SOP 1400 LIMS.

16.0 METHOD PERFORMANCE

16.1 Demonstration of Capability (DOC)

All parameters of interest must meet the method acceptance criteria before actual sample analysis begins. See SOP 1230 Training for the procedure to perform and document the DOC. The DOCs for the analysts performing this method are located in the analysts' training form folders located in the QA office files.

A quality control (QC) reference concentrate in air is required containing each compound at a concentration normally expected to be found in ambient air (0.2 to 40ppbv). The QC reference sample used is the LCS solution (see Section 10.7). The QC reference sample is made using stock standards prepared independently from those used for calibration. For this analysis, the LCS is the ICV standard which has a nominal concentration of 5 ppbv per compound. This analysis is performed in quadruplicate using 4 separately prepared canisters. For each analyte calculate the mean recovery. Note: X must be within 3.5 to 6.5 ppbv and s must be less than 1.5 ppbv and

the mean recovery must be in the range of 70 to 130%. If X and s and %R for all analytes meet the acceptance criteria, the system performance is acceptable and analysis of actual samples can begin. If any individual x or %R falls outside the range for accuracy or any individual s exceeds the precision limit, then the system performance is unacceptable for that analyte and corrective action must be taken.

Continuing Demonstration of Capability will be documented with four consecutive Laboratory Control Samples (LCS). This must be documented annually.

16.2 Comparison to Reference Method Data

EPA Method TO-15 provides guidance for the establishment of control limits for the LCS QC samples. Recovery limits of 70% to 130% are provided as initial benchmarks for performance (EPA Method TO-15 Section 11.4.2). These limits are designed for a wide variety of organic test methods. Individual compound performance may vary.

16.3 In-House Control Limits

Method performance data is on file in the laboratory QC department. Comparison of method performance data for the laboratory to the reference method criteria occurs when laboratory in-house acceptance limits are generated. In-house generated data is compared to the specifications of the reference method. If the in-house limits are within the specifications of the reference method, the control limits are updated in LIMS. If the in-house limits are not within specifications, an investigation is performed to determine the cause(s) of the problem and a corrective action is completed. The analysis may continue until enough data points are collected to regenerate new control limits. Any QC data generated outside of reference method limits during that time frame is flagged.

The laboratory maintains performance records to document the quality of data that is generated. Method accuracy for samples is assessed and records maintained. After the analysis of at least 20 laboratory control samples, calculate the average percent recovery (R) and the standard deviation of the percent recovery (S).

Control limits for method parameters are generated by the QC staff generates the method parameters and distributed to the analysts via updates to the LIMS control charts. The control limits are calculated based on in-house performance data. At a minimum, these limits are reviewed annually.

17.0 POLLUTION PREVENTION

The preparation of excessive volumes of laboratory reagents and standards shall be avoided so that waste and potential for pollution are minimized. Samples, reagents and standards shall be disposed in compliance with the lab waste disposal program, SOP 1130 Waste Management. With the consent of the client, the samples may be returned to their origin for treatment.

Uncontaminated paper waste, glass and cans should be separated for recycling. Laboratory staff is required to protect the laboratory and our clients' business information when disposing of recycled paper or waste from the facility.

18.0 DATA ASSESSMENT AND CRITERIA FOR QUALITY CONTROL MEASURES

Data assessment includes review of: proper sample condition, preservation, and storage; analysis within holding time limitations; deviations from the SOP, evaluation of performance based or in-house control limits, reference method limits or project specific limits.

The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When results of sample spikes indicate atypical method performance, a calibration verification standard is used to confirm the measurements were performed in an in-control mode of operation. The data review is conducted according to SOP 1250 Data Review.

18.1 Blanks

The method blank must contain less than the reporting limit for all target compounds. If the blank exceeds these limits, the source of contamination must be investigated and corrective actions taken. Re-analyze the method blank. If after re-analysis, the blank criteria is still exceeded, stop the analysis prior to sample analyses and correct the problem. Consult with the department manager for guidance. Refer to a client specific QAPP for additional guidance, if applicable.

If samples were analyzed with a contaminated method blank during unattended automated analysis, affected samples must be reanalyzed or data must be appropriately qualified if:

1) The concentration of a targeted compound in the blank is at or above the reporting limit as established by the SOP or by regulation, AND is greater than 1/10 of the amount measured in any sample.
2) The blank contamination otherwise affects the sample results as per the test method requirements or the individual project data quality objectives.

18.2 Laboratory Control Samples (LCS/LSCD)

The results of the individual batch LCS are calculated in percent recovery (%R) and compared to established acceptance criteria. Current acceptance criteria used are 70 - 130%; in-house LCS limits for air may be developed. For LCS Duplicate (LCSD), recovery limits must be met and the Relative Percent Difference (RPD) must be less than 25%. If the LCS is outside the acceptance criteria the analytical system is "out of control". Any affected samples associated with an out of control LCS must be reprocessed and reanalyzed or the results reported with appropriate data qualifiers. If after re-analysis the control criteria has not been met, the entire analysis batch must be re-analyzed. Always refer to a client specific QAPP for additional guidance.

18.3 Surrogates

Not applicable to this method.

18.4 Duplicates

The results from Laboratory Duplicates are designed to assess the precision of analytical results in a given matrix and are expressed as relative percent difference (RPD). See the QAM, Section 5.4 for the calculation for RPD.

Replicate samples will be analyzed whenever the client provides them. However, when they are not, then the LCS/LCSD pair must be analyzed per batch of 20 incoming samples. In both cases, reproducibility performance is defined as ± 25% RPD.

Note: It is an option to analyze the same can as a duplicate. The same acceptance criteria would apply.

For duplicates results outside established criteria corrective action must be documented or the data reported with appropriate data qualifying codes.

18.5 Matrix Spikes

Not applicable to this method.

18.6 Internal Standards

The results of the individual Internal Standard compounds on all samples, blanks, and spikes are calculated in percent recovery (%R) compared to the daily CCV sample and are compared to established acceptance criteria. If the internal standard recovery is outside the acceptance criteria, see Table 7, corrective action may be taken.

Table 7 Internal Standards

INTERNAL STD COMPOUND	CRITERIA (%)
Chlorobenzene-d_5	60 to 140
1,4-Dichlorobenzene-d_4	60 to 140
1,4-Difluorobenzene	60 to 140

18.6 Other

The laboratory will analyze standard reference materials and/or participate in relevant performance evaluation studies quarterly.

19.0 CORRECTIVE ACTIONS FOR OUT-OF-CONTROL DATA

The process for handling unacceptable and out of control data is found in SOP 230 Corrective Action.

If the CCV, MB, LCS/LCSD, lab duplicate, or internal standard recovery of any parameter falls outside the designated acceptance range, the laboratory performance for that parameter is judged to be out of control, and the problem must be immediately identified and corrected. The analytical result for that parameter in the samples is suspect and is only reported for regulatory compliance purposes with the appropriate corrective action form. Immediate corrective action includes reanalyzing all affected samples by using any retained sample before the expiration of the holding time. Final data results must be qualified in the client report for reported results not meeting the laboratory-defined criteria.

1) Review standards preparation logbooks. Check all calculations and ensure dilution factors are properly recorded.
2) Re-prepare the suspected standard or QC sample to identify possible preparation errors of the standard or QC sample.
3) Re-Analyze the samples when the CCV or LCS is not within acceptable limits, or the internal standard fails.
4) Perform routine preventative maintenance following manufacturer's specification. Record all maintenance in the instrument logbook.

20.0 CONTINGENCIES FOR HANDLING OUT-OF-CONTROL OR UNACCEPTABLE DATA

Every effort is made to prevent problems from occurring. When out of control or unacceptable data occurs the first option is to identify the problem and reanalyze the samples within the holding times. When this is not possible, the QA Manager and/or the Laboratory Director reviews data and discusses options with the client. Reanalysis or reporting the data with qualification are alternatives. Out of control or unacceptable data reported to the client must include the data qualifier, flag and discussion on the rationale for reporting.

Holding time exceedence, improper preservation and improper sample condition or storage are noted on the corrective action form and included on the final report.

Review the CCV standard response, LCS result, and internal standard recovery for acceptable performance for each batch of samples. Record any trends or unusual performance on a corrective action form. Final data results must be qualified in the client report for results not meeting the laboratory-defined criteria.

Manual integration must be minimized for standards and the method blank. Routine manual integration of the same parameters indicates a system performance problem. Correct this problem or note in the instrument analysis logbook the suspected causes for routine manual integration. Sign and date all manually integrated chromatograms.

20.1 The process for handling unacceptable and out of control data is found in the Laboratory QAM Section 11. The reporting of data that is out of control must be approved and documented by Quality Assurance Manager and either the Technical Manager or the Laboratory Director.

20.2 Client Requested Modifications:

20.2.1 Clients must request modifications from the laboratory SOP in writing to the lab.

20.2.2 The lab director, technical manager and quality assurance manager will evaluate the requested client deviations, determine the feasibly of the deviation and the potential effects on the data.

20.2.3 If it is determined that the lab will perform the requested deviations, the lab director, technical manager and quality assurance manager will decide if a method validation study is required.

20.2.4 The designated project manager will retain all documentation concerning the requested deviation, including all correspondence with the client, in the client folder.

20.2.5 The final analytical report must include the statement "*This report has analyses performed using client requested modifications* ".

21.0 WASTE MANAGEMENT

The STAT Analysis Corporation SOP 1130 Waste Disposal identifies proper waste management practices for the chemicals and biological materials used in this procedure. Samples are stored and discarded in accordance with SOP 1130 Waste Disposal.

22.0 REFERENCES

22.1 USEPA, 40CFR Part 136 Appendix B – Definition and Procedure for the Determination of the Method Detection Limit, Revision 1.11.

22.2 Method TO-15, Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Edition, 1999.

22.3 Method TO-14A, Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Edition, 1999.

22.4 Quality Assurance Manual, STAT Analysis Corporation, Revision 6, June 1, 2005.

22.5 SAP 003 Chemical Hygiene Plan

22.6 SOP 230 Corrective Action

22.7 SOP 1000 Control and Use of Laboratory Notebooks

22.8 SOP 1010 Analytical Standards and Reagents Receipt and Preparation

22.9 SOP 1040 General Laboratory Practices

22.10 SOP 1130 Waste Disposal

22.11 SOP 1210 Method Detection Limits

22.12 SOP 1230 Training

22.13 SOP 1250 Data Review

22.14 SOP 1255 Manual Integration

22.15 SOP 1400 LIMS

22.16 Manufacturers' Equipment Instruction Manuals

22.17 NIST Library of Reference Spectra, 1998

23.0 FORMS, FIGURES, TABLES, DIAGRAMS, FLOWCHARTS, ATTACHMENTS OR VALIDATION DATA

Attachment 1: MDLs And Reporting Limits for TO-14A and TO-15 Volatile Compounds

Attachment 2: Characteristic Ions For Volatile Compounds

Attachment 3: Volatile Internal Standards with Corresponding Compounds Assigned for Quantitation

Attachment 1
MDLs and REPORTING LIMITS FOR TO-14A and TO-15 VOLATILE COMPOUNDS

COMPOUND NAME	TO-14	TO-15	MDL, ppbv	Lower Reporting Limit, ppbv	Upper Reporting Limit, ppbv
Dichlorodifluoromethane	X	X	0.12665	0.20	50
Freon-114	X	X	0.02566	0.20	5
Vinyl Chloride	X	X	0.02473	0.20	50
Bromomethane	X	X	0.02376	0.20	50
Chloroethane	X	X	0.02828	0.20	50
Trichlorofluoromethane	X	X	0.02169	0.20	50
1,1-Dichloroethene	X	X	0.01534	0.20	50
Dichloromethane	X	X	0	2.00	50
Freon-113	X	X	0.01680	0.20	50
1,1-Dichloroethane	X	X	0.01680	0.20	50
cis-1,2-Dichloroethene	X	X	0.02169	0.20	50
trans-1,2-Dichloroethene		X	0.01680	0.20	50
Chloroform	X	X	0.02473	0.20	50
1,2-Dichloroethane	X	X	0.02376	0.20	50
1,1,1-Trichloroethane	X	X	0.01680	0.20	50
Benzene	X	X	0.02169	0.50	50
Carbon Tetrachloride	X	X	0.02376	0.20	50
1,2-Dichloropropane	X	X	0.02169	0.20	50
Trichloroethene	X	X	0.02473	0.20	50
cis-1,3-Dichloropropene	X	X	0.03360	0.20	50
trans-1,3-Dichloropropene	X	X	0.06994	0.20	50
1,1,2-Trichloroethane	X	X	0.01534	0.20	50
Toluene	X	X	0.02376	0.20	50
1,2-Dibromoethane	X	X	0.02376	0.20	50
Tetrachloroethene	X	X	0.01534	0.20	50
Chlorobenzene	X	X	0.02169	0.20	50
Ethylbenzene	X	X	0.04228	0.20	50
m,p-Xylene	X	X	0.11311	0.40	100
Styrene	X	X	0.09748	0.20	50
o-Xylene	X	X	0.05086	0.20	50
1,1,2,2-Tetrachloroethane	X	X	0.07226	0.20	50
1,3,5-Trimethylbenzene	X	X	0.12831	0.20	50
1,2,4-Trimethylbenzene	X	X	0.11436	0.20	50
1,3-Dichlorobenzene	X	X	0.05086	0.20	50
1,4-Dichlorobenzene	X	X	0.05086	0.20	50
1,2-Dichlorobenzene	X	X	0.05656	0.20	50
1,2,4-Trichlorobenzene	X	X	0.06135	0.20	50
Hexachlorobutadiene	X	X	0.08676	0.20	50
Propene		X	0.03067	1.00	50
Chloromethane	X	X	0.02376	0.20	50
1,3-Butadiene		X	0.02828	0.20	50
Isopropyl Alcohol		X	0.04946	0.20	50
Carbon Disulfide		X	0.01815	0.20	50

Attachment 1
MDLs and REPORTING LIMITS FOR TO-14A and TO-15 VOLATILE COMPOUNDS
(Continued)

COMPOUND NAME	TO-14	TO-15	MDL, ppbv	Lower Reporting Limit, ppbv	Upper Reporting Limit, ppbv
MTBE		X	0.07193	0.20	50
Vinyl Acetate		X	0.03564	2.00	50
2-Butanone		X	0.19664	0.50	50
Hexane		X	0.02376	1.00	50
Ethyl Acetate		X	0.20113	0.50	50
Tetrahydrofuran		X	0.14932	0.20	50
Cyclohexane		X	0.02169	0.20	50
Bromodichloromethane		X	0.03360	1.00	50
1,4-Dioxane		X	0.10219	0.20	50
Heptane		X	0.02169	0.20	50
4-Methyl-2-Pentanone		X	0.05940	1.00	50
2-Hexanone		X	0.04752	1.00	50
Dibromochloromethane		X	0.01680	0.20	50
Bromoform		X	0.02566	0.20	50
4-Ethyltoluene		X	0.09748	0.20	50
Benzyl Chloride		X	0.02376	0.20	50

Attachment 2: CHARACTERISTIC IONS FOR VOLATILE COMPOUNDS

#	Compounds	Retention Time (min.)	Primary Ion	Secondary Ion(s)
1	Freon-12	3.13	85	87
2	Freon-114	3.34	85	135
3	Vinyl Chloride	3.43	62	64
4	Bromomethane	3.74	94	96
5	Chloroethane	3.87	64	66
6	Trichlorofluoromethane	4.51	101	103
7	1,1-Dichloroethene	5.09	61	96,63
8	Dichloromethane	5.20	84	49
9	Freon-113	5.48	151	101,103
10	1,1-Dichloroethane	6.46	63	65
11	cis-1,2-Dichloroethene	7.39	96	61, 98
12	Chloroform	7.71	83	85, 47
13	1,2-Dichloroethane	8.5	62	64
14	1,1,1-Trichloroethane	8.77	97	99,61
15	Benzene	9.24	78	51
16	Carbon Tetrachloride	9.39	117	119
17	1,2-Dichloropropane	10.07	63	76
18	Trichloroethene	10.31	130	132,95
19	cis-1,3-Dichloropropene	11.16	75	77, 39
20	Trans-1,3-Dichloropropene	11.67	75	77,39
21	1,1,2-Trichloroethane	11.83	97	83,61
22	Toluene	12.10	91	92
23	1,2-Dibromoethane	12.77	107	109
24	Tetrachloroethene	13.26	164	129, 131, 166
25	Chlorobenzene	13.99	112	77,114
26	Ethylbenzene	14.41	91	106
27	m&p-Xylene	14.62	91	106
28	Styrene	15.05	104	78
29	o-Xylene	15.19	91	106
30	1,1,2,2-Tetrachloroethane	15.19	83	85
31	1,3,5-Trimethylbenzene	17.05	105	120
32	1,2,4-Trimethylbenzene	17.74	105	120
33	1,3-Dichlorobenzene	18.01	146	111, 148
34	1,4-Dichlorobenzene	18.14	146	111, 148
35	1,2-Dichlorobenzene	18.8	146	111, 148
36	1,2,4-Trichlorobenzene	22.89	180	182, 145
37	Hexachlorobutadiene	23.97	225	223, 227
38	Propene	3.36	41	42
39	Chloromethane	3.61	50	52
40	1,3-Butadiene	4.01	54	39
41	Isopropyl Alcohol	5.64	45	43, 59
42	Carbon Disulfide	6.58	76	78, 44
43	MTBE	7.71	73	57
44	Vinyl Acetate	7.85	43	86
45	2-Butanone	8.09	43	72
46	Trans-1,2-Dichloroethene	8.54	61	96, 98

Attachment 2: CHARACTERISTIC IONS FOR VOLATILE COMPOUNDS (Continued)

#	Compounds	Retention Time (min.)	Primary Ion	Secondary Ion(s)
47	Hexane	8.77	57	86, 41
48	Ethyl Acetate	8.83	43	88
49	Tetrahydrofuran	9.25	42	72, 71
50	Cyclohexane	10.59	84	41, 69
51	Bromodichloromethane	11.34	83	47, 129
52	1,4-Dioxane	11.38	88	58, 43
53	Heptane	11.69	71	100, 57
54	4-Methyl-2-Pentanone	12.27	58	85, 100
55	2-Hexanone	13.45	58	100, 85
56	Dibromochloromethane	13.61	129	81, 93
57	Bromoform	15.65	173	93
58	4-Ethyltoluene	17.47	120	105
59	Benzyl Chloride	18.23	126	91
	Internal Standards:			
38	Bromochloromethane	7.57	127	129,49
39	1,4-Difluorobenzene	9.62	114	88
40	Chlorobenzene-d5	13.94	117	119,82

Attachment 3: Volatile Internal Standards with Corresponding Compounds Assigned for Quantitation

Bromochloromethane (I)	1,4-Difluorobenzene (I)	Chlorobenzene-d5 (I)
Freon-12	1,2-Dichloropropane	Chlorobenzene
Freon-114	Trichloroethene	Ethylbenzene
Vinyl Chloride	Cis-1,3-Dichloropropene	m,p-Xylene
Bromomethane	Trans-1,3-Dichloropropene	Styrene
Chloroethane	1,1,2-Trichloroethane	o-Xylene
Trichlorofluoromethane	Toluene	1,1,2,2-Tetrachloroethane
1,1-Dichloroethene	1,2-Dibromoethane	1,3,5-Trimethylbenzene
Dichloromethane	Tetrachloroethene	1,2,4-Trimethylbenzene
Freon-113	Bromodichloromethane	1,3-Dichlorobenzene
1,1-Dichloroethane	1,4-Dioxane	1,4-Dichlorobenzene
Cis-1,2-Dichloroethene	Heptane	1,2-Dichlorobenzene
Chloroform	4-Methyl-2-Pentanone	1,2,4-Trichlorobenzene
1,2-Dichloroethane	2-Hexanone	Hexachlorobutadiene
1,1,1-Trichloroethane	Dibromochloromethane	Bromoform
Benzene		4-Ethyltoluene
Carbon Tetrachloride		Benzyl Chloride
Propene		
Chloromethane		
1,3-Butadiene		
Isopropyl Alcohol		
Carbon Disulfide		
MTBE		
Vinyl Acetate		
2-Butanone		
Trans-1,2-Dichloroethene		
Hexane		
Ethyl Acetate		
Tetrahydrofuran		
Cyclohexane		

(I) = Internal Standard

STA Analysis Corporation:

STANDARD OPERATING PROCEDURE 4020

SEMIVOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS) (EPA Method 8270C)

Draft
Revision 04
Effective Date: xxx, 2009

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1.0 IDENTIFICATION OF TEST METHOD

SOP Title: SemiVolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS) is abbreviated as SVOC in laboratory records.

2.0 APPLICABLE MATRICES

Methylene chloride and organic solvent extracts from soil, sediment, ground and surface water, and mobility extracts are analyzed using this method.

3.0 DETECTION LIMITS

The lab follows the procedure found in 40CFR Part 136B to determine the MDL for each matrix type on an annual basis. See the STAT Analysis SOP 1210 for the MDL procedure, frequency and acceptance criteria. The MDLs measured by the lab and all supporting documentation are in the laboratory QA files for review.

The laboratory determined MDL must always be less than the reporting limit (RL), which is determined by the lowest calibration standard. The RLs will usually range from three to ten times the laboratory measured MDLs but this relationship may vary dependent on dilution of sample aliquots, matrix interferences, moisture adjustments (in solid samples), or method-specified requirements. Attachment 1 contains the current MDLs and reporting limits (RLs) for this SOP.

4.0 SCOPE AND APPLICATION

4.1 This standard operating procedure describes in detail the precise methods used at STAT Analysis Corporation for the analysis of environmental samples for SemiVolatile Organic Compounds (SVOCs) by GC-MS. This SOP as written is to be applied when SW-846 Method 8270C is requested. This SOP is used to determine the concentration of SVOC's in extracts prepared from all types of solid waste matrices, soils, and ground water.

4.2 SOP 4020 can be used to quantitate SVOCs that are soluble in methylene chloride and other organic solvents and are capable of being eluted without derivatization as sharp peaks from a gas chromatographic fused-silica capillary column coated with a slightly polar silicone. See Attachment 2 for a list of compounds and their characteristic ions that have been evaluated on the specified GC/MS system.

4.3 The reporting limits (RLs) for this SOP are shown in Attachment 1 for soils and water. RLs will be proportionately higher for sample extracts and samples that require dilution or reduced sample size to avoid saturation of the detector.

4.4 This method is restricted to use by or under the supervision of analysts experienced in the use of a Gas Chromatograph/Mass Spectrometer (GC/MS) and skilled in the interpretation of mass spectra. Each analyst must demonstrate the ability to generate acceptable results with this method.

5.0 SUMMARY OF TEST METHOD

5.1 Prior to using this method, the samples must be prepared for the GC/MS using the appropriate sample preparation and cleanup SOPs (Section 14.1). Soil and solid samples are not pH adjusted before extracting with methylene chloride. Aqueous samples are acidified, extracted with methylene chloride then made basic and extracted again with methylene chloride. This method describes chromatographic conditions that will allow for the separation of the compounds in the extract and for their qualitative and quantitative analysis by gas chromatography/mass spectrometry. Identification of target analytes is accomplished by comparing component retention times to those of authentic standards and by comparing their mass spectra with the electron impact (or electron impact-like) spectra of authentic standards. Quantitation is accomplished by comparing the response of a major quantitation ion relative to an internal standard using a five-point calibration curve.

5.2 **Method Modifications from Reference** – This SOP is based on EPA Method 8270C except that no polychlorinated biphenyls (PCBs), pesticides, organophosphate esters or quinolines are reported. PCBs and Pesticides are reported using STAT Analysis SOP 4050. Organophosphate esters and quinolines are not reported by the lab. The Mass Spectrometer Tuning criteria used in this SOP is referenced from the CLP Statement of Work (SOW) for Organic Analyses Revision OLM04.2 May 1999. This is an option in Method SW-846 8270C.

6.0 DEFINITIONS

The STAT Analysis Quality Manual Section 19.0 contains all the definitions of standard terms used in SOPs.

7.0 INTERFERENCES

7.1 Raw GC/MS data from all blanks, samples, and spikes must be evaluated for interferences. Determine if the source of interference is in the preparation and/or cleanup of the samples and take corrective action to eliminate the problem.

7.2 Contamination by carryover can occur whenever high-concentration and low-concentration samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed out between samples with solvent. Whenever an unusually concentrated sample is encountered, the sample after it may need to be reanalyzed to check for cross contamination.

8.0 SAFETY

Methylene chloride is a suspected carcinogen as are numerous compounds analyzed by this method. Proper personal protective equipment including safety glasses, nitrile gloves and a lab coat are required during different parts of this method. Other safety precautions must be conducted in accordance with the Chemical Hygiene Plan (STAT QA SOP 003). Other actions can also be applied if deemed necessary. A reference file of Material Safety Data Sheets (MSDS) is available to all personnel involved in this method.

9.0 EQUIPMENT AND SUPPLIES

The following apparatus is recommended for performing this procedure. Equivalent items can be used, if with their use, the analytical and QA/QC requirements in this SOP can be met. All catalog numbers in this SOP are current as of the effective date and thereafter subject to change.

9.1 Gas Chromatograph/Mass Spectrometer system (GC/MS) (SVOC-2)

9.1.1 Gas chromatograph(GC) – Agilent 6890 and 6890N with electronic flow control gas chromatograph with the column directly coupled to the source. Equipped with an Agilent Autosampler Model 7683 and 7683B.

9.1.2 Column - 30 m x 0.25 mm ID (or 0.33mm ID) 0.25µm film thickness silicone-coated fused-silica capillary column (J&W Scientific HP-5MSI).

9.1.3 Mass spectrometer(MS) - Agilent 5973N and 5975 Inert Mass Selective Detector.

9.1.4 Data system - An Agilent Kayak computer system using G1701CA Chemstation Version C.00.01 to interpret data is attached to the GC.Agilent technologies Environmental Chem Station 0.02.00.237. LAN ID 105.1.100.

9.1.5 NIST Library of Reference Spectra, Edition Number NIST98

9.2 Gas Chromatograph/Mass Spectrometer system (GC/MS) (SVOC-5)

9.2.1 Gas chromatograph(GC) – Agilent 6890N with electronic flow control gas chromatograph with the column directly coupled to the source. Equipped with an Agilent Autosampler Model 7683B

9.2.2 Column - 30 m x 0.25 mm ID (or 0.33mm ID) 0.25µm film thickness silicone-coated fused-silica capillary column (J&W Scientific HP-5MSI).

9.2.3 Mass spectrometer(MS) - Agilent 5975i

9.2.4 Data system - An Agilent Kayak computer system using C1701DA Chemstation Version D.02.00.237 to interpret data is attached to the GC.

9.3 Micro syringes - 10 µL, 25 µL, 100 µL, 250 µL, 500 µL and 1,000 µL.

9.4 Volumetric flasks, Class A - 10 mL, 25 mL, 50 mL with ground glass stoppers.

9.5 Glass vials - 2-mL, for GC auto sampler with Teflon-lined screw caps or crimp tops.

9.6 Amber glass vials - 10 mL with Teflon-lined screw caps

10.0 REAGENTS AND STANDARDS

The following reagents and standards are required to perform this procedure. When instructions are given on how to prepare a specific volume of a reagent or standard, larger or smaller volumes can be prepared as needed so long as the final concentrations remain the same. Any other deviations from the reagents or standards listed in this SOP could be detrimental to the quality of the data produced. Such deviations would have to be approved and documented (see SOP QA 230 Corrective Action). Equivalent items can be used, if with their use, the analytical and QA/QC requirements in this SOP can be met.

Instructions for labeling and record keeping of reagents and standards are contained in SOP 1010 Analytical Standards and Reagents Receipt and Preparation.

10.1 Analytical reagent grade chemicals shall be used in all tests. Unless otherwise indicated, all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.

10.2 Organic-free reagent water - All references to water in this SOP refers to Type II reagent water (in-house system).

10.3 Stock Standard solutions - Standard solutions can be prepared from pure standard materials or purchased as certified solutions (e.g., SV standards). The routine laboratory practice is to purchase these standards from approved vendors. The standards used are: 8270 MegaMix (Restek Catalog # 31686), 605-Benzidines Standard (Restek Catalog # 31030), Custom 8270 Addition (Restek Catalog # 555680), Base/Neutral Surrogate Spike Mix (Restek Catalog # 31072) and Acids Surrogate Spike Mix (Restek Catalog # 31003). Stock standard solutions and QC solutions are stored at < -10°C and must be replaced after six months, or sooner if comparison with quality control check samples indicates a problem. Different storage conditions and expiration dates of other solutions are noted as warranted.

10.3.1 Secondary Stock Standard Solution – This solution is made using the individual Stock Standard solutions. Using microliter syringes, the following amounts of each Stock Standard solution is injected into a 10 mL volumetric flask. The solution is brought to volume with methylene chloride. The final concentration of each component is listed in Table 1. Note: this Secondary Stock Standard solution is also used as the high level calibration standard. It is also the source solution to prepare the calibration standards in Section 10.4. This standard is stored at < -10°C in a 10 mL amber screw cap vial equipped with a Teflon lined cap. It is freshly prepared every six months, or sooner if check standards indicate a problem.

Table 1 Secondary Stock Standard Solution

Stock Solution	Conc. Stock (µg/ml)	Vol. Stock (µL)	Final Conc. (µg/ml)
8270 Mega-mix	500-1000	1600	160
605 Benzidines	2000	800	160
Custom 8270 Addition	2000	800	160
B/N Surr.	5000	320	160
Acid Surr.	1500	1067	160

10.4 Calibration standards - A minimum of five calibration standards are prepared. The low standard is the RL and above the MDL. The others define the working range of the GC/MS system. Calibration standards in current use: 5, 10, 20, 50, 80, 120 and 160 µg/ml. (Table 2). Using microliter syringes, the following amount of the Secondary Stock solution is injected into a 1 ml syringe. The solution is brought to volume with Methylene chloride. The final concentration of each component is listed in Table 2. Each solution is transferred to an autosampler vial. Each 1 mL aliquot of calibration standard must be spiked with 10 µL of the internal standard solution (4000 µg/ml) prior to analysis. Storage is as indicated in 10.1.4. The continuing calibration verification standards (CCV) are prepared weekly and stored at 4°C. Levels 2, 3 and 4 (20, 50, 80 µg/mL) are used for the CCVs.

Table 2 Calibration Standards

Level	Volume (µL) Secondary Stock	Volume (µL) $MeCl_2$	Final Concentration (µg/ml)
1	31.25	968.75	5
2	62.5	937.5	10
3	125	875	20
4	312.5	687.5	50
5	500	500	80
6	750	250	120
7	1000	0	160

10.5 Surrogate standards - The surrogate standards phenol-d_6, 2-fluorophenol, 2,4,6-tribromophenol, nitrobenzene-d_5, 2-fluorobiphenyl and p-terphenyl-d_{14} (1,2-dichlorobenzene-d_4, 2-chlorophenol-d_4 are optional surrogate compounds). Surrogate stock solutions are purchased from Supelco (Cat. No. 4-7261 and 4-7262). The spike solution is prepared by injecting 1000 µL of the stock standard solution, concentration of 5000 µg/mL for Base/Neutrals and 10000 µg/mL for Acids, into a 100mL volumetric flask. The flask is diluted to the mark with methanol for a final concentration of 50 µg/mL for Base/Neutral surrogates and 100 µg/mL for Acid surrogates. All samples, blanks, LCSs, and MS/MSDs are spiked with 1.0 mL of the surrogate spike solution prior to extraction. This standard is stored at < -10°C in an amber glass vial with a Teflon lined screw cap.

10.6 Internal standard solutions - The internal standards used are 1,4-dichlorobenzene-d_4, naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, and perylene-d_{12}. The SV internal standards containing the recommended compounds at 4000 µg/mL are purchased from Supelco (cat. no. 4-7906). Just prior to analysis 10 µL of the solution (4000 µg/ml) is injected into each sample vial. Store at room temperature per manufacturer's instructions when not being used. The internal standards permit most of the compounds of interest in a chromatogram to have retention times of 0.80-1.20 relative to one of the internal standards. Use the base peak ion from the specific internal standard as the primary ion for quantitation (see Attachment 2, e.g., for 1,4-dichlorobenzene-d_4, use 152 m/z for quantitation). If interferences are noted, use the next most intense ion as the quantitation ion.

10.7 GC/MS tuning standard - A methylene chloride solution containing 50 ng/µL each of decafluorotriphenylphosphine (DFTPP), 4,4'-DDT, pentachlorophenol, and benzidine is used to tune the mass spectrometer, and to verify injection port inertness and GC column performance. The SV tuning standard is purchased from Supelco (Cat. No. 4-7387). Store at < -10°C when not being used. Inject 1 µL of this standard at the start of every 12 hours of operation.

10.8 Laboratory Control Sample/Matrix Spike standards - The LCS/matrix spike contains all compounds listed in Attachment 1. Samples will be spiked with acid compounds at 100 mg/sample, 3330 mg/kg for soil and 100 mg/L for water and base/neutral compounds at 50 mg/sample, 1670 mg/kg for soil and 50 mg/L for water (see SOP 3500 for LCS/Matrix Spike Solution preparation). This standard is stored at < -10°C in an amber glass vial with a Teflon lined screw cap.

10.9 Initial Calibration Verification Standard – A standard prepared from a different source at the midpoint of the calibration to verify the initial calibration. The solution concentration is 50 µg/mL. The ICV solution is made using the individual ICV Stock Standard solutions purchased from Supelco. Using microliter syringes, the following amounts of each Stock Standard solution is injected into a 10 mL volumetric flask. The solution is brought to volume with methylene chloride. The final concentration of each component is listed in Table 1a. This standard is stored at < -10°C.

Table 1a ICV Secondary Stock Standard Solution

Stock Solution	Conc. Stock (µg/ml)	Vol. Stock (µL)	Final Conc. (µg/ml)
TCL Base/Neutrals Mix 1	2000	250	50

TCL Base/Neutrals Mix 2	2000	250	50
TCL PNA Mix	2000	250	50
TCL Phenols Mix	2000	250	50
TCL Benzidine Mix	2000	250	50
TCL Hazardous Mix 1	2000	250	50
TCL Hazardous Mix 2	2000	250	50
3-Methyl Phenol Standard	5000	100	50
1-Chloronaphthalene Standard	2000	250	50
B/N Surrogate	5000	100	50
Acids Surrogate	10000	50	50

10.8 Acetone, hexane, methylene chloride, isooctane, toluene and other appropriate solvents, pesticide quality or equivalent.

10.9 Helium – UHP grade

11.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

11.1 Containers used to collect samples for the determination of semivolatile organic compounds are glass: 1 Liter bottles for water samples and various size jars for soil samples. They are equipped with screw caps with Teflon liners. Water samples containing residual chlorine should be field treated to remove the chlorine prior to collection. Plastic containers or lids may NOT be used for the storage of samples due to the possibility of sample contamination from the phthalate esters and other hydrocarbons within the plastic.

11.2 Samples must be stored under refrigeration at between 0.1 and 6.0°C. Extraction must be within 7 days from sampling date for water and 14 days for solids. Sample extracts are stored in the dark at between 0.1 and 6.0°C and must be analyzed within 40 days of extraction.

11.3 No chemical preservation is required for this method.

11.4 All samples are stored away from all standards, reagents, food, and other potentially contaminating sources in order to prevent cross contamination.

12.0 QUALITY CONTROL

The following details the QC requirements that apply to this analysis. Each Quality Control Indicator (QCI) provides information pertaining to either method or individual sample performance. Our goal is to produce defensible data of known and documented quality. The results of these Quality Control Indicator (QCI) samples are used to assess the acceptability of data.

12.1 Blanks

Method Blank analysis is performed to determine if any contamination is present in the analytical process and is used to evaluate acceptance of the batch of samples. A method blank shall be prepared once per preparation batch of 20 or less samples per matrix type. If more than 20 samples are prepared a second blank shall be prepared after the twentieth sample. The method blank shall be processed through all preparatory steps used for the samples, including cleanup procedures. The blank shall be analyzed using the same instrument and conditions as the samples.

The Solvent Blank, clean solvent injected into the GC/MS, is used to monitor the GC/MS system for potential cross-contamination from one sample to another or for residual contamination in the system.

12.2 Calibration Verification

An Initial Calibration Verification (ICV) standard containing all of the target analytes reported in this method (refer to section 10.9) shall be analyzed immediately after the completion of the initial calibration. The ICV shall be purchased from a second source to verify analyte concentrations.

A Continuing Calibration Verification (CCV) standard containing all of the target analytes reported in this method (refer to section 10.9) shall be analyzed at the start of every 12 hour analytical run, immediately following the tune check standard.

12.3 Laboratory Control Sample (LCS)

The LCS is used to evaluate the performance of the total analytical system, including all preparation and analysis steps. The LCS shall be prepared once per preparation batch of 20 or less samples per matrix type. If more than 20 samples are prepared a second LCS shall be prepared after the twentieth sample. The LCS shall be processed through all preparatory steps used for the samples, including cleanup procedures. The LCS shall be analyzed using the same instrument and conditions as the samples. Refer to section 10.8 for LCS analytes and concentrations.

12.4 Surrogates

The surrogates used for this method are added to all samples, standards, and blanks. Refer to section 10.5 for preparation and concentration instructions.

12.5 Duplicates

Duplicates of field samples or of the LCS must be prepared in compliance with the method requirements and client directives. Duplicate LCS's are prepared for sample where it would be impractical to prepare a matrix spike and matrix spike duplicate (e.g., wipes). Reproducibility performance would be the same as for a matrix spike/matrix spike duplicate.

12.6 Matrix Spike and Matrix Spike Duplicate (MS/MSD)

MS/MSDs indicate the effect of the sample matrix on the precision and accuracy of the results generated using the selected method. This information does not determine the validity of the entire batch. MS/MSDs must be analyzed at a minimum of 1 per 20 samples per matrix per preparation procedure, or one per preparation batch, or as specified by the required test method. For cases where the sample cannot be divided (e.g., wipes, air samples, not enough sample provided by customer) and

thus a MS/MSD pair cannot be prepared in the preparation batch, an LCS/LCSD pair is prepared and analyzed to measure precision. Samples chosen for matrix spiking are rotated among different clients and/or different client projects. This is accomplished through communication between the Department Manager and the analyst. In addition, designated samples, as indicated by client request or contract requirement, are matrix spiked. The MS/MSD pair shall be processed through all preparatory steps used for the samples. They shall be analyzed using the same instrument and conditions as the samples. Refer to section 10.8 for MS analytes and concentrations. Some clients may require different spiking levels and/or target analytes, these specific needs are documented on the request for analysis forms.

12.7 Internal Standards

The internal standards used for this method are added to all samples, standards, and blanks. Refer to section 10.6 for preparation and concentration instructions.

13.0 CALIBRATION AND STANDARDIZATION

13.1 Mass SpectrometerTuning

Each GC/MS system must be software-tuned to meet the criteria in Table 3 for a 50 ng injection of DFTPP. Analyses must not begin until all these criteria are met. Tuning criteria used in this SOP is referenced from the CLP Statement of Work (SOW) for Organic Analyses Revision OLM04.2 May 1999.

Using the ChemStation software to tune the GC/MS perform the following steps:
Set oven temperature to 250 °C (the elution temperature for DFTPP)
On the Instrument Control Panel click on View/Manual Tune…
On the Manual Tune Panel click on File/Load Tune Values/ and select DFTPP.u
On the Manual Tune Panel click on Tune/DFTPP Tune
The software automatically adjusts the tune parameters using PFTBA to meet the criteria in Table 3.
After the software has completed the tune click on File/Save Tune Values/ and select DFTPP.u and save the new parameters.
Click on View/Instrument Control to start analyzing standards and samples.

Table 3 Acceptance Criteria for DFTPP

Target Mass	Relative to Mass	Lower Limit%	Upper Limit%
51	198	30	80
68	69	0	2
69	198	0	100

70	69	0	2
127	198	25	75
197	198	0	1
198	198	100	100
199	198	5	9
275	198	10	30
365	198	1	100
441	443	0.01	100
442	198	40	110
443	442	15	24

Using the autosampler, inject 1 µL of DFTPP tuning standard solution on to the column. Analyze the solution using the DFTPP method which accelerates the elution of the compounds of interest.

Background subtraction must be straightforward and designed only to eliminate column bleed or instrument background ions. Obtain a background-corrected mass spectrum of DFTPP and confirm that all the key m/z criteria in Table 3 are achieved. Three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction is required, and must be accomplished using a single scan no more than 20 scans prior to the elution of DFTPP. Do not background subtract part of the DFTPP peak. Option: a single scan with background subtraction can also be used to evaluate the DFTPP spectrum. Note: the tuning file used to obtain and evaluate the DFTPP criteria must also be used to obtain and evaluate the sample data. If the criteria are not passed, the analyst must perform needed maintenance, retune the mass spectrometer and repeat the test until all criteria are achieved.

The GC/MS tuning standard must also be used to assess GC column performance and injection port inertness. Degradation of DDT to DDE and DDD must not exceed 20%. The following formula is used to calculate the percent breakdown:

$$\% \text{ breakdown of DDT} = \frac{\text{sum of degradation peak areas (DDE + DDD)} * 100\ \%}{\text{sum of all peak areas (DDT + DDE + DDD)}}$$

Benzidine and pentachlorophenol must be present at their normal responses, and no peak tailing must be visible. If degradation is excessive and/or poor chromatography is noted, the injection port may require cleaning. It may also be necessary to cut off an additional 10 to 20 cm of the capillary column.

To generate a custom report that calculates the % breakdown of DDT perform the following steps. Within the Data Review software click on Quant/QEdit Quant Result… Verify that all of the target peaks are correctly identified. Exit QEdit and click on CustRpt/Print Report. To review the report before printing click on CustRpt/Custom Reports…/ Select Edit Template DFTPP.CRT/OK. The report can be printed by clicking on the printer button or clicking on File/Print/OK.

Note: the 12 hour tune period begins at the start of the DFTPP analysis which is recorded as the data acquisition start time on the data file. The last valid calibration standard in the ICAL must have a data acquisition start time less than 12 hours from the start of the tune period.

13.2 **Initial Calibration (ICAL)**

13.2.1 Analyze 1 µL of each calibration standard and tabulate the area of the analyte against concentration for each compound. Calculate response factors (RFs) for each compound in each calibration standard as follows:

$$RF = \frac{A_x * C_{is}}{A_{is} * C_x}$$

where:
A_x = Area of the characteristic ion for the compound being measured.
A_{is} = Area of the characteristic ion for the specific internal standard.
C_{is} = Concentration of the specific internal standard (40 ng/µL for this method)
C_x = Concentration of the compound being measured (ng/µL = µg/mL = mg/L).

13.2.2 Calculate the average response factor ($\overline{RF}$) for each compound as follows:

$$\overline{RF} = (S\ RF_1 \text{ to } RF_n)/n$$

where: RF = RF for each of the calibration levels (i.e., 5)
n = Number of RF values (i.e., 5)

13.2.3 A system performance check must be performed to ensure that minimum average RFs are met before the calibration curve is used. For semivolatiles the System Performance Check Compounds (SPCCs) are: N-Nitroso-di-n-propylamine, Hexachlorocyclopentadiene, 2,4-Dinitrophenol, and 4-Nitrophenol. The minimum acceptable average RF for these compounds is 0.050. If it is determined that one calibration level has an unacceptable response, that level may be reanalyzed once. If the minimum average RF is still not met, corrective action must be taken and the calibration sequence repeated. If any major changes are made to the system (e.g. column changed or detector cleaned), recalibration of the system must take place.

13.2.4 Calibration Check Compound (CCC) responses are monitored to check the integrity of the system. The CCCs are as follows:

Base/Neutral Fraction	Acid Fraction
1,4-Dichlorobenzene	Phenol
Hexachlorobutadiene	2-Nitrophenol
Acenaphthene	2,4-Dichlorophenol
N-Nitrosodiphenylamine	4-Chloro-3-methylphenol

Fluoranthene	2,4,6-Trichlorophenol
Di-n-octyl phthalate	Pentachlorophenol
Benzo(a)pyrene	

Using the RFs from the initial calibration, calculate the percent relative standard deviation (%RSD) for the Calibration Check Compounds (CCC).

To calculate %RSD: $\%RSD = 100\% \times SD/\overline{RF}$

where:

%RSD = % Relative Standard Deviation

$\overline{RF}$ = average of initial RFs for a compound
SD = standard deviation (n-1) of average RFs for a compound

To calculate Standard Deviation (n-1 degrees of freedom)

$$SD = \sqrt{\sum_{i=1}^{N} \frac{(RF_i - \overline{RF})^2}{n-1}}$$

where: RF_i = RF for each of the 5 calibration levels
n = Number of RF values (i.e., 5)

13.2.5 If the %RSD of any CCC compound is > 30%, then the chromatographic system is too reactive for analysis to begin. Clean or replace the injector and/or capillary column, then repeat the calibration procedure beginning with section 13.2.1.

13.2.6 Linearity - If the %RSD of any compound is 15% or less, then the relative response factor is assumed to be constant over the calibration range, and the average relative response factor is used for quantitation. If the %RSD is greater than 15%, first order linear regression is used. The calibration curve must meet the requirements for curve fitting listed in SW-846 8000B and the correlation coefficient is = 0.99. The equation is not forced through the origin.

13.2.7 Retention Times: The Relative Retention Times (RRT) of each compound in each calibration standard should be within ± 0.06 RT units.

13.2.8 Before sample analysis can begin, a Initial Calibration Verification (ICV) (see Sec. 10.9) must be performed. The ICV results must be within the acceptance criteria as established for the CCV compounds (Section 13.3). Other components should be recovered within 70 to 130% of the true value. Note: Benzidine is one exception: Recovery of > 50% is acceptable for this compound.

NOTE:

1. All calibration curves must have a unique identifier. It is recommended that the calibration date be incorporated into the identifier for easy reference.
2. All initial calibration standards must be analyzed within the 12 hour DFTPP tune window.
3. Calibration must be completed (all standard levels analyzed) within 24 hours or the entire calibration sequence must be repeated. If the calibration was not completed in the first tune window it may continue into a second tune window. Standard calibration levels from either tune window can be used. An exception follows: If DFTPP criteria does not pass criteria for the second tune window and major maintenance was done to the instrument or the Mass Spectrometer tuning parameters were adjusted in order to obtain an acceptable tune for DFTPP, the entire calibration sequence must be repeated.
4. All initial calibration standards must be analyzed as a group. No field sample analyses are allowed during the calibration sequence.
5. Do not add calibration standards and update the curve after the original calibration date.
6. Multiple analyses of the same calibration level are not allowed to be included in the calibration curve.
7. Compound responses cannot be selected from different analyses of the same calibration level (i.e. all compound responses for level 1 must come from the same data file).
8. If more than five calibration levels are analyzed, it is permissible to either drop the low compound concentration (poor response) or the high compound concentration (detector saturation). It is not allowed to drop a point in the middle of the curve, unless as discussed in Item 8.
9. If more than five calibration levels are analyzed, it is permissible to drop an entire level if the analyst can document a specific reason or reasons why that level should be excluded. Mechanical failure, significant loss of all analyte responses possibly due to poor technique in standard preparation, or software malfunction during data acquisition (system did not acquire all compound data) are plausible reasons. The reason must be justified and documented. The supervisor should review this situation and approve the analyst's decision.
10. The need to analyze more than two analyses of the same calibration level indicates a potential problem with the secondary stock solution. Prepare a fresh secondary stock solution and repeat all seven calibration levels. It is recommended that all calibration standard levels come from the same secondary stock solution.
11. Manual integration must only be used if the software fails to properly integrate the peak. If manual integration is used for a particular compound, all levels of that compound do not have to be manually integrated, but all levels must be integrated in a similar manner. Example: the computer generated integration of a compound in the low level standard is not technically sound. A manual integration of the compound is performed (due to baseline noise, etc) in order to achieve a technically sound integration. Other levels of the compound are integrated correctly by the computer. The manual integration of the low level must match, as best as possible, the computer generated integrations for all other levels.
12. If any compound in the mid-point level is manually integrated, the integration of this compound must be reviewed for every continuing calibration standard and QC check solution (i.e. LCS, and Matrix Spike) to ensure that the integration is the same as the manual integration performed in the initial calibration (ICAL) mid-point. A consistent manner of integration must be achieved.

13. All manual integrations must be reviewed and approved at the supervisory level.

13.3 Continuing Calibration Verification (CCV)

13.3.1 The mass spectrometer must pass tune criteria (see Section 13.1) every 12 hours during analysis of samples.

13.3.2 A continuing calibration verification (CCV) sample is analyzed every 12 hours during analysis of samples. Different standards are analyzed for the CCV such that a wider range of the calibration curve is verified. For example: on successive days analyze the 20 µg/mL, then the 50 µg/mL and on the third day, the 80 µg/mL standard solution. Compare the response factors, of the SPCC's and the CCC's, and the internal standards from the CCV with the following criteria.

13.3.3 The SPCC compounds must have an RF = 0.05.

13.3.4 Control limits for the CCC compounds are ± 20% difference from the ICAL Response Factor (RF) if the average RF is used for quantitation, or ± 20% drift from the true concentration of the CCV compound if linear regression is used.

13.3.5 The areas of the internal standards in the CCV must be between –50% and +200% of the respective areas of the internal standards in the ICAL mid-point calibration standard.

13.3.6 The retention times of the internal standards in the CCV must be within ± 30 seconds of the respective retention times of the internal standards in the ICAL mid-point calibration standard.

13.3.7 If the CCV results obtained are outside the acceptance criteria, corrective actions must be performed. If routine corrective actions fail to produce an acceptable second consecutive (immediate) CCV, then either the lab has to demonstrate performance after corrective action with two consecutive successful CCVs, or a new ICAL must be performed. If the instrument has not demonstrated acceptable performance, sample analyses cannot continue until a new ICAL is established and verified with an ICV. However, sample data associated with an unacceptable CCV may be reported as qualified data under the following special conditions:

13.3.7.1 When the acceptance criteria for CCV are exceeded high, i.e., high bias, and there are associated samples that are non-detects, then those non-detects may be reported. Otherwise the samples affected by the unacceptable calibration verification must be reanalyzed after a new ICAL has been established, evaluated and accepted.

13.3.7.2 When the acceptance criteria for the CCV are exceeded low, i.e., low bias, those sample results may be reported if they exceed a maximum regulatory limit/decision level. Otherwise the samples affected by the unacceptable verification must be reanalyzed after a new ICAL is established and verified with an ICV.

13.3.7.3 When the acceptance criteria for the CCV are exceeded and it is not possible to reanalyze the sample due to limited sample quantity AND a new sample cannot be obtained by the laboratory, the data may be reported with the appropriate data qualifiers if the client has been contacted and agrees, in writing, to accept the qualified data.

13.4 Records: Initial and Continuing Calibration Records will contain, at a minimum, the following:

1) Calibration date
2) Test method
3) Instrument
4) Analysis date
5) Each analyte name
6) Analyst's initials or signature
7) Standard Concentration (appropriate units) and number of standards
8) Response (appropriate units)
9) Calibration curve or response factor
10) Evaluation of and Statistics for ICAL curve fit in order to judge calibration curve acceptance
11) Evaluation of and Acceptance Limits for ICV analysis in order to judge calibration curve acceptance
12) Evaluation of and Acceptance Limits for CCV analysis in order to judge continuing calibration acceptance

13.5 Thermometers - The thermometers in the sample refrigerators and the standards freezer must be checked daily. They must meet performance criteria.

14. PROCEDURE

14.1 Sample Preparation

14.1.1 Water, soil, sediment and waste samples must be prepared by SOP 3500 Extractions of Samples for Semi-Volatile Organic Analyses (EPA Methods 3510C, 3520C, 3550B, 3580A) prior to GC/MS analysis.

14.1.2 Extract Cleanup: Extracts may be cleaned up by any of the following methods prior to GC/MS analysis.

Compounds	**SOPs**
Semivolatile hydrocarbons	3330 Silicia Gel Clean-up for Semivolatile Organic Analyses

14.1.3 Direct Injection: In very limited applications direct injection of the sample into the GC/MS system with a 10 µL syringe may be appropriate (see SOP 3500 for preparation). The reporting limit is very high (approximately 100 to 1000 mg/L); therefore, it is only applicable where concentrations in excess of 100 mg/L are expected.

14.1.4 Extract Preparation: Sample extracts and the Internal Standard solution should be at ambient temperature prior to use. Using a 10 µL microliter syringe, inject 10 µL of the Internal Standard solution into the 1 mL sample extract prior to the start of the analytical batch. Ensure that there is no precipitation in the internal standard mixture. If there is precipitation then gently warm the standard until all is dissolved.

14.2 GC/MS Analysis

14.2.1 Instrument Conditions: The recommended GC/MS operating conditions:

EMV	1600 to 2500 (nominal)
Mass range:	35 to 500 amu (see Attachment 2 for ions monitored)
Scan time:	3.15 scans/sec
Initial temperature:	50°C hold for 0.4 minutes
Ramp 1 temperature program	25.0 °C/min
Final temperature 1:	320 °C hold for 3.8 minutes
Injector temperature:	280°C
Aux 2 temperature:	310 °C
Sample volume:	1 µL
Carrier gas:	Helium at 1.2 ml/min
Split flow:	Splitless
Flow Ramp	
Initial Flow	1.2 mL/min hold for 0.0 minutes
Ramp 1 Fow program	99 ml/min^2
Final Flow 1:	2.0 mL/min hold for 0.35 minutes
Ramp 2 Flow program	10 ml/min^2
Final Flow 2:	1.2 ml/min hold for 0.0 minutes

14.2.2 Access the computer and create a batch sequence file. Refer to section 14.3 for instructions.

14.2.3 Using the autosampler, inject 1 µL of the Tuning Standard (DFTPP) and evaluate using tune acceptance criteria. See Section 13.1

14.2.4 Inject 1 µL of the Continuing Calibration Verification Standard (CCV) and evaluate using CCV acceptance criteria. See Section 13.3.

14.2.5 If all criteria are met, continue with sample analysis, injecting 1 µL of each extract, as outlined below.

14.2.6 If the response for any quantitation ion exceeds the initial calibration curve range of the GC/MS system, extract dilution is an option. If extract dilution is required, additional internal standard must be added to the diluted extract to maintain the required 40 ng/µL of each internal standard in the extracted volume. Then the diluted extract is analyzed.

DILUTION PROCEDURE

1. Clean a 1ml syringe equipped with a luer lock needle with rinse and clean solvent. (dichloromethane or hexane) Fill syringe with clean solvent such that there is sufficient volume remaining for the dilution volume (see Table 4) and remove the needle. Place the needle on the counter top such that the tip of the syringe is elevated.

2. Clean an appropriate syringe (see Table 4) with rinse and clean solvent. Expel excess solvent by pumping the plunger several times. Puncture the sample vial with the syringe needle and withdraw the sample into the syringe.

3. Remove the syringe from the sample vial and insert the needle into the barrel of the 1ml syringe. Inject the sample into the clean solvent. Hold the 1ml syringe so that the tip is up and gently push up on the plunger to remove excess air from the barrel.

4. Replace the needle on the 1ml syringe and add sufficient clean solvent to a final volume of 1ml. Transfer the entire contents of the syringe into a labeled sample vial. Add an appropriate amount of internal standard (see Table 4) if necessary. Cap vial.

Table 4 STANDARD DILUTIONS

Dilution	Sample Volume mL	Total Volume µL	Amount of Internal Standard added µL
1:5	200	1000	8.0
1:10	100	1000	9.0
1:20	50	1000	9.5
1:50	20	1000	9.8
1:100	10	1000	9.9

14.2.7 Perform all qualitative and quantitative measurements as described in Sections 14.4 and 14.5. After analysis, store the extracts in the dark at 0.1- 6°C.

14.3 Analytical Sequence

START CHEMSTATION SOFTWARE:

From NT Desktop: Start/Programs/MSD ChemStation/Instrument #1/SVOC2
From XP Desktop: Start/Programs/MSD ChemStation/Instrument #1/SVOC5

The software will locate the instrument and all peripheral equipment. Once the software is fully loaded there will be two windows visible. (In XP only one window opens) Window one is the instrument control window. Instrument parameters are readily viewed from this window. The second window is the sequence control window. No instrument parameters are viewable from this window.

SEQUENCE SETUP - NT

From menu: Sequence/Run
Set current date in Data File Directory space (e.g., C:\MSDCHEM\1\DATA\060707\)
OK (to save changes)

From menu: Sequence/Edit Sample Log Table
Set data file name using current date using the following format MMDDYY## (e.g., 06070701)
Set up sequence order using the following format: (**NOTE:** Tune and CCV must always run first)

LINE	TYPE	VIAL	DATA FILE	METHOD	SAMPLE NAME
1	SAMPLE	1	06070701	DFTPP	TUNE STUNE01
2	SAMPLE	2	06070702	SVOC0804	CCV SSTD050
3	SAMPLE	3	06070703	SVOC0804	MBLK MB-14426-SVOC
4	SAMPLE	4	06070704	SVOC0804	LCS LCS-14426-SVOC
5	SAMPLE	5	06070705	SVOC0804	SAMP 0711034-001B
6	SAMPLE	6	06070706	SVOC0804	MS 0711034-001BMS
7	SAMPLE	7	06070707	SVOC0804	MSD 0711034-001BMSD
8	SAMPLE	8	06070708	SVOC0804	SAMP 0711034-002B
9	SAMPLE	9	06070709	SVOC0804	SAMP 0711034-003B
10	SAMPLE	10	06070710	SVOC0804	SAMP 0711034-004B
…		…		…	…
22	SAMPLE	22	06070722	SVOC0804	SAMP 0711123-001B

NOTE: All analyses must be injected within 12 hours of injecting the DFTPP sample
NOTE: The sample test code and dilution information is entered in the Miscellaneous Info field.

OK (to save changes)

From menu: Method/Set New Default Paths
Update the method and data file paths using the current date (e.g., C:\MSDCHEM\1\DATA\060707\)
OK (to save changes)

Using Windows Explorer copy all of the method files from the previous day's folder into the current day's folder.

SEQUENCE SETUP - XP

From menu: Sequence/Run
Set current date in Data File Directory space (e.g., C:\MSDCHEM\2\DATA\060707\)
OK (to save changes)

From menu: Sequence/Edit Sequence
Set data file name using current date using the following format MMDDYY## (e.g., 06070701)
Set up sequence order using the following format: (**NOTE:** Tune and CCV must always run first)

TYPE	VIAL	SAMPLE	METHOD/KEYWORD	DATA FILE	COMMENT
SAMPLE	1	TUNE STUNE01	DFTPP	06070701	DFTPP 58-18-139
SAMPLE	2	CCV SSTD050	SVOC0804	06070702	SVOC_QC 58-18-140
SAMPLE	3	MBLK MB-14426-SVOC	SVOC0804	06070703	SVOC_SOIL
SAMPLE	4	LCS LCS-14426-PCB	SVOC0804	06070704	SVOC_SOIL
SAMPLE	5	SAMP 0711034-001B	SVOC0804	06070705	SVOC_SOIL
SAMPLE	6	MS 0711034-001BMS	SVOC0804	06070706	SVOC_SOIL
SAMPLE	7	MSD 0711034-001BMSD	SVOC0804	06070707	SVOC_SOIL
SAMPLE	8	SAMP 0711034-002B	SVOC0804	06070708	SVOC_SOIL
SAMPLE	9	SAMP 0711034-003B	SVOC0804	06070709	SVOC_SOIL
SAMPLE	10	SAMP 0711034-004B	SVOC0804	06070710	SVOC_SOIL
…	…	…	…	…	…
SAMPLE	22	SAMP 0711045-010A	SVOC0804	06070722	SVOC_SOIL

NOTE: All analyses must be injected within 12 hours of injecting the DFTPP sample

1. OK (to save changes)

From menu: Method/Set New Default Paths

1. Update the method and data file paths using the current date (e.g., C:\MSDCHEM\2\DATA\060707\)
2. OK (to save changes)

Using Windows Explorer copy all of the method files from the previous day's folder into the current day's folder.

TO START SEQUENCE:

From menu: Sequence/Run/Run Sequence

Start of the 12 hour sequence (as documented as the date/time stamp on the data file for the Tune Standard):

The analytical sequence for Initial Calibration is:

DFTPP (Tune Standard)
Calibration standard (S1)
Calibration standard (S2)
Calibration standard (S3)
Calibration standard (S4)
Calibration standard (S5)
Calibration standard (S6) optional
Calibration standard (S7) optional
Initial Calibration Verification Standard (ICV)

The analytical sequence for Sample Analysis is:

DFTPP
Continuing Calibration Verification Standard (CCV)
Method Blank (MB)
LCS
LCS Duplicate (if applicable)
Sample #1
Sample #1 Matrix Spike (MS)
Sample #1 Matrix Spike Duplicate (MSD)
Sample #1 Laboratory Duplicate (if applicable)
Samples #2, #3, etc. until the end of 12 hour tune period

DFTPP
CCV
Samples up to #20
Method Blank (MB) #2
LCS #2
LCSD #2 (if applicable)
Sample #21
Sample #21 Matrix Spike (MS)
Sample #21 Matrix Spike Duplicate (MSD)
Sample #21 Laboratory Duplicate (if applicable)
Samples #22, #23, etc. until the end of 12 hour tune period

14.4 Data Interpretation - Qualitative Analysis

14.4.1 An analyte is identified based upon Relative Retention Time (RRT) and by comparison of the sample mass ions with the mass ions of a standard of the suspected compound (standard reference ions). The reference mass ion ratio must be generated by the laboratory using the conditions of this method. The characteristic ions from the reference mass ion are defined to be the two or three ions of greatest relative intensity. See Attachment 2 for the ions to be monitored. Two criteria must be satisfied to verify identification:
(1) elution of sample component at the same GC relative retention time (RRT) as those of the standard component; and (2) correspondence of the sample component and the standard component mass ions. Intensities of the characteristic ions must maximize in the same scan or within one scan of each other.

14.4.2 The RRT of the sample component is within ± 0.06 RRT units of the RRT of the standard component.

14.4.3 The relative intensities of the characteristic ions must agree within 30% of the relative intensities of these ions in the reference spectrum. (Example: For an ion abundance of 50% in the reference, the corresponding abundance in a sample spectrum can range between 20% and 80%.)

14.4.4 Structural isomers that produce very similar mass spectra must be identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs. An exception to this guidance occurs for the compounds Benzo(b)fluoranthene and Benzo(k)fluoranthene. Although the GC resolution may be minimal between the two, they are routinely reported as individual compounds. The Manual Integration SOP 1255 is used for guidance in the integration of these two peaks and for other situations that may require analyst efforts to correct computer generated integrations that are not technically sound.

14.4.5 Identification is hampered when sample components are not resolved chromatographically or coelute and produce mass spectra containing ions contributed by more than one analyte. When gas chromatographic peaks obviously represent more than one sample component (i.e., a broadened peak with shoulder(s) or a valley between two or more maxima), appropriate selection of analyte spectra and background spectra is important. Examination of extracted ion current profiles of appropriate ions can aid in the selection of spectra, and in qualitative identification of compounds, but each analyte spectrum will contain extraneous ions contributed by the coeluting compound.

14.4.6 For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the purpose of the analyses being conducted. Computer generated library search routines must not use normalization routines that would misrepresent the library or unknown spectra when compared to each other. For example, the RCRA permit or waste delisting requirements may require the reporting of nontarget analytes. Only after visual comparison of sample spectra with the nearest library searches will the mass spectral interpretation specialist assign a tentative identification. Guidelines for making tentative identification are:

14.4.6.1 Relative intensities of major ions in the reference spectrum (ions >10% of the most abundant ion) must be present in the sample spectrum.

14.4.6.2 The relative intensities of the major ions must agree within ± 20%. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30 and 70%).

14.4.6.3 Molecular ions present in the reference spectrum must be present in the sample spectrum.

14.4.6.4 Ions present in the sample spectrum but not in the reference spectrum must be reviewed for possible background contamination or presence of coeluting compounds.

14.4.6.5 Ions present in the reference spectrum but not in the sample spectrum must be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks. Data system library reduction programs can sometimes create these discrepancies.

14.5 Data Interpretation - Quantitative Analysis

14.5.1 Once a compound has been identified, the quantitation of that compound must be based on the integrated abundance from the EICP of the primary characteristic ion. The internal standard used shall be the one nearest the retention time of that of a given analyte.

14.5.2 If the RSD of a compound's response factor is 15% or less, then the concentration in the extract is determined using the average response factor (RF) from initial calibration data (13.2). See Method 8000, Sec. 7.0, for the equations describing internal standard calibration and either linear or non-linear calibrations.

14.5.3 Where applicable or required, the concentration of any non-target analytes (TICs) identified in the sample are estimated. The same formulae must be used with the following modifications: The areas A_x and A_{is} must be from the total ion chromatograms, and the RF for the compound must be assumed to be 1. The resulting concentration must be reported indicating: (1) that the value is an estimate, and (2) which internal standard was used to determine concentration. Use the nearest internal standard free of interferences.

14.6 Record the following information in the appropriate logbook or data file. Include any deviations from this procedure. Analyst initials, date of analysis, sample number or ID, initial sample volume or weight processed, final extract volume, calibration standard sample or solution identifier, QC sample or solution identifier, surrogate solution identifier, internal standard solution identifier, any dilution information, readings from support equipment, data file name, instrument method name, visual observations, and any other information as deemed necessary.

14.7 Troubleshooting

The experience of the analyst performing GC/MS analyses is invaluable to the success of the methods. Each day that the analysis is performed, the daily calibration standard (CCV) must be evaluated to determine if the chromatographic system is operating properly. Questions that must be asked: Do the peaks look normal? Is the response obtained comparable to the response from previous calibrations? Careful examination of the standard chromatogram can indicate whether the column is still good the injector is leaking, the injector septum needs replacing, etc. If any major changes are made to the system (e.g. column changed or detector cleaned), recalibration of the system must take place.

14.8 Routine Maintenance - Record all maintenance

14.8.1 Daily, or as needed according to sample throughput, change the septum and or the injection port liner. Trim a short section from the analytical column as necessary. Alternatively, the use of a guard column helps to protect the analytical column from residue buildup. A short section, 10 to 20 cm, of the guard column may be trimmed as to improve column performance.

14.8.2 Clean the source on an as needed basis (loss of sensitivity).

14.8.3 Inspect the autosampler syringe for wear; replace as necessary.

14.8.4 Check the carrier gas supply; replace as necessary.

15. DATA REDUCTIONS, CALCULATIONS, AND LOADING

15.1 The data system performs the calculations.

15.1.1 If the %RSD of a compound's relative response factor is 15% or less, then the concentration in the extract may be determined using the average response factor (RF) from the initial calibration data (13.2) and the following equation:

$$C_{ex}(mg/L) = \frac{A_x \times C_{is}}{A_{is} \times RF}$$

where C_{ex} is the concentration of the compound in the extract, and the other terms are defined in Sec. 13.2.

15.1.2 Alternatively, linear regression (Sec. 13.2) may be used for determination of the extract concentration.

15.2 Compute the concentration of the analyte in the sample using the equations in Secs. 15.2.1 and 15.2.2.

15.2.1 The concentration of the analyte in the liquid samples is calculated using the concentration of the analyte in the extract and the volume of liquid extracted, as follows:

$$\text{Concentration in liquid (mg/L)} = \frac{C_{ex} * V_f}{V_i}$$

or

$$\text{Concentration in liquid (µg/L)} = \frac{C_{ex} * V_f * 1000}{V_i}$$

where:

V_f = final extract volume in mL (includes any dilution volumes)
V_i = initial volume of liquid extracted, in mL.

15.2.2 The concentration of the analyte in the solid sample is calculated using the concentration of the analyte in the extract and the weight of the solid extracted, as follows:

$$\text{Concentration in solid (mg/Kg)} = \frac{C_{ex} * V_f}{W_i}$$

or

$$\text{Concentration in solid (µg/Kg)} = \frac{C_{ex} * V_f * 1000}{W_i}$$

where:

V_f = final extract volume in mL (includes any dilution volumes)
W_i = initial sample weight, in g.

For soil samples reported on dry weight basis, divide the Concentration by the decimal equivalent of the Percent Solids. For example: a sample contains 90% solids, thus

$$\text{Concentration in solid (mg/Kg) dry weight} = \frac{C_{ex} * V_f}{W_i * 0.90}$$

16. METHOD PERFORMANCE

Demonstration of Capability (DOC)

All parameters of interest must meet the method acceptance criteria before actual sample analysis begins. See SOP 1230 Training for the procedure to perform and document the DOC. The DOCs for the analysts performing this method are located in the analysts' training form folders located in the QA office files.

A quality control (QC) reference concentrate is required containing each analyte at a concentration of 50 µg/mL in acetone. The QC reference sample used is the Semivolatiles ICV (refer to Section 10.9 for composition) diluted to the Reporting Limit (RL). The QC reference sample is made using stock standards prepared independently from those used for calibration.

For each analyte calculate the mean recovery (x) and standard deviation (s) and the average % Recovery (%R). Compare X and s and %R with the corresponding acceptance criteria for accuracy and precision, respectively. Note: x must be within 1.5 and 7.5 µg/mL and s must be less than 1.25 µg/L and %R must be within 30 TO 150%**.** If x and s and %R for all analytes meet the acceptance criteria, the system performance is acceptable and analysis of actual samples can begin. If any individual x or %R falls outside the range for accuracy or any individual s exceeds the precision limit, then the system performance is unacceptable for that analyte and corrective action must be taken.

Locate and correct the source of the problem and repeat the test only for those analytes that failed to meet criteria. Repeated failure, however, will confirm a general problem with the measurement system. If this occurs, locate and correct the source of the problem and repeat the test for all compounds of interest.

Comparison to Reference Method Data

EPA Method 8000B provides guidance for the establishment of control limits for the LCS and MS QC samples. Recovery limits of 70% to 130% are provided as initial benchmarks for performance (8000B Section 8.5.4). These limits are designed for a wide variety of organic test methods. Individual analyte performance may vary. The control limits stated in Section 18 of this SOP are referenced from the CLP Statement of Work (SOW) for Organic Analyses Revision OLM04.2 May 1999 and in-house recovery data.

In-House Control Limits

Method performance data is on file in the laboratory QC department. Comparison of method performance data for the laboratory to the reference method criteria occurs when laboratory in-house acceptance limits are generated. In-house generated data is compared to the specifications of the reference method. If the in-house limits are within the specifications of the reference method, the control limits are updated in LIMS. If the in-house limits are not within specifications, an investigation is performed to determine the cause(s) of the problem and a corrective action is completed. The analysis may continue until enough data points are collected to regenerate new control limits. Any QC data generated outside of reference method limits during that time frame is flagged.

The laboratory maintains performance records to document the quality of data that is generated. Method accuracy for samples is assessed and records maintained. After the analysis of at least 20 laboratory control samples and surrogates, calculate the average percent recovery (R) and the standard deviation of the percent recovery (S).

Control limits for the method parameters are generated by the QC staff and distributed to the analysts via updates to the LIMS control charts. The control limits are calculated based on in-house performance data. At a minimum, these limits are reviewed annually.

17. POLLUTION PREVENTION

The preparation of excessive volumes of laboratory reagents and standards shall be avoided so that waste and potential for pollution are minimized. Samples, reagents and standards shall be disposed in compliance with the lab waste disposal program, SOP 1130 Waste Disposal. With the consent of the client, the samples may be returned to their origin for treatment.

Uncontaminated paper waste, glass and cans should be separated for recycling. Laboratory staff are required to protect the laboratory's and our clients' business information when disposing recycled paper or waste from the facility.

18. DATA ASSESSMENT AND CRITERIA FOR QUALITY CONTROL MEASURES

Data assessment includes review of: proper sample condition, preservation, and storage; analysis within holding time limitations; deviations from the SOP, evaluation of performance based or in-house control limits, reference method limits or project specific limits.

The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When results of sample spikes indicate atypical method performance, a calibration verification standard is used to confirm the measurements were performed in an in-control mode of operation. The data review is conducted according to SOP 1250 Data Review.

18.1 Blanks

If the blank exceeds the RL (usually the lowest calibration standard or specifically defined in this test method SOP), the source of contamination must be investigated and corrective actions taken. The compound concentrations in the method blank of an extraction batch must be less than the RL's listed in Attachment 1, except for common laboratory contaminants, i.e. bis-2-ethylhexyl phthalate which must be less than 5 times the RL listed in Attachment 1. If this criteria is exceeded, re-analyze the method blank. If after re-analysis, the blank criteria is still exceeded, then the entire extraction batch must be re-extracted. Always refer to a client specific QAPP for additional guidance.

If the surrogate recovery is outside the QA limits as defined in this test method the source of the nonconformance must be investigated and corrective actions taken. If this criteria is exceeded, re-analyze the method blank. If after re-analysis, the blank criteria is still exceeded, then the entire extraction batch must be re-extracted. Always refer to a client specific QAPP for additional guidance.

Affected samples must be reprocessed and reanalyzed **or** Data must be appropriately qualified if:

1) The concentration of a targeted analyte in the blank is at or above the reporting limit as established by the SOP or by regulation, AND is greater than 1/10 of the amount measured in any sample.

2) The blank contamination otherwise affects the sample results as per the test method requirements or the individual project data quality objectives.

18.2 Laboratory Control Samples (LCS)

The results of the individual batch LCS are calculated in percent recovery (%R) and compared to established acceptance criteria from in house analyses. If the LCS is outside the acceptance criteria, see Table 5 for current acceptance criteria, the analytical system is "out of control." Any affected samples associated with an out of control LCS must be reprocessed and reanalyzed or the results reported with appropriate data qualifiers. If after re-analysis the control criteria has not been met, the entire extraction batch must be re-extracted. Always refer to a client specific QAPP for additional guidance.

Table 5 LCS

Compound	Soil % Recovery	Water % Recovery
Phenol	60 – 91	12 – 101
2-Chlorophenol	61 – 91	30 – 97
1,4-Dichlorobenzene	55 – 90	27 – 99
N-Nitrosodi-n-propylamine	55 – 100	36 – 104
1,2,4-Trichlorobenzene	55 – 106	31 – 101
4-Chloro-3-methylphenol	62 – 100	43 – 113
Acenaphthene	65 – 101	43 – 122
4-Nitrophenol	53 – 123	10 – 129
2,4-Dinitrotoluene	55 – 101	10 – 123
Pentachlorophenol	40 – 120	50 – 113
Pyrene	50 – 131	54 – 131

18.3 Surrogates

18.3.1 The results of the individual Surrogate compounds are calculated in percent recovery (%R) and are compared to established acceptance criteria from the CLP Statement of Work (SOW) for Organic Analyses Revision OLM04.2 May 1999. Surrogates outside the acceptance criteria, see Table 6 for current acceptance criteria, must be evaluated for the effect indicated for the individual sample results.

Table 6 Surrogates

Surrogate Compound	Soil % Recovery	Water % Recovery
Nitrobenzene-d_5	23 – 120	35-114
2-Fluorobiphenyl	30 – 115	43-116
Terphenyl-d_{14}	18 – 137	33-141
Phenol-d_5	24 – 113	10-110
2-Fluorphenol	25 – 121	21-110
2,4,6-Tribromophenol	19 – 122	10-123
1,2-Dichlorobenzene-d_4	20 – 130	16-110
2-Chlorophenol-d_4	20 – 130	33-110

If surrogate recoveries are not within the established acceptance criteria, proceed as follows (SW-846 8000B):

1) Check to be sure that there are no errors in the calculations, surrogate solutions or internal standards. If errors are found, recalculate the data accordingly. Examine chromatograms for interfering peaks and integrated peak areas.

2) Check instrument performance. If an instrument performance problem is identified, correct the problem and re-analyze the extract (or re-analyze the sample for volatiles).

3) Some samples may require dilution in order to bring one or more target analytes within the calibration range or to overcome significant interferences with some analytes. This may result in the dilution of the surrogate responses to the point that the recoveries cannot be measured. If the surrogate recoveries are available from a less diluted or undiluted aliquot of the sample or sample extract, those recoveries may be used to demonstrate that the surrogates were within the QC limits, and no further action is required. However, the results of both the diluted and undiluted (or less-diluted) analyses should be provided to the data user.

4) If no instrument problem is found and if sufficient sample is available, the sample should be re-extracted and re-analyzed.

18.3.2 If, upon re-analysis (in either 2 or 4 above), the recovery is again not within limits, report the data as an "estimated concentration." If the recovery is within the limits in the re-analysis, provide the re-analysis data to the data user. If the holding time for the method has expired prior to the re-analysis, provide both the original and reanalysis results to the data user, and note the holding time problem.

18.4 Duplicates

The results from laboratory duplicates are designed to assess the precision of analytical results in a given matrix and are expressed as relative percent difference (RPD). See the STAT Quality Assurance Manual, Section 5.4 for the calculation for RPD. Results are compared to established acceptance criteria as listed in the MS/MSD Tables 7 and 8. For duplicates results outside established criteria, corrective action must be documented or the data reported with appropriate data qualifying codes.

For this test method, the analysis of the MS/MSD pair is used for determination of method precision. For cases where the sample cannot be divided (e.g., wipes, air samples, not enough sample provided by customer) and thus a MS/MSD pair is cannot be prepared in the preparation batch, an LCS/LCSD pair is prepared and analyzed to measure precision. Precision data from Tables 7 and 8 will be used for RPD acceptance criteria for LCS/LCSD.

18.5 Matrix Spikes

18.5.1 The results from MS/MSD are primarily designed to assess the precision and accuracy of analytical results in a given matrix and are expressed as percent recovery (%R) and relative percent difference (RPD). See the STAT Quality Assurance Manual, Section 5.4 for the calculation for RPD. Results are compared to established acceptance criteria from the CLP Statement of Work (SOW) for Organic Analyses Revision OLM04.2 May 1999. For matrix spike

results outside established criteria corrective action must be documented or the data reported with appropriate data qualifying codes.

18.5.2 Tables 7 and 8 show the compounds spiked, the levels and the current QC criteria for soils and water samples.

Table 7 Matrix Spike - Soil

Compound	Amount added µg/Kg	RPD Limit	% Recovery
Phenol	3330	35	60 – 91
2-Chlorophenol	3330	50	61 – 91
1,4-Dichlorobenzene	1670	27	55 – 90
N-Nitrosodi-n-propylamine	1670	38	55 – 100
1,2,4-Trichlorobenzene	1670	23	55 – 106
4-Chloro-3-methylphenol	3330	33	62 – 100
Acenaphthene	1670	19	65 – 101
4-Nitrophenol	3330	50	53 – 123
2,4-Dinitrotoluene	1670	47	55 – 101
Pentachlorophenol	3330	47	40 – 120
Pyrene	1670	36	50 – 130

Table 8 Matrix Spike - Water

Compound	Amount added µg/L	RPD Limit	% Recovery
Phenol	200	42	12 – 101
2-Chlorophenol	200	40	30 – 97
1,4-Dichlorobenzene	100	28	27 – 99
N-Nitrosodi-n-propylamine	100	38	36 – 104
1,2,4-Trichlorobenzene	100	28	31 – 101
4-Chloro-3-methylphenol	200	42	43 – 113
Acenaphthene	100	31	43 – 122
4-Nitrophenol	200	50	10 – 129
2,4-Dinitrotoluene	100	38	10 – 123
Pentachlorophenol	200	50	50 – 113
Pyrene	100	31	54 – 131

18.6 Internal Standards

The results of the individual Internal Standard compounds on all samples, blanks, and spikes are calculated in percent recovery (%R) and are compared to established acceptance criteria. If the Internal Standard recovery is outside the acceptance criteria, see Table 9, corrective action should be taken. Note: the recovery of internal standards in these samples within the stated limits is not mandatory per the reference method, 8270C. It can be a useful diagnostic tool. Client specific project criteria may require the adherence to these limits. If so, then corrective action must be documented or the data reported with appropriate data qualifying codes.

Table 9 Internal Standards

INTERNAL STD COMPOUND	CRITERIA (%)
Acenaphthene-d_{10}	-50 to +200
Chrysene-d_{12}	-50 to +200
1,4-Dichlorobenzene-d_4	-50 to +200
Naphthalene-d_8	-50 to +200
Perylene-d_{12}	-50 to +200
Phenathrene-d_{10}	-50 to +200

18.7 Other

The laboratory will analyze standard reference materials and participate in relevant performance evaluation studies quarterly.

19 CORRECTIVE ACTIONS FOR OUT-OF-CONTROL DATA

The process for handling unacceptable and out of control data is found in SOP 230 Corrective Action.

If the CCV, MB, LCS/LCSD, MS/MSD, lab duplicate, surrogate, internal standard, or recovery of any parameter falls outside the designated acceptance range, the laboratory performance for that parameter is judged to be out of control, and the problem must be immediately identified and corrected. The analytical result for that parameter in the samples is suspect and is only reported for regulatory compliance purposes with the appropriate corrective action form. Immediate corrective action includes reanalyzing all affected samples by using any retained sample before the expiration of the holding time. Final data results must be qualified in the client report for reported results not meeting the laboratory defined criteria.

1) Review standards preparation logbooks. Check all calculations and ensure dilution factors are properly recorded.
2) Re-prepare the suspected standard or QC sample to identify possible preparation errors of the standard or QC sample.
3) Re-Analyze the samples when the CCV or LCS is not within acceptable limits.

4) Perform routine preventative maintenance following manufacturer's specification. Record all maintenance in the instrument logbook.

20 CONTINGENCIES FOR HANDLING OUT-OF-CONTROL OR UNACCEPTABLE DATA

Every effort is made to prevent problems from occurring. When out of control or unacceptable data occurs the first option is to identify the problem and reanalyze the samples within the holding times. When this is not possible, the QA Manager and/or the Laboratory Director reviews data and discusses options with the client. Reanalysis or reporting the data with qualification are alternatives. Out of control or unacceptable data reported to the client must include the data qualifier, flag and discussion on the rationale for reporting.

Holding time exceedence, improper preservation and improper sample condition or storage are noted on the corrective action form and included on the final report.

Review the CCV standard response, LCS result, the surrogate recovery, and internal standard recovery for acceptable performance for each batch of samples. Record any trends or unusual performance on a corrective action form. Final data results must be qualified in the client report for results not meeting the laboratory defined criteria.

Manual integration must be minimized for standards, reagent blanks and surrogates. Routine manual integration of the same parameters indicates a system performance problem. Correct this problem or note in the instrument analysis logbook the suspected causes for routine manual integration. Sign and date all manually integrated chromatograms.

20.1 The process for handling unacceptable and out of control data is found in the Laboratory QAM Section 11. The reporting of data that is out of control must be approved and documented by Quality Assurance Manager and either the Technical Manager or the Laboratory Director.

20.2 Client Requested Modifications:

20.2.1 Clients must request modifications from the laboratory SOP in writing to the lab.

20.2.2 The lab director, technical manager and quality assurance manager will evaluate the requested client deviations, determine the feasibly of the deviation and the potential effects on the data.

20.2.3 If it is determined that the lab will perform the requested deviations, lab director, technical manager and quality assurance manager will decide if a method validation study is required.

20.2.4 The designated project manager will retain all documentation concerning the requested deviation, including all correspondence with the client, in the client folder.

20.2.5 The final analytical report must include the statement *"This report has analyses performed using client requested modifications"*.

21 WASTE MANAGEMENT

The STAT Analysis Corporation Waste Disposal SOP 1130 identifies proper waste management practices for the chemicals and biological materials used in this procedure. Samples are stored and discarded accordance with SOP 1130 Waste Disposal.

22 REFERENCES

22.1 Method 8270C, Revision 3, December 1996; U.S. EPA SW-846 "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods" Update III, December 1996.
22.2 STAT SOP 3500 Extraction of Samples for Organic Analyses
22.3 STAT SOP 3330 Silica Gel Cleanup
22.4 SOP 230 Corrective Actions
22.5 SOP 1010 Standard and Reagent Preparation
22.6 SOP 1400 LIMS
22.7 SOP 1130 Waste Disposal
22.8 SAP 003 Chemical Hygiene Plan
22.9 SOP 1250 Data Review
22.10 Manufacturers' Equipment Instruction Manuals
22.11 SOP 1255 Manual Integration
22.12 SW-846 8000B Determinative Chromatographic Separations
22.13 SOP 1230 Training
22.14 "USEPA Contract Laboratory Program Statement of Work for Organic Analysis" Revision OLM04.2 May 1999, U. S. Environmental Protection Agency. Office of Solid Waste, Washington DC 20460.
22.15 NIST Library of Reference Spectra, Edition Number NIST98

23 FORMS, FIGURES, TABLES, DIAGRAMS, FLOWCHARTS, ATTACHMENTS OR VALIDATION DATA

Attachment 1: Summary of Changes from Revision 03

- Instrument and software information are updated.
- Specifications for the source standard used for initial calibration and ICV have changed.
- GC operating conditions have been modified.
- Minor editorial changes.

Attachment 2: MDLs and REPORTING LIMITS FOR SEMIVOLATILE COMPOUNDS

CASN	Compounds	MDL (mg/L)	RL (mg/L)	RL (mg/L)	MDL (mg/Kg)	RL (mg/Kg)	RL (mg/Kg)
83-32-9	Acenaphthene	1.03	5	0.005	15	170	0.17
208-96-8	Acenaphthylene	0.99	5	0.005	10	170	0.17
62-53-3	Aniline	0.76	5	0.005	35	170	0.17
120-12-7	Anthracene	0.49	5	0.005	9	170	0.17
65-85-0	Benzoic acid	2.35	25	0.025	45	800	0.80
56-55-3	Benzo(a)anthracene	0.25	5	0.005	15	170	0.17
205-99-2	Benzo(b)fluoranthene	0.50	5	0.005	23	170	0.17
207-08-9	Benzo(k)fluoranthene	1.01	5	0.005	56	170	0.17
191-24-2	Benzo(g,h,i)perylene	0.33	5	0.005	13	170	0.17
50-32-8	Benzo(a)pyrene	0.46	5	0.005	13	170	0.17
100-51-6	Benzyl alcohol	0.69	5	0.005	23	170	0.17
111-91-1	Bis(2-chloroethoxy)methane	0.78	5	0.005	20	170	0.17
111-44-4	Bis(2-chloroethyl) ether	0.52	5	0.005	84	170	0.17
108-60-1	2,2'-oxybis(1-Chloropropane)	0.72	5	0.005	24	170	0.17
117-81-7	Bis(2-ethylhexyl)phthalate	1.95	5	0.005	50	330	0.33
101-55-3	4-Bromophenyl phenyl ether	1.03	5	0.005	17	170	0.17
85-68-7	Butyl benzyl phthalate	0.90	5	0.005	14	170	0.17
106-47-8	4-Chloroaniline	1.06	5	0.005	25	170	0.17
59-50-7	4-Chloro-3-methylphenol	1.21	5	0.005	12	170	0.17
91-58-7	2-Chloronaphthalene	0.99	5	0.005	11	170	0.17
95-57-8	2-Chlorophenol	1.28	5	0.005	46	170	0.17
7005-72-3	4-Chlorophenyl phenyl ether	1.18	5	0.005	10	170	0.17
86-74-8	Carbazole	0.62	5	0.005	7	170	0.17
218-01-9	Chrysene	0.32	5	0.005	11	170	0.17
53-70-3	Dibenz(a,h)anthracene	0.44	5	0.005	9	170	0.17
132-64-9	Dibenzofuran	1.05	5	0.005	12	170	0.17
84-74-2	Di-n-butyl phthalate	6.41	10	0.010	130	170	0.17
95-50-1	1,2-Dichlorobenzene	1.01	5	0.005	27	170	0.17
541-73-1	1,3-Dichlorobenzene	0.95	5	0.005	28	170	0.17
106-46-7	1,4-Dichlorobenzene	0.87	5	0.005	23	170	0.17
91-94-1	3,3'-Dichlorobenzidine	1.20	10	0.005	22	660	0.66
120-83-2	2,4-Dichlorophenol	1.80	5	0.005	12	800	0.80
84-66-2	Diethyl phthalate	0.72	5	0.005	26	170	0.17
131-11-3	Dimethyl phthalate	0.93	5	0.005	13	170	0.17
534-52-1	4,6-Dinitro-2-methylphenol	1.0	25	0.025	60	800	0.80
51-28-5	2,4-Dinitrophenol	1.0	25	0.025	10	800	0.80
121-14-2	2,4-Dinitrotoluene	0.46	5	0.005	12	170	0.17
606-20-2	2,6-Dinitrotoluene	0.80	5	0.005	18	170	0.17
117-84-0	Di-n-octyl phthalate	0.75	5	0.005	13	170	0.17
206-44-0	Fluoranthene	0.78	5	0.005	10	170	0.17
86-73-7	Fluorene	0.83	5	0.005	15	170	0.17
CASN	**Compounds**	**MDL (mg/L)**	**RL (mg/L)**	**RL (mg/L)**	**MDL (mg/Kg)**	**RL (mg/Kg)**	**RL (mg/Kg)**

118-74-1	Hexachlorobenzene	0.73	5	0.005	11	170	0.17
87-68-3	Hexachlorobutadiene	1.09	5	0.005	19	170	0.17
77-47-4	Hexachlorocyclopentadiene	0.89	5	0.005	11	170	0.17
67-72-1	Hexachloroethane	0.92	5	0.005	27	170	0.17
193-39-5	Indeno(1,2,3-cd)pyrene	0.32	5	0.005	11	170	0.17
95-48-7	2-Methylphenol	1.31	5	0.005	37	170	0.17
108-39-4	3-Methylphenol	3.81	5	0.005	40	170	0.17
106-44-5	4-Methylphenol	3.81	5	0.005	40	170	0.17
91-20-3	Naphthalene	1.05	5	0.005	19	170	0.17
88-74-4	2-Nitroaniline	0.61	25	0.025	7	800	0.80
99-09-2	3-Nitroaniline	0.66	25	0.025	17	800	0.80
100-01-6	4-Nitroaniline	0.71	25	0.025	21	800	0.80
98-95-3	Nitrobenzene	0.71	5	0.005	32	170	0.17
88-75-5	2-Nitrophenol	1.16	5	0.005	52	170	0.17
100-02-7	4-Nitrophenol	1.29	25	0.025	66	800	0.80
62-75-9	N-Nitrosodimethylamine	0.48	5	0.005	52	330	0.33
86-30-6	N-Nitrosodiphenylamine	0.62	5	0.005	6	170	0.17
621-64-7	N-Nitrosodi-n-propylamine	0.63	5	0.005	95	330	0.33
87-86-5	Pentachlorophenol	1.74	25	0.025	30	800	0.80
85-01-8	Phenanthrene	0.58	5	0.005	9	170	0.17
108-95-2	Phenol	0.66	5	0.005	49	170	0.17
129-00-0	Pyrene	0.61	5	0.005	7	170	0.17
110-86-1	Pyridine	0.72	5	0.005	122	330	0.33
120-82-1	1,2,4-Trichlorobenzene	1.27	5	0.005	29	170	0.17
95-95-4	2,4,5-Trichlorophenol	1.76	10	0.010	39	330	0.33
88-06-2	2,4,6-Trichlorophenol	1.25	5	0.005	22	170	0.17
103-33-3	Azobenzene	0.61	5	0.005	10	170	0.17

Attachment 3: CHARACTERISTIC IONS FOR SEMIVOLATILE COMPOUNDS

#	Compounds	Retention Time (min.)	Primary Ion	Secondary Ion(s)
1	1,4-Dichlorobenzene-d4 (ISTD)	3.675	152	150, 154
2	2-Ethoxyethanol	1.797	59	45, 72
3	N-Nitrosodimethylamine	1.958	74	79, 42
4	Pyridine	1.974	79	51, 52
5	Cyclohexanone	2.899	55	42, 98
6	2-Fluorophenol (SURR)	2.744	112	64, 92
7	Phenol-d5 (SURR)	3.413	99	42, 71
8	Phenol (MS)	3.423	94	65, 66
9	Aniline	3.445	66	65, 39
10	bis-(2-Chloroethyl)ether	3.482	63	65
11	2-Chlorophenol (MS)	3.536	128	64, 130, 132
12	1,3-Dichlorobenzene	3.648	146	148, 75, 111
13	1,4-Dichlorobenzene (MS)	3.691	146	148, 111
14	Benzyl Alcohol	3.803	108	107, 79
15	1,2-Dichlorobenzene-d4 (SURR)	3.840	152	154, 115
16	2-Chlorophenol-d4 (SURR)	3.525	132	134
17	1,2-Dichlorobenzene	3.851	146	148, 111
18	2-Methylphenol	3.910	107	108, 79
19	2,2'-oxybis(1-Chloropropane)	3.931	45	41, 121
20	3- & 4-Methylphenol	4.038	107	108, 77
21	N-Nitrosodi-n-propylamine (MS)	4.054	70	43, 42
22	Hexachloroethane	4.108	117	119, 121
23	Nitrobenzene-d5 (SURR)	4.172	82	128, 54
24	Nitrobenzene	4.188	77	123, 51
25	Isophorone	4.397	82	138, 95
26	2-Nitrophenol	4.477	139	109, 65
27	2,4-Dimethylphenol	4.509	122	107, 121
28	Benzoic acid	4.632	105	122, 77
29	bis(2-Chloroethoxy)methane	4.595	93	63, 95
30	2,4-Dichlorophenol	4.691	162	98, 164, 166
31	1,2,4-Trichlorobenzene (MS)	4.766	180	182, 184
32	Naphthalene-d8 (ISTD)	4.803	136	68
33	Naphthalene	4.825	128	129, 127
34	4-Chloroaniline	4.894	127	129, 65
35	Hexachlorobutadiene	4.990	225	223, 227
36	4-Chloro-3-methylphenol (MS)	5.359	107	142, 144
37	2-Methylnaphthalene	5.472	142	115, 141
38	Hexachlorocylopentadiene	5.686	237	235, 239
39	2,4,6-Trichlorophenol	5.771	196	198, 200
40	2,4,5-Trichlorophenol	5.814	196	132, 97, 198
41	2-Fluorobiphenyl (SURR)	5.846	172	171, 170
42	2-Chloronaphthalene	5.937	162	127, 164

43	1-Chloronaphthalene	6.017	162	127, 164
44	2-Nitroaniline	6.076	138	92, 65
45	Dimethyl phthalate	6.279	163	194, 77
46	Acenaphthylene	6.344	152	151, 76
47	2,6-Dinitrotoluene	6.344	165	89, 63
#	Compounds	Retention Time (min.)	Primary Ion	Secondary Ion(s)
48	3-Nitroaniline	6.076	138	92, 65
49	Acenaphthene-d10 (ISTD)	6.493	164	162, 160
50	Acenaphthene (MS)	6.525	153	154, 152
51	2,4-Dinitrophenol	6.579	184	154, 63
52	Dibenzofuran	6.681	168	139
53	4-Nitrophenol (MS)	6.665	109	65, 39
54	2,4-Dinitrotoluene (MS)	6.723	165	89, 63
55	Diethyl phthalate	6.969	149	177, 150
56	4-Chlorophenyl phenyl ether	7.018	204	206, 141
57	Fluorene	7.012	166	165, 167
58	4-Nitroaniline	7.087	138	108, 92
59	N-Nitrosodiphenylamine	7.141	169	168, 167
60	4,6-Dinitro-2-methylphenol	7.119	198	51, 105
61	Azobenzene	7.167	77	51, 182
62	2,4,6-Tribromophenol (SURR)	7.274	330	332, 328
63	4-Bromophenyl phenyl ether	7.488	248	250, 141
64	Hexachlorobenzene	7.627	284	286, 282
65	Pentachlorophenol (MS)	7.809	266	264, 268
66	Phenanthrene-d10 (ISTD)	7.921	188	94, 80
67	Phenanthrene	7.948	178	176, 152
68	Anthracene	7.991	178	176, 179
69	Carbazole	8.157	167	166, 168
70	Di-n-butyl phthalate	8.553	149	104, 150
71	Fluoranthene	9.114	202	200, 203
72	Benzidine	9.494	184	185, 183
73	Pyrene (MS)	9.333	202	200, 203
74	p-Terphenyl-d14 (SURR)	9.494	244	240, 243
75	Butyl benzyl phthalate	10.013	149	206, 91
76	3,3'-Dichlorobenzidine	10.553	252	254, 256
77	Chrysene-d12 (ISTD)	10.532	240	236, 120
78	Benzo(a)anthracene	10.510	228	226, 229
79	Chrysene	10.553	228	226, 229
80	bis-(2-Ethylhexyl)phthalate	10.590	149	167, 279
81	Di-n-octyl phthalate	11.152	149	279, 43
82	Benzo(b)fluoranthene	11.532	252	250, 126
83	Benzo(k)fluoranthene	11.553	252	250, 126
84	Benzo(a)pyrene	11.837	252	126, 113
85	Perylene-d12 (ISTD)	11.895	264	260, 265
86	Indeno(1,2,3-cd)pyrene	13.094	276	138, 277

87	Dibenz(a,h)anthracene	13.110	278	139, 279
88	Benzo(g,h,i)perylene	13.431	276	138, 277

ISTD = Internal Standard
SURR = Surrogate
MS = Matrix Spike

STA Analysis Corporation:

STANDARD OPERATING PROCEDURE 4060
EPA Method 3C

DETERMINATION OF CARBON DIOXIDE, METHANE, NITROGEN, AND OXYGEN IN AIR BY GC WITH THERMAL CONDUCTIVITY DETECTION

Revision 00
Effective Date: December 29, 2008

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Attachment 1: MDLs and Reporting Limits for 3C Compounds 17

1.0 IDENTIFICATION OF TEST METHOD

SOP Title: SOP 4060; Determination of carbon dioxide, methane, nitrogen, and oxygen in air by GC with thermal conductivity detection.

2.0 APPLICABLE MATRICES

This method is applicable to air samples (source monitoring, ambient outdoor/indoor, landfill gas, etc.) collected in Tedlar™ bags, stainless steel (including Silcosteel™) sampling canisters at sub-ambient (passively sampled) or positive pressure (actively sampled).

3.0 DETECTION LIMITS

The lab follows the procedure found in 40CFR Part 136B to determine the MDL for each matrix type on an annual basis. See the STAT Analysis SOP 1210 for the MDL procedure, frequency and acceptance criteria. The MDLs measured by the lab and all supporting documentation are in the laboratory QA files for review.

The laboratory determined MDL must always be less than the reporting limit (RL), which may be determined by the lowest standard. Attachment 1 contains the current MDLs and reporting limits (RLs) for this SOP for Method 3C compounds.

4.0 SCOPE AND APPLICATION

4.1 This SOP describes in detail the methods used at STAT Analysis Corporation for the analysis of air samples for carbon dioxide, methane, nitrogen, and oxygen in air by TCD. This SOP as written is to be applied when EPA Method 3C analysis is requested. This method is applicable to all types of air matrices.

4.2 SOP 4060 may be extended to other very volatile gases (with proper validation) when high levels (ppm to percent levels) are of interest. In cases where the level of interest is lower (e.g., carbon monoxide in homes, carbon dioxide in IAQ studies), EPA Method 25C may be more appropriate.

4.3 The reporting limits (RLs) for this SOP are shown in Attachment 1. RLs will be proportionately higher for samples that require dilution or reduced sample size to avoid saturation of the detector.

4.4 This method is restricted to use by or under the supervision of analysts experienced in the use of a Gas Chromatograph/Thermal Conductivity Detector (GC/TCD) and skilled in the use of air delivery systems. Each analyst must demonstrate the ability to generate acceptable results with this method.

5.0 SUMMARY OF TEST METHOD

5.1 Samples must be prepared for the GC/TCD using the appropriate sample preparation technique (see Section 14.1). Air samples are introduced to the GC using a sample loop, and gases are detected with a TCD. Peaks are integrated on the chemstation. Samples are analyzed in duplicate.

5.2 This method describes chromatographic conditions that will allow for the separation of the compounds and for their quantitative analysis by GC/TCD. Identification of target compounds is accomplished by comparing component retention times to those of authentic standards. Quantitation is accomplished by comparing the response to a calibration curve containing a minimum of 3 points for each target compound.

5.3 **Method Modifications from Reference** – This SOP is based on EPA Methods 3C with the following modifications:
1) A second source standard is analyzed after the calibration curve.
2) Argon is used to quantify oxygen.

6.0 DEFINITIONS

The STAT Analysis Quality Manual Section 19.0 contains all of the definitions of standard terms used in SOPs. In EPA Method 3C, duplicate refers to the re-analysis of the sample, as received (without a separate preparation.).

7.0 INTERFERENCES

7.1 All blanks, samples, and spikes must be evaluated for interferences. Interferences will vary from source to source depending upon the particular sample being tested. Determine if the source of interference is laboratory induced. If the source of the interference is laboratory found, take corrective action to eliminate the problem.

7.2 Contamination by carryover can occur whenever high-concentration and low-concentration samples are sequentially analyzed. A Method blank (helium) must be analyzed to demonstrate that carryover has been eliminated. Reanalysis must be performed on all affected samples to demonstrate that the compound concentration is from the sample and not due to carryover.

7.3 A method blank, consisting of high purity helium is prepared in a previously cleaned and certified sampling canister. It is analyzed daily to ensure that system is not contaminated.

7.4 All sampling canisters are cleaned in batches on a manifold. They are cleaned using repeated cycles of pressurization with humidified zero air followed by evacuation. All canisters in the batch are pressurized to 30psia (15.3 psig) with humidified zero air and the canister valves are closed. The canisters are allowed to stand overnight, and then the pressure in each canister is individually checked. A pressure-drop of >1.0psi in any canister over a 12-hour period is indicative of a leak. Any leaking canister should be taken out of service and tagged for a leak test. If the canister can be repaired and subsequently demonstrated to pass the leak test, it can again be cleaned and certified and placed back in service.

8.0 SAFETY

The concentrations of hazardous chemicals in most air samples are minimal and the analyst should not be exposed to the sample due to the closed nature of the sample canisters and analytical system; however, samples analyzed by this method may include known or suspected carcinogens and other toxic compounds. Proper personal protective equipment including safety glasses and a lab coat are suggested. Other safety precautions must be conducted in accordance with the SOP 003 Chemical Hygiene Plan. Other actions can also be applied if deemed necessary. A reference file of Material Safety Data Sheets (MSDS) is available to all personnel involved in this method. This method requires the safe handling and use of pressurized cylinders.

9.0 EQUIPMENT AND SUPPLIES

The following apparatus is recommended for performing this procedure. Equivalent items can be used, if with their use, the analytical and QA/QC requirements in this SOP can be met. All catalog numbers in this SOP are current as of the effective date and thereafter subject to change.

9.1 Gas Chromatograph/Thermal Conductivity Detector

9.1.1 Gas chromatograph(GC) – Agilent 5890 gas chromatograph or equivalent.

9.1.2 Column – 2 m x 2 mm id ShinCarbon ST 80/100

9.1.3 Thermal Conductivity Detector

9.1.4 Data system – A computer system using Enviroquant Chemstation Software (G1701BA Version B.01.00) is used to collect and process data.

9.2 Sample canisters - Stainless steel air sampling canisters (e.g., Restek TO-Can, Entech) or Tedlar bags

9.3 Cleaning manifold – in-house design capable of automated cleaning of canisters in batches of at least 8.

9.4 Pressure gauge 0 – 30psi, 0.1% accuracy.

9.5 Two-stage gas regulator with gauges 0-3000 psi and 0-150 psi or other suitable range.

9.6 Gas Supplies
Ultra-High Purity Helium (99.99%)
Reagent Grade Zero air or ultra grade air (for canister cleaning)

10.0 REAGENTS AND STANDARDS

The following reagents and standards are required to perform this procedure. When instructions are given on how to prepare a specific volume of a reagent or standard, larger or smaller volumes can be prepared as needed so long as the final concentrations remain the same—this is especially applicable if standards are being prepared in 1L or 33L canisters as opposed to the usual 6L canisters. Any other deviations from the reagents or standards listed in this SOP could be detrimental to the quality of the data produced. Such deviations would have to be approved and documented (see 230 Corrective Action SOP).

Instructions for labeling and record keeping of reagents and standards are contained in SOP 1010 Analytical Standards and Reagents Receipt and Preparation.

NOTE: All concentration listed below are nominal concentrations. Any stock standard where an individual compound differs from the listed nominal concentration by greater than 10% will be rejected or the spike value in LIMS must be corrected to match the reported concentration on the COA.

10.1 Analytical reagent grade chemicals shall be used in all tests. Unless otherwise indicated, all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.

10.2 Stock Standard mixtures - Standard mixtures are purchased in cylinders from certified vendors traceable to NIST, where possible. The primary standard mixtures used is the Matheson Tri Gas 3C Calibration Mix. Secondary source standard mixture is Scott Specialty Gases certified working dass calibration standard. Calibration standards and Quality Control Standards are prepared from the Stock Standard mixtures in clean, certified 6L canisters, diluted to appropriate concentration with high purity helium or used directly from the stock cylinders. The prepared standards must be replaced monthly or sooner if comparison with quality control check samples indicates a problem. Quality Control Standards must be from different source (lot numbers) than Calibration Standards.

10.3 Calibration Standards – A minimum of three calibration standards are required, additional standards can be prepared from stock standards by dilution (10.4). The concentration of individual compounds can vary in calibration mixtures from different suppliers. The composition of mixtures should satisfy reporting limits shown in attachment 1. (Note: argon is used to quantitate oxygen). (Example of calibration mixtures in Table 1).

10.4 A static dilution system is used to prepare the calibration standards. The system incorporates a very accurate (0.1% gauge) test pressure gauge and uses pressure differential to calculate dilutions. Working standards are prepared by adding into, certified, evacuated canister calculated amount of calibration standard and pressurizing to 30psia with high purity helium. The prep factor is equal to the gauge pressure differential of Stock Standard mixture divided by the final canister pressure. Calibration standards and quality control standards in canisters can be used for one month from the date of preparation, or until the pressure in the canister falls to 0 psig. The pressure in the canister should be checked periodically in order to prevent the system from appearing to be out of control due to low standard pressure.

Table 1 Calibration Standards

Compound	Concentration, %						
	Matheson TG # 1	Matheson TG # 2	Matheson TG # 3	# 3 1:5	# 3 1:50	# 3 1:500	Scott SG (ICV)
Carbon dioxide	5	35	15	3	0.3	0.03	35
Methane	93	50	25	5	0.5	0.05	50
Argon	1	5	20	4	0.4	0.04	5
Nitrogen	1	10	40	8	0.8	0.08	10

10.5 Method Blank. A canister containing high purity helium will be analyzed during each series of analytical runs. Each sequence will have a continuing calibration check, and then the blank canister. The blank must contain less than the reporting limit of each target analyte for analysis to continue.

11.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

11.1 Containers used to collect sample: clean, certified air sampling canisters, Tedlar bags. Tedlar bags and air sampling canisters are available from a variety of vendors.

11.1.1 The lab may provide clean, evacuated canisters to the client(s) for sampling. If the client(s) choose to use their own sampling containers, the client may be issued a statement of potentially inaccurate results in the case narrative.

11.1.2 The lab may provide sample collection devices (passive or active samplers) to the client(s) or provide for initial and periodic certification (see section 7.4) of sampling equipment belonging to clients. Samples may not be deemed of known quality for analysis if either the sampler or canister used for sample collection is not properly documented as clean and/or certified.

11.2 All samples are generally kept free of contamination because the sample containers must be leak-free. See section 14.9 for details of how to perform the leak-test procedure.

11.3 Sample analysis must be within 30 days from the date of sample collection. After client approval or 30 days have elapsed, the sample will be disposed.

12.0 QUALITY CONTROL

The following details the QC requirements that apply to this analysis. Each Quality Control Indicator (QCI) provides information pertaining to either method or individual sample performance. Our goal is to produce defensible data of known and documented quality. The results of these QCI samples are used to assess the acceptability of data.

12.1 Calibration Verification

An Initial Calibration Verification (ICV) standard containing all of the target compounds reported in this method shall be analyzed immediately after the completion of the initial calibration. The ICV shall be purchased from a second source to verify compound concentrations. Continuing calibration verification is performed daily.

12.2 Blanks

Method Blank analysis is performed to determine if any contamination is present in the analytical process and is used to evaluate acceptance of the batch of samples. A method blank shall be analyzed once per analytical batch. The method blank shall be processed through all preparatory steps used for the samples. The blank shall be analyzed using the same instrument and conditions as the samples.

12.3 Laboratory Control Sample (LCS)

Not applicable to this method.

12.4 Duplicates

Samples are analyzed in duplicates. The analysis is acceptable when results of two consecutive injections of the sample agree within 5% of their average.

12.5 Matrix Spike and Matrix Spike Duplicate (MS/MSD)

Not applicable to this method.

12.6 Internal Standards

Not applicable to this method.

13.0 CALIBRATION AND STANDARDIZATION

13.1 **Initial Calibration (ICAL)** Analyze each calibration standard according to the procedure listed in Section 14 (standards are analyzed under the same conditions as samples). Verify the detector linearity over the range of suspected sample concentrations with at least three points per compound of interest. All susequent calibrations performed using a single-point standard gas provided the calibration point within 20% of the sample component concentration. For each instrument calibration, record the carrier and detector flow rates, detector temperature, attenuation factor, injection time, chart speed, sample loop volume, and component concentrations. Plot a linear regression of the standard concentrations versus area values to obtain the response factor of each compound. Alternatively, response factors of uncorrected component concentrations may be generated using instrumental integration. Peak height may be used instead of peak area.

13.1.1 Calculate the average calibration factor ($\overline{CF}$) for each compound as follows:

$$\overline{CF} = (S\ CF_1 \text{ to } CF_n)/n$$

where:
CF = CF for each of the calibration levels
n = Number of CF values (minimum 3)

13.1.2 Calibration Check Compound (CCC) responses are monitored to check the integrity of the system. All compounds are considered calibration check compounds.

Using the CFs from the initial calibration, calculate the percent relative standard deviation (%RSD) for the CCCs.

To calculate %RSD: $\%RSD = 100\% \times SD/\overline{CF}$

where:
%RSD = % Relative Standard Deviation

$\overline{CF}$ = average of initial CFs for a compound
SD = standard deviation (n-1) of average CFs for a compound

To calculate Standard Deviation (n-1 degrees of freedom)

$$SD = \sqrt{\sum_{i=1}^{N} \frac{(CF_i - \overline{CF})^2}{N-1}}$$

where: CF_i = CF for each of the calibration levels
N = Number of CF values (minimum 3)

13.1.3 The %RSD of all CCC compound should be < 20%. If the response of any CCC compound varies by more than 20%, the system is considered too reactive for analysis to continue. Perform the initial calibration procedure beginning with section 13.1.

13.1.4 Retention Times: The Relative Retention Times (RRT) of each compound in each calibration standard should be within ± 0.06 RT units.

13.1.5 Before sample analysis can begin, a Initial Calibration Verification (ICV) must be performed. The ICV results must be within the acceptance criteria as established for the CCV compounds (Section 13.3).

13.1.6 **NOTES**:

1. All calibration curves must have a unique identifier. The calibration date is incorporated into the method identifier for easy reference.
2. All initial calibration standards must be analyzed within the 8 hours.
3. Calibration must be completed (all standard levels analyzed) within 8 hours or the entire calibration sequence must be repeated. All initial calibration standards must be analyzed and verified prior to field sample analyses.
4. Do not add calibration standards and update the curve after the original calibration date.
5. Multiple analyses of the same calibration level are not allowed to be included in the calibration curve.
6. Compound responses cannot be selected from different analyses of the same calibration level (i.e. all compound responses for level 1 must come from the same data file). If more than three calibration levels are analyzed, it is permissible to either drop the low compound concentration (poor response) or the high compound concentration (detector saturation). Do not drop a point in the middle of the curve.

7. If more than three calibration levels are analyzed, it is permissible to drop an entire level if the analyst can document a specific reason or reasons why that level should be excluded. Mechanical failures, significant loss of all compound responses possibly due to poor technique in standard preparation, or software malfunction during data acquisition (system did not acquire all compound data) are plausible reasons. The reason must be justified and documented. The supervisor should review this situation and approve the analyst's decision.
8. The need to reanalyze the same calibration level more than once indicates a potential problem with the Working Standard mixture. Prepare a fresh Working Standard and repeat all calibration levels. All calibration standard levels must come from the same Working Standard.
9. Manual integration must only be used if the software fails to properly integrate the peak (See SOP 1255 Manual Integration). If manual integration is used for a particular compound, all levels of that compound do not have to be manually integrated. Example: the computer generated integration of a compound in the low level standard is not technically sound. A manual integration of the compound is performed (due to baseline noise, etc) in order to achieve a technically sound integration. The computer integrates other levels of the compound correctly. The manual integration of the low level must match, as best as possible, the computer generated integrations for all other levels.
10. If any compound in the mid-point level is manually integrated, the integration of this compound must be reviewed for every continuing calibration standard and QC check solution to ensure that the integration is the same as the manual integration performed in the initial calibration (ICAL) mid-point. A consistent manner of integration must be achieved.
11. All manual integrations must be reviewed and approved according to SOP 1255 Manual Integration.

13.2 Continuing Calibration Verification (CCV)

13.2.1 A continuing calibration verification (CCV) sample is analyzed for every batch of samples. Different standards are analyzed for the CCV such that a wider range of the calibration curve is verified.

13.2.2 Control limits for the CCC compounds are ± 20% difference from the ICAL Calibration Factor (CF).

13.2.3 If the CCV results obtained are outside the acceptance criteria, corrective actions must be performed. If routine corrective actions fail to produce an acceptable *second consecutive (immediate)* CCV, then either the lab has to demonstrate performance after corrective action with two consecutive successful CCVs, or a new ICAL must be performed. If the instrument has not demonstrated acceptable performance, sample analyses cannot continue until a new ICAL is established and verified with an ICV. However, sample data associated with an unacceptable CCV may be reported as qualified data under the following special conditions:

13.2.3.1 When the acceptance criteria for CCV are exceeded high, i.e., high bias, and there are associated samples that are non-detects, then those non-detects may be reported. Otherwise the samples affected by the unacceptable calibration verification must be reanalyzed after a new ICAL has been established, evaluated and accepted.

13.2.3.2 When the acceptance criteria for the CCV are exceeded low, i.e., low bias, those sample results may be reported if they exceed a maximum regulatory limit/decision level. Otherwise the samples affected by the unacceptable verification must be reanalyzed after a new ICAL is established and verified with an ICV.

13.2.3.3 When the acceptance criteria for the CCV are exceeded and it is not possible to reanalyze the sample due to limited sample quantity and the laboratory cannot obtain a new sample, the data may be reported with the appropriate data qualifiers if the client has been contacted and agrees to accept the qualified data.

13.3 Records: Initial and Continuing Calibration Records will contain, at a minimum, the following:

1) Calibration date
2) Test method
3) Instrument

4) Analysis date
5) Each compound name
6) Analyst's initials or signature
7) Standard Concentration (appropriate units) and number of standards
8) Response (appropriate units)
9) Calibration curve or response factor
10) Evaluation of and Statistics for ICAL curve fit in order to judge calibration curve acceptance
11) Evaluation of and Acceptance Limits for ICV analysis in order to judge calibration curve acceptance.
12) Evaluation of and Acceptance Limits for CCV analysis in order to judge continuing calibration acceptance.

14.0 PROCEDURE

14.1 Sample Preparation

14.1.1 Incoming samples will have their pressure checked using the test pressure gauge.
Samples in Tedlar can be connected directly to the instrument for analysis. Alternatively, the contents of the Tedlar bag can be transferred to a clean, evacuated canister. The pressure in the canister is recorded, and the canister is pressurized with helium, final pressure is recorded to calculate preparation factor.

14.1.2 High purity helium is added to each incoming canister sample, the final pressure of every sample is recorded. The initial and final sample volumes are recorded in LIMS and used to calculate the sample prep factor.

14.2 Sample Analysis

14.2.1 Access the Chemstation software to generate a sample analysis sequence.

14.2.2 Analyze the Continuing Calibration Verification Standard (CCV) and evaluate using CCV acceptance criteria (See Section 13.2).

14.2.3 Analyze the Method Blank. The method blank must contain less than the reporting level for all target compounds. If target parameters achieve these limits, recovery and retention times of the compounds are within acceptance limits, and the chromatography (baseline noise and compound tailing) is acceptable, continue the analysis. If any one of these criteria is not met, take appropriate corrective action to identify and correct the problem.

14.2.4 Purge the sample loop with sample, and allow to come to atmospheric pressure before each injection. Analyze each sample in duplicate. The analysis is acceptable when results of two consecutive injections of the sample agree within 5% of their average.

14.2.5 If the response for any compound exceeds the initial calibration curve range, sample dilution and reanalysis is an option.

14.2.6 Perform all qualitative and quantitative measurements as described in Sections 14.4 and 14.5. Samples may be retained for up to 30 days from the date of sample collection for repeat analysis should the sample fail data review for any reason. After client approval or 30 days has elapsed, the canister should be cleaned along with a batch of other canisters, and one canister from each batch should be certified as described in section 7.4.

14.3 Analytical Sequence

START CHEMSTATION SOFTWARE:
From Desktop: C:\HPCHEM\MSEXE\MSTPO.EXE

The software will locate the instrument. Once the software is fully loaded there will be two windows visible. Window one is the instrument control window. Instrument parameters are readily viewed from this window. The second window is the sequence control window.

SEQUENCE SETUP

From menu: Method/Load
1. Load the method you want to use for analysis (e.g., A112108.m)
2. OK (to save changes)

From menu: Sequence/Run
3. Set current date in Data File Directory space (e.g., C:\MSDCHEM\2\DATA\081222\)
4. OK (to save changes)

From menu: Sequence/Edit Sample Log Table
1. Set data file name using current date using the following format MMDDYY##.d (e.g., 12220801.d)
2. Set up sequence order using the following format: (**NOTE:** CCV must always run first, followed by analysis of the method blank. The only exception to this is the ICAL sequence.)

LINE	TYPE	VIAL	DATA FILE	METHOD	SAMPLE NAME-INSTRUMENT
1	Sample	1	12220801	A112108	CCV TO3STD…
2	Sample	2	12220802	A112108	MBLK TO3BLK122208
4	Sample	3	12220803	A112108	SAMP ##########
5	Sample	3	12220804	A112108	SAMP ##########
…	Sample	…	…	A112108	…
…	Sample	…	122208…	A112108	SAMP ##########
…	Sample	…	122208…	A112108	SAMP ##########

NOTE: Ten samples, not including CCV and method blank can be analyzed within the 8-hour window.
3. OK (to save changes)

From menu: Method/Set New Default Paths
1. Update the method and data file paths using the current date (e.g., C:\MSDCHEM\1\DATA\122208\)
2. OK (to save changes)

Using Windows Explorer copy all of the method files from the previous day's folder into the current day's folder. Note: After each ICAL, the method is saved using the following format: matrix instrument MMDDYY of last ICAL (e.g., A112108.m).

TO START SEQUENCE:

From menu: Sequence/Run/Run Sequence
The analytical sequence for Initial Calibration is:

Calibration standard (S1)
Calibration standard (S2)
Calibration standard (S3)
……..
Calibration Standard (SN)
Initial Calibration Verification Standard (ICV)
Method Blank (MBLK)

The analytical sequence for Sample Analysis is:

Continuing Calibration Verification Standard (CCV)
Method Blank (MBLK)
Sample #1
Sample #1 Duplicate
Sample #2
Sample #2 Duplicate
……..
Sample #N
Sample #N Duplicate

14.4 Data Interpretation - Qualitative Analysis

14.4.1 A compound is identified based upon Relative Retention Time (RRT). The criteria must be satisfied to verify identification: elution of sample component at the same GC relative retention time (RRT) as those of the standard component.

14.4.2 The RRT of the sample component is within ± 0.06 RRT units of the RRT of the standard component.

14.5 Data Interpretation - Quantitative Analysis

14.5.1 Once a compound has been identified, the quantitation of that compound must be based on the integrated abundance.

14.5.2 The concentration in the sample is determined using the average CF from initial calibration data (13.0).

14.6 Record the following information in the appropriate logbook or data file. Include any deviations from this procedure. Analyst initials, date of analysis, sample number or ID, initial sample volume or weight processed, calibration standard sample or solution identifier, QC sample or solution identifier, any dilution information, readings from support equipment, data file name, instrument method name, visual observations, and any other information as deemed necessary.

14.7 Troubleshooting - The experience of the analyst performing analyses is invaluable to the success of the methods. Each day that the analysis is performed, the daily calibration standard (CCV) must be evaluated to determine if the chromatographic system is operating properly. Questions that must be asked: Do the peaks look normal? Is the response obtained comparable to the response from previous calibrations? Careful examination of the chromatogram can indicate whether the column is still good, the injector is leaking, the injector septum needs replacing, etc. If any major changes are made to the system (e.g. column changed or detector cleaned), recalibration of the system must take place.

14.8 Record all maintenance, including the problem encountered, steps taken to correct the problem, and verification that the problem has been corrected.

15.0 DATA REDUCTIONS, CALCULATIONS, AND LOADING

15.1 The LIMS data system performs the calculations. Since each sample may have a preparation factor, this must be accounted for in the calculations.

15.1.1 The concentration in the sample is determined using the average CF from the initial calibration data (13.0)

15.1.2 Additional calculations can be fulfiled by customers request and the following equation. Additional data must be provided:

$$C_0 = \frac{A}{R(1-B_w)}$$

where:
A = Average sample area
R = Mean calibration response factor for specific sample component area/%vol
B_w = Moisture content in the sample

$$B_W = \frac{P_w}{P_{bar}}$$

Where:
P_w = Wapor pressure of H_2O (from Table 2), mm Hg
P_{bar} = Barometric pressure, mm Hg

If the sample was diluted with helium using procedures in Method 25C:

$$C = \frac{C_0 P_{tf}}{T_{tf}\left(\frac{P_t}{T_t} - \frac{P_{ti}}{T_{ti}}\right)}$$

Where:
P_{tf} = final gas sample tank pressure after pressurizing, mm Hg absolute
P_t = gas sample tank pressure after sampling, but before pressurizing, mm Hg absolute
P_{ti} = gas sample tank pressure after evacuation, mm Hg absolute
T_{tf} = sample tank temperature after pressurizing, ^{0}K
T_t = sample tank temperature at completion of sampling, ^{0}K
T_{ti} = sample tank temperature before sampling, ^{0}K

Table 2 Moisture correction

Temperature, ^{o}C	Vapor pressure of H_2O, mm Hg	Temperature, ^{o}C	Vapor pressure of H_2O, mm Hg
4	6.1	18	15.5
6	7.0	20	17.5
8	8.0	22	19.8
10	9.2	24	22.4
12	10.5	26	25.2
14	12.0	28	28.3
16	13.6	30	31.8

15.3 The concentration of the compound in the sample is reported in percent (%). If conversion to mg/m^3 is required, calculate as follows:

$$\text{Concentration (mg/m}^3) = \frac{\text{Conc. (\%)} * 10000 * \text{MW}}{}$$

$$\frac{24.45}{MW}$$

Where:

24.45 is the volume in L of 1 mole of an ideal gas at 25 ºC and standard pressure.
Conversion of L to m^3 is cancelled out by conversion of mg to mg.
MW is the molecular weight

15.4 The procedure for uploading data into the LIMS system is detailed in SOP 1400 LIMS.

16.0 METHOD PERFORMANCE

16.1 Demonstration of Capability (DOC)

All parameters of interest must meet the method acceptance criteria before actual sample analysis begins. See SOP 1230 Training for the procedure to perform and document the DOC. The DOCs for the analysts performing this method are located in the analysts' training form folders located in the QA office files.

The QC reference sample used is the ICV. The QC reference sample is made using stock standards prepared independently from those used for calibration. This analysis is performed in quadruplicate using 4 separately prepared canisters. For each analyte calculate the mean recovery (X), the average percent recovery (R) and the standard deviation of the percent recovery (S). Note mean recovery must be in the range of 80 to 120%. If X, S and %R for all analytes meet the acceptance criteria, the system performance is acceptable and analysis of actual samples can begin. If any individual X, S or R falls outside the range for accuracy, then the system performance is unacceptable for that analyte and corrective action must be taken.

16.2 Comparison to Reference Method Data

EPA Method 3C provides guidance for the establishment of control limits for the QC samples. Recovery limits of 80% to 120% are provided as initial benchmarks for performance.

17.0 POLLUTION PREVENTION

The preparation of excessive volumes of laboratory reagents and standards shall be avoided so that waste and potential for pollution are minimized. Samples, reagents and standards shall be disposed in compliance with the lab waste disposal program, SOP 1130 Waste Management. With the consent of the client, the samples may be returned to their origin for treatment.

Uncontaminated paper waste, glass and cans should be separated for recycling. Laboratory staff is required to protect the laboratory and our clients' business information when disposing of recycled paper or waste from the facility.

18.0 DATA ASSESSMENT AND CRITERIA FOR QUALITY CONTROL MEASURES

Data assessment includes review of: proper sample condition, preservation, and storage; analysis within holding time limitations; deviations from the SOP, evaluation of performance based or in-house control limits, reference method limits or project specific limits.

The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When results of sample spikes indicate atypical method performance, a calibration verification standard is used to confirm the measurements were performed in an in-control mode of operation. The data review is conducted according to SOP 1250 Data Review.

18.1 Blanks

The method blank must contain less than the reporting limit for all target compounds. If the blank exceeds these limits, the source of contamination must be investigated and corrective actions taken. Re-analyze the method blank. If after re-analysis, the blank criteria is still exceeded, stop the analysis prior to sample analyses and correct the problem. Consult with the department manager for guidance. Refer to a client specific QAPP for additional guidance, if applicable.

If samples were analyzed with a contaminated method blank during unattended automated analysis, affected samples must be reanalyzed or data must be appropriately qualified if:

1) The concentration of a targeted compound in the blank is at or above the reporting limit as established by the SOP or by regulation, AND is greater than 1/10 of the amount measured in any sample.
2) The blank contamination otherwise affects the sample results as per the test method requirements or the individual project data quality objectives.

18.2 Laboratory Control Samples (LCS/LSCD)

Not applicable to this method.

18.3 Surrogates

Not applicable to this method.

18.4 Duplicates

The results from Laboratory Duplicates are designed to assess the precision of analytical results in a given matrix and are expressed as relative percent difference (RPD). See the QAM, Section 5.4 for the calculation for RPD.
For duplicates results outside established criteria (>5%), corrective action must be documented or the data reported with appropriate data qualifying codes.

18.5 Matrix Spikes

Not applicable to this method.

18.6 Internal Standards

Not applicable to this method.

18.6 Other

The laboratory will analyze standard reference materials and/or participate in relevant performance evaluation studies quarterly.

19.0 CORRECTIVE ACTIONS FOR OUT-OF-CONTROL DATA

The process for handling unacceptable and out of control data is found in SOP 230 Corrective Action.

If the CCV, MB or lab duplicate, recovery of any parameter falls outside the designated acceptance range, the laboratory performance for that parameter is judged to be out of control, and the problem must be immediately identified and corrected. The analytical result for that parameter in the samples is suspect and is only reported for regulatory compliance purposes with the appropriate corrective action form. Immediate corrective action includes reanalyzing all affected samples by using any retained sample before the expiration of the holding time. Final data results must be qualified in the client report for reported results not meeting the laboratory-defined criteria.

1) Review standards preparation logbooks. Check all calculations and ensure dilution factors are properly recorded.

2) Re-prepare the suspected standard or QC sample to identify possible preparation errors of the standard or QC sample.

   Re-Analyze the samples when the CCV is not within acceptable limits, or analysis of two consecutive injections of the sample is not within 5% of their average.

3) Perform routine preventative maintenance following manufacturer's specification. Record all maintenance in the instrument logbook.

20.0 CONTINGENCIES FOR HANDLING OUT-OF-CONTROL OR UNACCEPTABLE DATA

Every effort is made to prevent problems from occurring. When out of control or unacceptable data occurs the first option is to identify the problem and reanalyze the samples within the holding times. When this is not possible, the QA Manager and/or the Laboratory Director reviews data and discusses options with the client. Reanalysis or reporting the data with qualification are alternatives. Out of control or unacceptable data reported to the client must include the data qualifier, flag and discussion on the rationale for reporting.

Holding time exceedence, improper preservation and improper sample condition or storage are noted on the corrective action form and included on the final report.

Review the CCV standard response, for acceptable performance for each batch of samples. Record any trends or unusual performance on a corrective action form. Final data results must be qualified in the client report for results not meeting the laboratory-defined criteria.

Manual integration must be minimized for standards and the method blank. Routine manual integration of the same parameters indicates a system performance problem. Correct this problem or note in the instrument analysis logbook the suspected causes for routine manual integration. Sign and date all manually integrated chromatograms.

20.1 The process for handling unacceptable and out of control data is found in the Laboratory QAM Section 11. The reporting of data that is out of control must be approved and documented by Quality Assurance Manager and either the Technical Manager or the Laboratory Director.

20.2 Client Requested Modifications:

20.2.1 Clients must request modifications from the laboratory SOP in writing to the lab.

20.2.2 The lab director, technical manager and quality assurance manager will evaluate the requested client deviations, determine the feasibly of the deviation and the potential effects on the data.

20.2.3 If it is determined that the lab will perform the requested deviations, the lab director, technical manager and quality assurance manager will decide if a method validation study is required.

20.2.4 The designated project manager will retain all documentation concerning the requested deviation, including all correspondence with the client, in the client folder.

20.2.5 The final analytical report must include the statement *"This report has analyses performed using client requested modifications"*.

21.0 WASTE MANAGEMENT

The STAT Analysis Corporation SOP 1130 Waste Disposal identifies proper waste management practices for the chemicals and biological materials used in this procedure. Samples are stored and discarded in accordance with SOP 1130 Waste Disposal.

22.0 REFERENCES

22.1 USEPA, 40CFR Part 136 Appendix B – Definition and Procedure for the Determination of the Method Detection Limit, Revision 1.11.
22.2 Method 3C, Determination of carbon dioxide, methane, nitrogen and oxygen from stationary sources.
22.3 SOP 001, Quality Assurance Manual, STAT Analysis Corporation
22.4 SOP 003 Chemical Hygiene Plan
22.5 SOP 230 Corrective Action
22.6 SOP 1000 Control and Use of Laboratory Notebooks
22.7 SOP 1010 Analytical Standards and Reagents Receipt and Preparation
22.8 SOP 1040 General Laboratory Practices
22.9 SOP 1130 Waste Disposal
22.10 SOP 1210 Method Detection Limits
22.11 SOP 1230 Training
22.12 SOP 1250 Data Review
22.13 SOP 1255 Manual Integration
22.14 SOP 1400 LIMS
22.15 Manufacturers' Equipment Instruction Manuals

23.0 FORMS, FIGURES, TABLES, DIAGRAMS, FLOWCHARTS, ATTACHMENTS OR VALIDATION DATA

Attachment 1

MDLs and REPORTING LIMITS FOR 3C COMPOUNDS

COMPOUND NAME	MDL, %	Lower Reporting Limit, ppmv
Carbon dioxide	0.004	0.04
Methane	0.011	0.05
Nitrogen	0.098	1.0
Oxygen	0.027	0.3

STAT Analysis Corporation

STANDARD OPERATING PROCEDURE 4430

ALKALINITY ANALYSIS

Revision 00
Effective Date: December 29, 2008

Printed Name	**Signature/Date**
Bruce Anderson **Inorganics Manager**	_____
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1.0 Identification of Test Method

SOP Title: Alkalinity Analysis

2.0 Applicable Matrix or Matrices

This method is used to measure alkalinity in aqueous samples, waste, and leachate.

3.0 Detection Limits

The lab follows the procedure found in 40CFR Part 136B to determine the MDL for each matrix type on an annual basis. See the STAT Analysis SOP 1210 for the MDL procedure, frequency and acceptance criteria. The MDLs measured by the lab and all supporting documentation are in the laboratory QA files for review. The MDL for this method is 3.63 mg/L as $CaCO_3$.

The laboratory determined MDL must always be less than the reporting limit (RL). The RL will usually range from three to ten times the laboratory measured MDL but this relationship may vary dependent on dilution of sample aliquots, matrix interferences, moisture adjustments (in solid samples), or method-specified requirements. The RL for this method is 10 mg/L as $CaCO_3$.

4.0 Scope and Application

The method, based on Standard Methods 2320 B is designed for the analysis of alkalinity in water. Because the alkalinity of many surface waters is primarily a function of carbonate, bicarbonate, and hydroxide content, it is taken as an indication of the concentration of these constituents.

5.0 Summary of Method

Hydroxyls ions present in a sample as a result of dissociation or hydrolysis of solutes react with additions of standard acid. Alkalinity thus depends on the end-point pH used. When alkalinity is due entirely to carbonate or bicarbonate content, the pH at equivalence point of the titration is determined by the concentration of carbon dioxide (CO_2) at that stage. CO_2 concentration depends, in turn, on the total carbonate species originally present and any losses that may have occurred during titration

6.0 Definitions

The STAT Analysis Corporation Quality Assurance Manual (QAM) contains the definitions of standard terms used in this SOP.

7.0 Interferences

7.1 Soaps, oily matters, suspended solids, or precipitates may interfere.

7.2 Do not filter, dilute, concentrate, or alter sample.

7.3 Method interference may be caused by contaminants in the reagent water, reagents, glassware, and other sample processing apparatus that bias analyte response.

8.0 Safety

8.1 All samples must be assumed as hazardous and appropriate precautions taken during handling.

8.2 Safety glasses, gloves, lab coats and closed toe shoes are to be worn.

8.3 Other safety precautions must be conducted in accordance with the SOP 003 Chemical Hygiene Plan. Other actions can also be applied if deemed necessary. A reference file of material safety data sheets (MSDS) is available in the laboratory for personnel involved in an analysis using chemicals.

8.4 The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable. Cautions are included for materials known to be extremely hazardous.

8.5 The following chemicals have the potential to be highly toxic or hazardous, for detailed explanation consults the MSDS.

8.5.1 Sulfuric acid is a strong oxidizer. Use extreme caution when handling this chemical. Avoid eye and skin contact. Wash exposed areas immediately with copious amounts of water

9.0 Equipment and Supplies

9.1 Titration vessel, 500 mL beaker

9.2 Pipets, volumetric

9.3 Flasks, volumetric, 1000-, 200-,100-mL

9.4 Burets, borosilicate glass, 50-, 25-, 10-mL

9.5 Polyolefin bottle, 1-L

9.6 Transfer Pipets

9.7 pH paper

9.8 Analytical balance

10.0 Reagents and Standards

The following reagents and standards are required to perform this procedure. When instructions are given on how to prepare a specific volume of a reagent or standard, larger or smaller volumes can be prepared as needed so long as the final concentrations remain the same. Any other deviations from the reagents or standards listed in this SOP could be detrimental to the quality of the data produced. Such deviations would have to be approved and documented (see 230 Corrective Action SOP).

10.1 Instructions for labeling and record keeping of reagents and standards are contained in SOP 1010 Analytical Standards and Reagents Receipt and Preparation.

10.2 Reagents - In methods where the purity of reagents is not specified, analytical reagent grade shall be used. Reagents of lesser purity than those specified by the test method shall not be used.

10.3 Stock Alkalinity Standard: Sodium Carbonate, as 0.5N $CaCO_3$ (preferable by ampule).

10.4 **Working Alkalinity Solution-Sodium Carbonate (0.05N):** In 100 mL volumetric flask, add 10 mL of 0.5N Na_2CO_3 solution from commercially purchased ampoules, diluting to 100 mL of DI.

1) **Alternate Sodium Carbonate Solution (0.05N):** Dry 3 to 5 g Na_2CO_3 at 250°C for 4 h and cool in a desiccator. Weigh 2.5 ± 0.2 g (to the nearest mg), transfer to a 1-L volumetric flask, fill to the mark with distilled water, and dissolve and mix reagent. Do not keep longer than 1 week.

10.5 **Reagent 1. Standard Sulfuric Acid (0.02N):** Commercially purchased.

10.6 **Reagent 2. Mixed Bromocresol Green-Methyl Red Indicator Solution:** Commercially purchased.

10.7 **Reagent 3. Phenolphthalein Solution Alcoholic:** Commercially purchased.

1) Alternative: Dissolve 5 g phenolphthalein disodium salt in 500 mL 95% ethyl or isopropyl alcohol and add 500 mL DI water.

11.0 Sample Collection, Shipment, Preservation and Storage

Samples shall be placed on ice immediately after collection. The holding time is 14 days for a refrigerated sample (0.1 - 6°C). Collect samples in polyethylene or borosilicate glass bottles and store at a low temperature. Fill bottles completely and cap tightly. Because waste samples may be subject to microbial action and to loss or gain of CO_2 or other gases when exposed to air, analyze samples without delay, preferably within 1 day. If biological activity is suspected analyze within 6 hours. Avoid sample agitation and prolonged exposure to air.

12.0 Quality Control

The following details the QC requirements that apply to this analysis. Each Quality Control Indicator (QCI) provides information pertaining to either method or individual sample performance. Our goal is to produce defensible data of known and documented quality.

The results of these QCI samples are used to assess the acceptability of data.

12.1 Blanks

Method Blank analysis is performed to determine if any contamination is present in the analytical process and is used to evaluate acceptance of the batch of samples. A method blank shall be prepared once per preparation batch of 20 or less samples per matrix type. If more than 20 samples are prepared a second blank shall be prepared after the twentieth sample. The method blank shall be processed through all preparatory steps used for the samples, including cleanup procedures. The blank shall be analyzed using the same instrument and conditions as the samples.

12.2 Laboratory Control Sample (LCS)

The LCS is used to evaluate the performance of the total analytical system, including all preparation and analysis steps. The LCS shall be prepared once per preparation batch of 20 or less samples per matrix type. If more than 20 samples are prepared a second LCS shall be prepared after the twentieth sample. The LCS shall be processed through all preparatory steps used for the samples, including cleanup procedures. The LCS shall be analyzed using the same instrument and conditions as the samples.

Theoretical Value of LCS is 25 mg/L as $CaCO_3$ .Use 1 mL of working alkalinity solution (see 10.4) to 100 mL DI.

12.3 Duplicates

Duplicates of field samples or of the LCS must be prepared in compliance with the method requirements and client directives. Note: The analysis of the Matrix Spike Duplicate (MSD) is used as a substitute for the laboratory duplicate.

12.4 Matrix Spike and Matrix Spike Duplicate (MS/MSD)

MS/MSDs indicate the effect of the sample matrix on the precision and accuracy of the results generated using the selected method. This information does not determine the validity of the entire batch. MS/MSD's must be analyzed at a minimum of 1 per 20 samples per matrix per preparation procedure, or as specified by the required test method. For cases where the sample cannot be divided (e.g., wipes, air samples, not enough sample provided by customer) and thus a MS/MSD pair cannot be prepared in the preparation batch, an LCS/LCSD pair is prepared and analyzed to measure precision.

The MS/MSD pair shall be processed through all preparatory steps used for the samples. They shall be analyzed using the same instrument and conditions as the samples.

Theoretical Value is 25 mg/L $CaCO_3$. Use 1 mL of working alkalinity solution (see 10.4) to 100 mL of sample.

13.0 Calibration and Standardization

Titration reagents are purchased pre-standardized. Certificates are kept at the laboratory.

Standard Support Equipment

Autopipettes - Check autopipette to ensure standardization is within control limits (see SOP 1040 General Laboratory Practices for Pipette Calibration).

Balances - Be sure the balance is checked prior to use and performance criteria are met (see SOP 1040 General Laboratory Practices for Calibration of Balances).

14.0 Procedure

14.1 Using pH paper, determine pH of the sample. If pH is 4.5<pH<8.3, pour 100 mL of sample into beaker, add 10 drops of Reagent 2 and titrate with 0.02N H_2SO_4 until color change (green to yellow-red).

14.2 If pH is greater than 8.3, pour 100 mL of the sample into a beaker, add 1 drop of Reagent 3, titrate with 0.02N H_2SO_4 until pink color disappears. Add 10 drops of reagent 2 and titrate until color change (green to yellow-red).

14.3 Record initial and final buret readings of 0.02N H_2SO_4 used for titration in logbook. Record titrant used.

14.4 Smaller volumes may be used for high sample concentrations.

14.5 If pH <4.5, alkalinity can not be determined.

15.0 Data Reduction, Calculations and Loading

15.1 Titration to end-point pH:

Alkalinity, mg $CaCO_3$/L = **A** x **N** x 50000 / mL sample

where:
A = mL standard acid used and
N = normality of standard acid

15.1.1 Enter the volumes into spreadsheet at Harrison/D/Inorganic/Inorganic data/Alkalinity/Alkalinity worksheet to automatically calculate values of Alkalinity.

15.2 Calculations of alkalinity relationships: This task can be done per client request. The results obtained from the phenolphthalein and total alkalinity determinations offer a means for stoichiometric classification of the three principal; forms of alkalinity present in many

waters. The classification ascribes the entire alkalinity to bicarbonate, carbonate, and hydroxide, and assumes the absence of other (weak) inorganic or organic acids, such as silicic, phosphoric, and boric acids. It further presupposes the compatibility of hydroxide and bicarbonate alkalinities. Because the calculations are made on a stoichiometric basis, ion concentration in the strictest sense are not represented in the results, which may differ significantly from actual concentrations especially pH>10. According to this scheme:

1) Carbonate (CO32-) alkalinity is present when phenolphthalein alkalinity is not zero but is less than the total alkalinity.
2) Hydroxide (OH-) alkalinity is present if phenolphthalein alkalinity is more than half the total alkalinity.
3) Bicarbonate (HCO3-) alkalinity is present if phenolphthalein alkalinity is less than or half of the total alkalinity. These relationships may be calculated by the following scheme, where P is phenolphthalein alkalinity and T is the total alkalinity.

Select the smaller value of P or (T-P). Then, carbonate alkalinity equals twice the smaller value. When the smaller value is P, the balance (T – 2P) is bicarbonate. When the smaller value is (T – P), the balance (2P-T) is hydroxide. All results are expressed as $CaCO_3$. The mathematical conversion of the results is shown in Table 1.

Table 1:Alkalinity Relationships

Results of Titration	Hydroxide Alkalinity as $CaCO_3$	Carbonate Alkalinity as $CaCo_3$	Bicarbonate Concentration as $CaCO_3$
P = 0	0	0	T
P < ½ T	0	2P	T – 2P
P = ½ T	0	2P	0
P > ½ T	2P – T	2(T – P)	0
P = T	T	0	0

Alkalinity relationships also may be computed nomographically. Accurately measure pH, calculate OH- concentration as milligrams CaCO3 per liter, and calculate concentration of CO32- and HCO3- as milligrams CaCO3 per liter from the OH- concentration, and the phenolphthalein and total alkalinities by the following equations:

$$\mathbf{CO_3^{2-}} = 2P - 2[OH^-]$$

$$\mathbf{HCO_3^-} = T - 2P + [OH^-]$$

Similarly, if difficultly is experienced with the phenolphthalein end point, or if a check on the phenolphthalein titration is desired, calculate phenolphthalein alkalinity as CaCO3 from the results of the nomographic determinations of carbonate and hydroxide ion concentrations:

$$\mathbf{P} = ½ [CO_3^{2-}] + [OH^-]$$

16.0 Method Performance

Demonstration of Capability (DOC)

Note: Each analyst must demonstrate the ability to generate acceptable results with this method.

All parameters of interest must meet the method acceptance criteria before actual sample analysis begins. See SOP 1230 Training for the procedure to perform and document the DOC. The DOCs for the analysts performing this method are located in the analysts' training form folders located in the QA office files.

Prepare 4 LCS's. Titrate according to Section 14.

Calculate the mean recovery (X), standard deviation (s), relative standard deviation (RSD), and the average % Recovery (%R). Compare X and s and %R with the corresponding acceptance criteria for accuracy and precision, respectively. Note: RSD must be equal to or less than 20% and the %R must be within 100 ± 20%. These limits are taken from established in-house criteria If RSD and %R meet the acceptance criteria, the system performance is acceptable and analysis of actual samples can begin. If RSD or %R falls outside the range for accuracy and precision, then the system performance is unacceptable and corrective action must be taken.

Comparison to Reference Method Data
There are no stated reference method criteria for blanks, LCS, Duplicate Sample or MS/MSD recoveries in Method 2320 B.

In-House Control Limits
Method performance data is on file in the laboratory QC department. Comparison of method performance data for the laboratory to the reference method criteria occurs when laboratory in-house acceptance limits are generated. In-house generated data is compared to the specifications of the reference method. If the in-house limits are within the specifications of the reference method, the control limits are updated in LIMS. If the in-house limits are not within specifications, an investigation is performed to determine the cause(s) of the problem and a corrective action is completed. The analysis may continue until enough data points are collected to regenerate new control limits. Any QC data generated outside of reference method limits during that time frame is flagged.

The laboratory maintains performance records to document the quality of data that is generated. Method accuracy for samples is assessed and records maintained.

17.0 Pollution Prevention

The preparation of excessive volumes of laboratory reagents and standards shall be avoided so that waste and potential for pollution are minimized. Samples, reagents and standards shall be disposed in compliance with the laboratory waste disposal program and applicable waste disposal regulations. With the consent of the client, the samples may be returned to their origin for treatment.

Uncontaminated paper waste, glass and cans should be separated for recycling. Laboratory staff are required to protect the laboratory's and our clients' business information when disposing of recycling or waste from the facility.

18.0 Data Assessment and Criteria for Quality Control Measures

The laboratory maintains records to document the quality of data that is generated. Ongoing quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. The data review is conducted according to SOP 1250 Data Review.

Method Blank (MB)
If the blank exceeds the RL, the source of contamination must be investigated and corrective actions taken.

Affected samples must be reprocessed and reanalyzed or Data must be appropriately qualified if:

1) The concentration of a targeted analyte in the blank is at or above the reporting limit as established by the SOP or by regulation, AND is greater than 1/10 of the amount measured in any sample.

2) The blank contamination otherwise affects the sample results as per the test method requirements or the individual project data quality objectives.

Laboratory Control Sample (LCS)
The results of the individual batch LCS are calculated in percent recovery (%R) and compared to established acceptance criteria (in-house limits). LCS %R limits are 100 ± 20%. If the LCS is outside the acceptance criteria, the analytical system is "out-of-control". Any affected samples associated with an out of control LCS must be reprocessed and reanalyzed or the results reported with appropriate data qualifiers.

Matrix Spikes
The results from MS/MSD are primarily designed to assess the precision and accuracy of analytical results in a given matrix and are expressed as percent recovery (%R) and relative percent difference (RPD). See the STAT QAM, Section 5.4 for the calculation for RPD. Results are compared to established acceptance criteria (in-house limits). For aqueous samples, MS/MSD %R limits are 100 ± 25% and RPD limits are 20%. For soil samples, MS/MSD %R limits are 100 ± 25% and RPD limits are 20%. For matrix spike results outside established criteria corrective action must be documented, or the data for the spiked sample is reported with appropriate data qualifying codes.

Duplicates

The results from laboratory Duplicates are designed to assess the precision of analytical results in a given matrix and are expressed as relative percent difference (RPD). See the STAT QAM, Section 5.4 for the calculation for RPD. Results are compared to established acceptance criteria (in-house limits). RPD limits are 20%. For duplicates results outside established criteria

corrective action must be documented or the data for the duplicate sample is reported with appropriate data qualifying codes.

19.0 Corrective Actions for Out-of-Control Data

The process for handling corrective actions is found in SOP 230 Corrective Action.

If the MB, LCS/LCSD, MS/MSD, or lab duplicate recovery of any parameter falls outside the designated acceptance range, the laboratory performance for that parameter is judged to be out of control, and the problem must be immediately identified and corrected. The analytical result for that parameter in the samples is suspect and is only reported for regulatory compliance purposes with the appropriate corrective action form. Immediate corrective action includes reanalyzing all affected samples by using any retained sample before the expiration of the holding time. Final data results must be qualified in the client report for reported results not meeting the laboratory-defined criteria.

1) Review standards preparation logbooks. Check all calculations and ensure dilution factors are properly recorded.

2) Re-prepare the suspected standard or QC sample to identify possible preparation errors of the standard or QC sample.

3) Re-Analyze the samples when the CCV or LCS is not within acceptable limits.

4) Perform routine preventative maintenance following manufacturer's specification. Record all maintenance in the instrument logbook.

20.0 Contingencies for Handling Out-of-Control Or Unacceptable Data

Every effort is made to prevent problems from occurring. When out of control or unacceptable data occurs the first option is to identify the problem and reanalyze the samples within the holding times. When this is not possible, the QA Manager and/or the Laboratory Director reviews data and discuss options with the client. Reanalysis or reporting the data with qualification is alternatives. Out-of-control or unacceptable data reported to the client must include the data qualifier, flag and discussion on the rationale for reporting.

The process for handling unacceptable and out of control data is found in section 11 of the Laboratory QAM. The reporting of data that is out of control must be approved and documented by Quality Assurance Manager and either the Technical Manager or the Laboratory Director.

21.0 Waste Management

The STAT Analysis Corporation SOP 1130 Waste Disposal identifies proper waste management practices for the chemicals and biological materials used in this procedure. Samples are stored and discarded accordance with SOP 1130 Waste Disposal.

22.0 References

20.1 Method 2320B-Alkalinity, Standard Methods for the Examination of Water and Wastewater (20th Edition).
20.2 STAT Analysis Corporation Quality Assurance Manual
20.3 STAT SOP 003 Chemical Hygiene Plan
20.4 STAT SOP 230 Corrective Actions
20.5 STAT SOP 1000 Control and Use of Laboratory Notebooks
20.6 STAT SOP 1010 Standard and Reagent Preparation
20.7 STAT SOP 1020 Glassware Cleaning
20.8 STAT SOP 1040 General Laboratory Procedures
20.9 STAT SOP 1130 Waste Disposal
20.10 STAT SOP 1210 Method Detection Limits (MDL's)
20.11 STAT SOP 1230 Training
20.12 STAT SOP 1250 Data Review
20.13 STAT SOP 1400 LIMS

23.0 Forms, Figures, Tables, Diagrams, Flowcharts, Attachments or Validation Data

Not applicable to this SOP.

STAT Analysis Corporation

Standard Operating Procedure 4480:

Gravimetric Determinations for Moisture, Solids, Ash, and Fractional Organic Carbon (FOC)

(EPA METHOD 160.4, SW 3550B, & ASTM D2216, D2974)

Revision 00
Effective Date: December 23, 2008

Printed Name	Signature/Date
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1.0 Identification of Test Method

SOP Title: Gravimetric Determinations for Moisture, Solids, Ash, and Fractional Organic Carbon/Organic Matter.

2.0 Applicable Matrix or Matrices

This method is applicable to the following matrices: Solids, sludge, and multiphasic wastes.

3.0 Detection Limits

The lab follows the procedure found in 40CFR Part 136B to determine the MDL for each matrix type on an annual basis. See STAT Analysis SOP 1210 for the MDL Procedure, frequency and acceptance criteria. The MDLs measured by the laboratory and all supporting documentation are in the laboratory QA files for review.

The laboratory determined MDL must always be less than the reporting limit (RL). The RLs will usually range from three to ten times the laboratory measured MDLs, but this relationship may vary dependent on dilution of sample aliquots, matrix interferences, or method specific requirements.

The reporting limit for Percent Moisture for this method is 0.2 %. The method detection limit for Percent Moisture is 0.13 %.

Reporting limits for ash and fractional organic carbon have not been determined.

4.0 Scope and Application

Percent moisture is determined to provide dry weight correction for results on other analytical methods performed by the laboratory.

Soils and sediments contain a large variety of organic materials ranging from simple sugars and carbohydrates to the more complex proteins, fats, waxes, and organic acids. Important characteristics of the organic matter include their ability to: form water-soluble and water insoluble complexes with metal ions and hydrous oxides; interact with clay minerals and bind particles together; sorb and desorb both naturally-occurring and anthropogenically-introduced organic compounds; absorb and release plant nutrients; and hold water in the soil environment. As a result of these characteristics, the determination of total organic carbon (a measure of one of the chemical components of organic matter that is often used as an indicator of its presence in a soil or sediment) is an essential part of any site characterization since its presence or absence can markedly influence how chemicals will react in the soil or sediment. Soil and sediment total organic carbon (TOC) determinations are typically requested with contaminant analyses as part of a risk assessment data package. TOC contents may be used qualitatively to assess the nature of

the sampling location (e.g., was a depositional area) or may be used to normalize portions of the analytical chemistry data set (e.g., equilibrium partitioning).

The loss-on-ignition (LOI) method for the determination of organic matter involves the heated destruction of all organic matter in the soil or sediment. A known weight of sample is placed in a ceramic crucible (or similar vessel), which is then heated to 440 °C.

The sample is then cooled in a desiccator and weighed. Organic matter content is calculated as the difference between the initial and final sample weights divided by the initial sample weight times 100%. All weights should be corrected for moisture/water content prior to organic matter content calculation.

NOTE: Each analyst must demonstrate the ability to generate acceptable results with this method.

5.0 Summary of Test Method

5.1 Percent Moisture/Percent Solids

Approximately 5-10 grams of sample is dried in an oven overnight at a temperature of 105 ± 10°C). Allow the sample to cool to room temperature, weigh, and perform calculations.

5.2 Ash/Fractional Organic Carbon (FOC)

Approximately 20-30 grams of sample is dried in an oven overnight at a temperature of 105 ± 10°C). Then the sample is heated in a **muffle furnace** at 440°C for 4 hours. Allow the sample to cool to room temperature, weigh, and perform calculations.

Method modifications from Reference – Samples analyzed for moisture content are dried overnight in the oven, not necessarily for 16 hours. Same day moisture content samples are dried for a minimum of 4 hours

6.0 Definitions

The STAT Analysis Corporation Quality Assurance Manual (QAM) contains the definitions of standard terms used in this SOP.

Oven dried sample -total residue remaining after oven drying at 103-105°C, expressed as grams

Ash - material remaining after ignition in a muffle furnace at 440°C of the oven dried sample, expressed as weight percent

Organic Carbon/Organic Matter - also referred to as organic carbon content is one hundred minus the percentage of ash.

Percent Solids (Psolids) - also referred to as total solids or total residue is the percent solids remaining after oven drying at 105°C

Percent Moisture (Pmoist) - the weight percent of moisture lost after oven drying at 105°C

7.0 Interferences

7.1 Highly mineralized waters with large amounts of calcium, magnesium, chloride and/or sulfate may be hygroscopic and require longer drying, desiccation, and rapid weighing.

7.2 Too much residue in the aluminum dish can reduce the amount of water that can be evaporated during drying. Samples containing high amounts of minerals and other hygroscopic materials may require a smaller sample size to help insure removal of all moisture.

8.0 Safety

8.1 All samples must be assumed as hazardous and appropriate precautions taken during handling.

8.2 Safety glasses, gloves, lab coats and closed toe shoes are to be worn.

8.3 Other safety precautions must be conducted in accordance with the Chemical Hygiene Plan. Other actions can also be applied if deemed necessary. A reference file of material safety data sheets (MSDS) is available in each room for personnel involved in an analysis using chemicals.

8.4 The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable. Cautions are included for known extremely hazardous materials.

8.5 A reference file of material safety data sheets (MSDS) is available in the lab for personnel involved in any analysis using chemicals.

9.0 Equipment and Supplies

The following apparatus is recommended for performing this procedure. Equivalent items can be used, if with their use, the analytical and QA/QC requirements in this SOP can be met.

9.1 Thermometer ($^{-}10^{o}$C to 260°C)

9.2 Disposable aluminum dishes – 75mm diameter

9.3 Porcelain crucibles – (31 x 26 mm) diameter x height (mL 10) and (35 x 29) (mL 15)

9.4 Oven for operation to 105 ± 5°C

9.5 Muffle furnace for operation up to 440°C

9.5 Tongue depressors

9.6 Forceps

9.7 Analytical balance capable of weighing to ± 0.0001g.

9.8 Desiccant Blue (97% $CaSO_4$ and 3% $CoCl_2$) and white (100% $CaSO_4$) A mixture of 10% blue and 90% white should be used in the desiccator. When the desiccant turns from blue to pink (indicating water absorption), heat in an oven at 180 °C overnight to drive off moisture.

9.9 Desiccator

10.0 Reagents and Standards

10.1 Deionized water – ASTM type 2 reagent grade water

10.2 Sodium Chloride – (reagent grade) Dry in an oven at 180°C for 1 hour and store in a tightly sealed container in a dessicator. Shelf life is 5 years.

10.3 Ottawa Sand - Dry in an oven at 180°C for 1 hours and store in a tightly sealed container in a dessicator. Shelf life is 5 years.

10.4 Laboratory Control Sample Solid (LCSS) for Pmoist/Psolids –Weigh out 475 grams to the nearest 0.5 grams of Ottawa sand. Place in a 500 ml plastic bottle. Weigh out 25 grams of reagent water and add to the plastic bottle. Cap tightly and shake to mix. Store at room temperature. Shelf life is 6 months from the preparation date. T.V. for pmoist is 5 % Quality Control(QC) limit is ±20 %

10.5 Stock solution for Laboratory Control Sample (LCSW) for Pmoist/Psolids – Weigh out 2 grams of Sodium Chloride. Add to 1000 ml of reagent water, mix well and store in a plastic bottle at room temperature. Shelf life is one year. T.V. is 02% Quality Control(QC) limit is ±20 %

11.0 Sample Collection, Preservation and Handling

Samples should be analyzed as soon as possible. No preservation is needed. Samples must be analyzed within seven days from the time of collection. Store at 0.1 – 6 °C until analysis.

12.0 Quality Control

12.1 **Method Blank** A Method Blank analysis is performed to determine if any contamination is present in the analytical process and is used to evaluate acceptance of the batch of samples.
A Method Blank must be processed through the same conditions as the associated samples for TSS and TDS using reagent water. The Method Blank is of a similar matrix (e.g. reagent water) and is free of analytes of interest.

12.2 **Duplicates** - Duplicates are defined as replicate aliquots of the same sample taken through the entire analytical procedure. The result from this analysis is an indication of the precision of the analytical method. The duplicate provides a usable measure of precision only when target analytes are found in the sample chosen for duplication. Duplicates are performed on replicate aliquots of actual samples. The duplicate analysis must be analyzed at a frequency of at least once per 20 samples per preparation batch.

12.3 **Laboratory Control Sample (LCS)** - The LCS is used to evaluate the performance of the total analytical system, including all preparation and analysis steps. The LCS is a controlled matrix (e.g., reagent water, Ottawa sand, glass beads, etc.), known to be free of analytes of interest, spiked with known and verified concentrations of analytes. Alternatively, the LCS may consist of a media containing known and verified concentrations of analytes or as Certified Reference Material (CRM). All LCS analyte concentrations must be within the calibration range. The LCS must be analyzed at a minimum of once per preparation batch.

12.4 MS/MSDs are not applicable to this method.

13.0 Calibration and Standardization

13.1 Balances need to be checked daily with the appropriate weights prior to use (refer to SOP 1040 General Laboratory Practices).

13.2 Thermometers - Check thermometers to ensure the calibration is not expired or for correction factors (refer to SOP 1040 General Laboratory Practices for Thermometer Calibration).

13.3 Check the Microsoft Excel “Dry Weight Conversion” program to ensure file is not corrupted. Click on <tools>, <macros--CHECK, the four columns should read as follows all the way down the page. If not the file is corrupted and needs to be corrected.

% Solids	% Moisture	% Ash	% FOC
66.67	33.33	50.00	50.00
66.67	33.33	50.00	50.00

Click on the <CHECK OFF> button to begin entering data into the spreadsheet. **Always exit the program without saving changes after you finish using the spreadsheet**.

14.0 Procedure

Analysis for all procedures should be done on a well-mixed sample.

Percent Moisture/Percent Solids (Pmoist/Psolid)

14.1 Label, then weigh an empty aluminum dish or use a prelabeled dish. Record the weight in the logbook.

14.2 Weigh approximately 5-7 grams of the sample and record the weight. (A larger or smaller sample size may be used if needed)

14.3 Dry at 105 $\pm$ 10°C in an oven. The drying process should be overnight unless same day results are requested.

14.4 Allow the sample to cool and re-weigh, and record weight. If the sample has conjoined together or appears to have an amorphous appearance, reprepare with a smaller sample size. Spread the sample out over the dish to insure complete evaporation of the moisture that may have been trapped on the larger sample size.

14.5 Percent Moisture represents the amount of sample that has been evaporated and Percent Solid represents the solid amount that remains after heating.

Organic Carbon (FOC)/Ash

14.6 Follow the same procedure for Percent Moisture/Percent Solid. However, porcelain crucibles are used in place of aluminum dishes, and 25-30grams of sample is used.
14.7 Weigh an empty porcelain crucible as your Method Blank.
14.8 After the sample has been oven dried overnight, cool and record the weight in the logbook. Transfer the sample to a **muffle furnace**.
14.9 Heat the sample to 440°C for 4 hours.
14.10 Cool the sample to room temperature in a dessicator, weigh, and record in the logbook.

15.0 Data Reduction, Calculations, and Loading

15.1 **Percent Moisture/ Percent Solid**

Percent Solids (reported as Total Solids) in wt % = B/A x 100
Percent Moisture (Moisture Content) in wt % = [(A-B) x 100] /A

Where A = mass of the as-received test specimen in grams

B = mass of the oven-dried specimen in grams

This calculation is used primarily for dry weight correction

(An alternative calculation according to ASTM D2216 is [(A-B) x 100]/B
This calculation is mainly for geotechnical purposes and the result should be referred to as the moisture content as a percentage of oven-dried mass.)

15.2 **Ash Content** in wt % = (C x 100) /B
Where: C = ash in grams
B = oven-dried test specimen in grams

15.3 **Organic Carbon**
Organic Carbon (Organic carbon content) in wt %= 100-Ash

The procedure for uploading data into the LIMS system is detailed in SOP 1400 LIMS.

16.0 Method Performance

All parameters of interest must meet the method acceptance criteria before actual sample analysis begins. See SOP 1230 Training for the procedure to perform and document the DOC. The DOCs for the analysts performing this method are located in the analysts' training form folders located in the QA office files.

A quality control (QC) reference concentrate is required for Percent Moisture. Weight out 99 grams of oven dried Ottawa sand into a 150mL plastic bottle. Add 1grams of reagent water, cap and shake. Record in the reagent prep logbook.

Analyze four aliquots.
Calculate the mean recovery (X) and standard deviation (s) and the average % Recovery (%R). Compare X and s and %R with the corresponding acceptance criteria for accuracy and precision, respectively. Note: X must be within 1% ± 0.3 % and s must be less than 0.3 % and %R must be within 100 ± 30%.

These limits are taken from established in-house criteria. If X and s and %R for all analytes meet the acceptance criteria, the system performance is acceptable and analysis of actual samples can begin. If any individual X or %R falls outside the range for accuracy, or any individual s exceeds the precision limit, then the system performance is unacceptable for that analyte and corrective action must be taken.

17.0 Pollution Prevention

Samples shall be disposed in compliance with the lab waste disposal program and applicable waste disposal regulations.

18.0 Data Assessment and Criteria for Quality Control Measures

The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When results of QC samples indicate atypical method performance, a calibration verification standard is used to confirm the measurements were performed in an in-control mode of operation. The data review is conducted according to SOP 1250 Data Review.

Method Blank (MB)

If the blank exceeds the RL (usually the lowest calibration standard), the source of contamination must be investigated and corrective actions taken.

Affected samples must be reprocessed and reanalyzed **or** Data must be appropriately qualified if:

1. The concentration of a targeted analyte in the blank is at or above the reporting limit as established by the SOP or by regulation, AND is greater than 1/10 of the amount measured in any sample.

2. The blank contamination otherwise affects the sample results as per the test method requirements or the individual project data quality objectives.

Laboratory Control Sample (LCS)

The results of the individual batch LCS are calculated in percent recovery (%R) and compared to established acceptance criteria (in-house limits). LCS %R limits are 100 ± 20% for both aqueous and soil samples. If the LCS is outside the acceptance criteria, the analytical system is "out of control". Any affected samples associated with an out of control LCS must be reprocessed and reanalyzed or the results reported with appropriate data qualifiers.

Matrix Spikes

Not applicable to this method.

Duplicates

The results from laboratory Duplicates are designed to assess the precision of analytical results in a given matrix and are expressed as relative percent difference (RPD). See the STAT QAM, Section 5.4 for the calculation for RPD. Results are compared to established acceptance criteria (in-house limits). RPD limits are 20 %(25% for samples with less than 10% moisture or FOC). For samples with less than 3% FOC the RPD limit is 30%. Duplicates results outside established criteria corrective action must be documented, or the data for the duplicate sample is reported with appropriate data qualifying codes.

19.0 Corrective Actions for Out of Control Data

The process for handling out of control data is found in SOP 230 Corrective Action.
If the Method Blank, LCS, or lab duplicate of any parameter falls outside the designated acceptance range, the laboratory performance for that parameter is judged to be out of control, and the problem must be immediately identified and corrected. The analytical result for that parameter in the samples is suspect and is only reported for regulatory compliance purposes with the appropriate corrective action form. Immediate corrective action includes reanalyzing all affected samples by using any retained sample before the expiration of the holding time. Final data results must be qualified in the client report for reported results not meeting the laboratory-defined criteria.

19.1 Review standards preparation logbooks. Check all calculations and ensure dilution factors are properly recorded.
19.2 Re-prepare the suspected standard or QC sample to identify possible preparation errors of the standard or QC sample.
19.3 Re-Analyze the samples when the LCS or Duplicate is not within acceptable limits.
19.4 Perform routine preventative maintenance following manufacturer's specification. Record all maintenance in the instrument logbook.

20.0 Contingencies for Handling Out-of-Control or Unacceptable Data

Every effort is made to prevent problems from occurring. When out of control or unacceptable data occurs the first option is to identify the problem and reanalyze the samples within the holding times. When this is not possible, the QA Manager and/or the Laboratory Director review the data and discuss options with the client. Reanalysis or reporting the data with qualifications is an alternative. Out of control or unacceptable data reported to the client must include the data qualifier, flag and discussion on the rationale for reporting.

Holding time exceedance, or improper preservation are noted on the corrective action form and included on the final report.

20.1 The process for handling unacceptable and out of control data is found in the Laboratory QAM Section 11. The reporting of data that is out of control must be approved and documented by the Quality Assurance Manager and either the Technical Manager or the Laboratory Director.

20.2 Client Requested Modifications:

20.2.1 Clients must request modifications from the laboratory SOP in writing to the lab.
20.2.2 The Laboratory Director, Technical Manager and Quality Assurance Manager

will evaluate the requested client deviations; determine the feasibility of the deviation and the potential effects on the data.

20.2.3 If it is determined that the laboratory will perform the requested deviations, the Laboratory Director, Technical Manager and Quality Assurance Manager will decide if a method validation study is required.

20.2.4 The designated project manager will retain all documentation concerning the requested deviation, including all correspondence with the client, in the client folder.

20.2.5 The final analytical report must include the statement *"This report has analyses performed using client requested modifications"*.

21.0 Waste Management

The STAT Analysis Corporation SOP 1130 Waste Disposal identifies proper waste management practices for the chemicals and biological materials used in this procedure. Samples are stored and discarded accordance with SOP 1130 Waste Disposal.

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22.0 References

22.1 Standard Test Methods for Moisture, Ash, and Organic Matter of Peat and Other Organic Soils, ASTM D 2974.

22.2 Standard Methods for the Examination of Water and Wastewater, 20th Edition (1998).

22.3 Methods for the Determination of Total Organic Carbon (TOC) in Soils and Sediments, Brian A. Schumacher, Ph.D., Ecological Risk Assessment Support Center Office of Research and Development USEPA, NCEA-C- 1282 EMASC-001 April 2002., p. 3

22.4 Methods for Chemical Analysis of Water and Wastewater, U.S. Environmental Protection Agency, EPA methods 160.1, 160.2, 160.3, 160.4

22.5 STAT SOP 1000 Control and Use of Laboratory Notebooks

22.6 SOP 1400 LIMS

22.7 STAT SOP 1210 Method Detection Limits (MDLs)

22.8 SOP 1040 General Laboratory Practices

22.9 STAT SOP 1020 Glassware Cleaning

22.10 STAT SOP 1250 Data Review

22.11 SOP 230 Corrective Actions

22.12 SOP 1130 Waste Disposal

22.13 SOP 1230 Training

22.14 SOP 003 Chemical Hygiene Plan

22.15 SOP 1010 Standard and Reagent Preparation

22.16 STAT Analysis Corporation Quality Assurance Manual

23.0 Forms, Figures, Tables, Diagrams, Flowcharts

None.

STA Analysis Corporation:

STANDARD OPERATING PROCEDURE 4500

POLYNUCLEAR AROMATIC COMPOUNDS BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS) with SELECTIVE ION MONITORING (SIM) (EPA Method 8270C SIM)

Revision 04

Effective Date: March 5, 2004

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1.0 IDENTIFICATION OF TEST METHOD

SOP Title: Polynuclear Aromatic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS) with Selective Ion Monitoring (SIM) (EPA Method 8270C SIM) is abbreviated as PNA (SIM) in laboratory records.

2.0 APPLICABLE MATRICES

Methylene chloride and organic solvent extracts from soil, sediment, ground and surface water, and mobility extracts are analyzed using this method.

3.0 DETECTION LIMITS

The lab follows the procedure found in 40CFR Part 136B to determine the method detection limits (MDL's) for each matrix type on an annual basis. See the STAT Analysis SOP 1210 Method Detection Limits for the MDL procedure, frequency and acceptance criteria. The MDL's measured by the lab and all supporting documentation are in the laboratory QA files for review.

The laboratory determined MDL must always be less than the reporting limit (RL), which maybe determined by the lowest standard. The RL's will usually range from three to ten times the laboratory measured MDLs but this relationship may vary dependent on dilution of sample aliquots, matrix interferences, moisture adjustments (in solid samples), or method-specified requirements. Attachment 1 contains the current MDLs and reporting limits (RLs) for this SOP.

4.0 SCOPE AND APPLICATION

4.1 This standard operating procedure describes in detail the precise methods used at STAT Analysis Corporation for the analysis of environmental samples for Polynuclear Aromatic Compounds (PNAs) by GC-MS. This SOP as written is to be applied when SW-846 Method 8270C (SIM) is requested. This SOP is used to determine the concentration of (PNAs) in extracts prepared from all types of solid waste matrices, soils, and ground water.

4.2 SOP 4500 can be used to quantitate PNAs that are soluble in methylene chloride and other organic solvents and are capable of being eluted without derivatization as sharp peaks from a gas chromatographic fused-silica capillary column coated with a slightly polar silicone. See Attachment 2 for a list of compounds and their characteristic ions that have been evaluated on the specified GC/MS system.

4.3 The reporting limits (RLs) for this SOP are shown in Attachment 1 for soils and water. RLs will be proportionately higher for sample extracts and samples that require dilution, reduced sample size, or final volume of extracts greater than 1 mL.

4.4 This method is restricted to use by or under the supervision of analysts experienced in the use of a Gas Chromatograph/Mass Spectrometer (GC/MS) and skilled in the interpretation of mass spectra. Each analyst must demonstrate the ability to generate acceptable results with this method.

5.0 SUMMARY OF TEST METHOD

5.1 Prior to using this method, the samples must be prepared for the GC/MS using the appropriate sample preparation and cleanup SOPs (Section 14.1). Samples are not pH adjusted prior to extraction with methylene chloride. This method describes chromatographic conditions that will allow for the separation of the compounds in the extract and for their qualitative and quantitative analysis by gas chromatography/mass spectrometry. Identification of target analytes is accomplished by comparing component retention times to those of authentic standards and by comparing their mass spectra with the electron impact (or electron impact-like) spectra of authentic standards. Quantitation is accomplished by comparing the response of a major (quantitation) ion relative to an internal standard using a five-point calibration curve.

5.2 **Method Modifications from Reference** – This SOP is based on EPA Method 8270C except that no polychlorinated biphenyls (PCBs), pesticides, organophosphate esters or quinolines are reported. PCBs and Pesticides are reported using STAT Analysis SOP 4050 Organochlorine and PolyChlorinated Biphenyls by Gas Chromatography/Electron Capture Detector (EPA Methods 8081A/8082). The lab does not report organophosphate esters and quinolines. The reported compounds are listed in Attachment 1. The Mass Spectrometer Tuning criteria used in this SOP are referenced from the CLP Statement of Work (SOW) for Organic Analyses Revision OLM04.2 May 1999. This is an option in Method SW-846 8270C. The analytes are measured using Selective Ion Monitoring (SIM) MS detection instead of full scan MS to increase sensitivity. The SPCC's and CCC's from 8270C are not used; instead all compounds are CCC's and SPCC's.

6.0 DEFINITIONS

The STAT Analysis Quality Manual Section 19.0 contains all the definitions of standard terms used in SOPs.

7.0 INTERFERENCES

7.1 Raw GC/MS data from all blanks, samples, and spikes must be evaluated for interferences. The analyst must determine if the source of interference is in the preparation and/or cleanup of the samples and take corrective action to eliminate the problem.

7.2 Contamination by carryover can occur whenever high-concentration and low-concentration samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed out between samples with solvent. Whenever an unusually concentrated sample is encountered, the sample after it must be reanalyzed to check for cross contamination.

8.0 SAFETY

Methylene chloride is a suspected carcinogen as are numerous compounds analyzed by this method. Proper personal protective equipment including safety glasses, nitrile gloves and a lab coat are required during different parts of this method. Other safety precautions must be conducted in accordance with the Chemical Hygiene Plan (STAT QA SAP 003). Other actions can also be applied if deemed necessary. A reference file of Material Safety Data Sheets (MSDS) is available to all personnel involved in this method.

9.0 EQUIPMENT AND SUPPLIES

The following apparatus is recommended for performing this procedure. Equivalent items can be used, if with their use, the analytical and QA/QC requirements in this SOP can be met. All catalog numbers in this SOP are current as of the effective date and thereafter subject to change.

9.1 Gas Chromatograph/Mass Spectrometer system (Agilent 6890 GC/MS)

9.1.1 Gas chromatograph(GC) – Agilent 6890 with electronic flow control gas chromatograph with the column directly coupled to the source. Equipped with an Agilent Autosampler Model 7683.

9.1.2 Column - 30 m x 0.25 mm ID (or 0.33mm ID) 0.5µm film thickness silicone-coated fused-silica capillary column (J&W Scientific HP-5MS).

9.1.3 Mass spectrometer(MS) - Agilent 5973N.

9.1.4 Data system - An Agilent Kayak computer system using 3365 Chemstation Version C.00.00 to interpret data is attached to the GC.

9.1.5 NIST Library of Reference Spectra, Edition Number NIST98

9.2 Gas Chromatograph/Mass Spectrometer system (Hewlett Packard 5890 GC/MS)

9.2.1 Gas chromatograph(GC) – Hewlett Packard 5890 Series II with pneumatic flow control gas chromatograph with the column directly coupled to the source. Equipped with a Hewlett Packard Autosampler 6890 Series Injector.

9.2.2 Column - 30 m x 0.25 mm ID (or 0.33mm ID) 0.5µm film thickness silicone-coated fused-silica capillary column (J&W Scientific HP-5MS).

9.2.3 Mass spectrometer(MS) – Hewlett Packard 5971

9.2.4 Data system – A Hewlett Packard Vectra VE computer system using G1032C Chemstation Version C.01.00 to interpret data is attached to the GC.

9.2.5 NBS Library of Reference Spectra, Edition Number NBS75K

9.3 Micro syringes - 10 µL, 25 µL, 100 µL, 250 µL, 500 µL and 1,000 µL.

9.4 Volumetric flasks, Class A - 10 mL, 25 mL, 50 mL with ground glass stoppers.

9.5 Glass vials - 2-mL, for GC auto sampler with Teflon-lined screw caps or crimp tops.

9.6 Amber glass vials - 10 mL with Teflon-lined screw caps

10.0 REAGENTS AND STANDARDS

The following reagents and standards are required to perform this procedure. When instructions are given on how to prepare a specific volume of a reagent or standard, larger or smaller volumes can be prepared as needed so long as the final concentrations remain the same. Any other deviations from the reagents or standards listed in this SOP could be detrimental to the quality of the data produced. Such deviations would have to be approved and documented (see SOP QA 230 Corrective Action). Equivalent items can be used, if with their use, the analytical and QA/QC requirements in this SOP can be met.

Instructions for labeling and record keeping of reagents and standards are contained in SOP 1010 Analytical Standards and Reagents Receipt and Preparation.

10.1 Analytical reagent grade chemicals shall be used in all tests. Unless otherwise indicated, all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.

10.2 Organic-free reagent water - All references to water in this SOP refers to Type II reagent water (in-house system).

10.3 Stock Standard solutions - Standard solutions can be prepared from pure standard materials or purchased as certified solutions (e.g. SV standards). The routine laboratory practice is to purchase these standards from approved vendors. The standards used are: 8270 Calibration Mix #5 (Restek Catalog # 31622), Custom Dibenzofuran Standard (Restek Catalog # 555319), B/N Surrogate Standard (Restek Catalog # 31072), and Acids Surrogate Spike Mix (Restek Catalog # 31003). Stock standard solutions and QC solutions are stored at < -10°C and must be replaced after six months, or sooner if comparison with quality control check samples indicates a problem. Different storage conditions and expiration dates of other solutions are noted as warranted.

10.3.1 Secondary Stock Standard Solution – This solution is made using the individual Stock Standard solutions. Using microliter syringes, the following amounts of each Stock Standard solution is injected into a 10 mL volumetric flask. The solution is brought to volume with methylene chloride. The final concentration of each component is listed in Table 1.

Note: This Secondary Stock Standard solution is also used as the high-level calibration standard. It is also the source solution to prepare the calibration standards in Section 10.4. This standard is stored at < -10°C in a 10 mL amber screw cap vial equipped with a Teflon lined cap. It is freshly prepared every six months, or sooner if check standards indicate a problem.

Table 1 Secondary Stock Standard Solution

Stock Solution	Conc. Stock (µg/ml)	Vol. Stock (µL)	Final Conc. (µg/ml)
8270 Calibration Mix #5	2000	50	10
Custom Dibenzofuran	2000	50	10
B/N Surr.	5000	20	10
Acid Surr.	1500	66.7	10

10.4 Calibration standards - A minimum of five calibration standards are prepared. The low standard is at or below the RL and above the MDL. The others define the working range of the GC/MS system. Calibration standards in current use: 0.1, 0.5, 1.0, 5.0, 7.5, and 10 µg/ml. (Table 2). Using microliter syringes, the following amount of the Secondary Stock solution is injected into a 1 ml syringe. The solution is brought to volume with Methylene chloride. The final concentration of each component is listed in Table 2. Each solution is transferred to an autosampler vial. Each 1 mL aliquot of calibration standard must be spiked with 10 µL of the internal standard solution (400 µg/ml) (Section 10.6) prior to analysis. Storage is as indicated in 10.3.1. The continuing calibration verification standards (CCV) are prepared weekly and stored at 4°C. Levels 3, 4 and 5 (1.0, 50, 7.5 µg/mL) are used for the CCVs. Because of this levels 3, 4 and 5 expire after 1 week. However, levels 1,2 and 6 have a 6 month expiration date.

Table 2 Calibration Standards

Level	Volume (µL) Secondary Stock	Volume (µL) $MeCl_2$	Final Concentration (µg/ml)
1	10	990	0.1
2	50	950	0.5
3	100	900	1.0
4	500	500	5.0
5	750	250	7.5
6	1000	0	10

10.5 Surrogate standards - The surrogate standards are nitrobenzene-d_5, 2-fluorobiphenyl, p-terphenyl-d_{14} and 1,2-dichlorobenzene-d_4. Surrogate stock solutions are purchased from Supelco (Cat. No. 4-7261 and 4-7262, store at room temp until dilution is prepared). The spike solution is prepared by diluting 100 µL of the stock standard solution for Base/Neutrals (5000 µg/mL) and 50 µL of the stock standard solution for Acids (10000 µg/mL), into a 100mL volumetric flask. The flask is diluted to the mark with methanol for a final concentration of 5.0 µg/mL for Base/Neutral and Acid surrogates. All samples, blanks, LCS's, and MS/MSDs are spiked with 1.0 mL of the surrogate spike solution prior to extraction. This standard is stored at < -10°C in an amber glass vial with a Teflon lined screw cap.

10.6 Internal standard solutions - The internal standards used are 1,4-dichlorobenzene-d_4, naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, and perylene-d_{12}. The SV internal standards containing the recommended compounds at 4000 µg/mL are purchased from Supelco (cat. no. 4-7906). PNA internal standard is prepared by diluting 100 µL of the stock internal standard solution with methylene chloride to a final volume of 1.0 ml. Just prior to analysis 10 µL of the solution (400 µg/ml) is injected into each sample vial. Store at room temperature per manufacturer's instructions when not being used. The internal standards permit most of the compounds of interest in a chromatogram to have retention times of 0.80-1.20 relative to one of the internal standards. Use the base peak ion from the specific internal standard as the primary ion for quantitation (see Attachment 2, i.e. for 1,4-dichlorobenzene-d_4, use 152 m/z for quantitation). If interferences are noted, use the next most intense ion as the quantitation ion.

10.7 GC/MS tuning standard - A methylene chloride solution containing 50 ng/µL each of decafluorotriphenylphosphine (DFTPP), 4,4'-DDT, pentachlorophenol, and benzidine is used to tune the mass spectrometer, and to verify injection port inertness and GC column performance. The SV tuning standard is purchased from Supelco (Cat. No. 4-7387). Store at < -10°C when not being used. Inject 1 µL of this standard at the start of every 12 hours of operation.

10.8 Laboratory Control Sample/Matrix Spike standards - The LCS/matrix spike compounds are all reportable compounds. Refer to Attachment 3 for the complete compound list. Samples will be spiked at 5.0 µg/sample, 167.0 µg/kg for soil and 5.0 µg/L for water (see SOP 3500 for LCS/Matrix Spike Solution preparation). This standard is stored at < -10°C in an amber glass vial with a Teflon lined screw cap.

10.9 Initial Calibration Verification Standard – A standard prepared from a different source at the midpoint of the calibration to verify the initial calibration. This solution concentration is 10.0 µg/mL The solution is made using the individual ICV Stock Standard solutions purchased from Supelco. The stock standards used are TCL Polynuclear Aromatic Hydrocarbons Mix (Catalog # 48905-U), Custom Mix (Quote # 20217206), Semivolatile Base/Neutrals (Catalog # 4-7262) and Semivolatile Acids Surrogate Spike Mix HC (Catalog # 4-7261). Using microliter syringes, the following amounts of each Stock Standard solution is injected into a 10 mL volumetric flask. The solution is brought to volume with methylene chloride. The final concentration of each component is listed in Table 3. This standard is stored at < -10°C.

Table 3 ICV Secondary Stock Standard Solutions

Stock Solution	Conc. Stock	Vol. Stock (µL)	Final Conc.

	(µg/ml)		(µg/ml)
TCL PAH Mix	2000	50	10
Custom Mix	2000	50	10
B/N Surrogate	5000	20	10
Acids Surrogate	10000	10	10

The working ICV solution is prepared by diluting 500 µL of the ICV Secondary Stock Standard Solution to 1000 µL with methylene chloride. The solution is transferred to an autosampler vial. Each 1 mL aliquot of calibration standard must be spiked with 10 µL of the internal standard solution (400 µg/ml) prior to analysis. Storage is as indicated in 10.3.1.

10.10 Acetone, hexane, methylene chloride, isooctane, carbon disulfide, toluene and other appropriate solvents, pesticide quality or equivalent.

10.11 Helium – UHP grade, 99.999% pure (Grade 5, Medox)

11.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

11.1 Containers used to collect samples for the determination of polynuclear aromatic compounds are glass: 1 Liter bottles for water samples and various size jars for soil samples. They are equipped with screw caps with Teflon liners. Water samples containing residual chlorine should be field treated to remove the chlorine prior to collection. Plastic containers or lids may NOT be used for the storage of samples due to the possibility of sample contamination from the phthalate esters and other hydrocarbons within the plastic.

11.2 Samples must be stored under refrigeration at between 0.1 and 6.0°C. Extraction must be within 7 days from sampling date for water and 14 days for solids. Sample extracts are stored in the dark at between 0.1 and 6.0°C and must be analyzed within 40 days of extraction.

11.3 No chemical preservation is required for this method.

11.4 All samples are stored away from all standards, reagents, food, and other potentially contaminating sources in order to prevent cross contamination.

12.0 QUALITY CONTROL

The following details the QC requirements that apply to this analysis. Each Quality Control Indicator (QCI) provides information pertaining to either method or individual sample performance. Our goal is to produce defensible data of known and documented quality. The results of these Quality Control Indicator (QCI) samples are used to assess the acceptability of data.

12.1 Blanks

Method Blank analysis is performed to determine if any contamination is present in the analytical process and is used to evaluate acceptance of the batch of samples. A method blank shall be prepared once per preparation batch of 20 or less samples per matrix type. If more than 20 samples are prepared a second blank shall be prepared after the twentieth sample. The method blank shall be processed through all preparatory steps used for the samples, including cleanup procedures. The blank shall be analyzed using the same instrument and conditions as the samples.

The Solvent Blank, clean solvent injected into the GC/MS prior to analysis, is used to monitor the GC/MS system for potential cross-contamination from one sample to another or for residual contamination in the system.

12.2 Calibration Verification

An Initial Calibration Verification (ICV) standard containing all of the target analytes reported in this method (refer to section 10.9) shall be analyzed immediately after the completion of the initial calibration. The ICV shall be purchased from a second source to verify analyte concentrations.

12.3 Laboratory Control Sample (LCS)

The LCS is used to evaluate the performance of the total analytical system, including all preparation and analysis steps. The LCS shall be prepared once per preparation batch of 20 or less samples per matrix type. If more than 20 samples are prepared a second LCS shall be prepared after the twentieth sample. The LCS shall be processed through all preparatory steps used for the samples, including cleanup procedures. The LCS shall be analyzed using the same instrument and conditions as the samples. Refer to section 10.8 for LCS analytes and concentrations.

12.4 Surrogates

The surrogates used for this method are added to all samples, standards, and blanks. Refer to section 10.5 for preparation and concentration instructions.

12.5 Duplicates

Duplicates of field samples or of the LCS must be prepared in compliance with the method requirements and client directives. Reproducibility performance would be the same as for a matrix spike/matrix spike duplicate.

12.6 Matrix Spike and Matrix Spike Duplicate (MS/MSD)

MS/MSDs indicate the effect of the sample matrix on the precision and accuracy of the results generated using the selected method. This information does not determine the validity of the entire batch. MS/MSDs must be analyzed at a minimum of 1 per 20 samples per matrix per preparation procedure, or one per preparation batch, or as specified by the required test method. For cases where the sample cannot be divided (e.g., wipes, air samples, not enough sample provided by customer) and thus a MS/MSD pair cannot be prepared in the preparation batch, an LCS/LCSD pair is prepared and analyzed to measure precision. Samples chosen for matrix spiking are rotated among different clients and/or different client projects. This is accomplished through communication between the Department Manager and the analyst. In addition, designated samples, as indicated by client request or contract requirement, are matrix spiked. The MS/MSD pair shall be processed through all preparatory steps used for the samples. They shall be analyzed using the same instrument and conditions as the samples. Refer to section 10.8 for MS analytes and concentrations. Some clients may require different spiking levels and/or target analytes; these specific needs are documented on the request for analysis forms.

12.7 Internal Standards

The internal standards used for this method are added to all samples, standards, and blanks. Refer to section 10.6 for preparation and concentration instructions.

13.0 CALIBRATION AND STANDARDIZATION

13.1 Mass Spectrometer Tuning

Each GC/MS system must be software-tuned to meet the criteria in Table 4 for a 50 ng injection of DFTPP. Analyses must not begin until all these criteria are met. Tuning criteria used in this SOP is referenced from the CLP Statement of Work (SOW) for Organic Analyses Revision OLM04.2 May 1999.

Using the ChemStation software to tune the GC/MS perform the following steps:
Set oven temperature to 250 °C (the elution temperature for DFTPP)
On the Instrument Control Panel click on View/Manual Tune…
On the Manual Tune Panel click on File/Load Tune Values/ and select DFTPP.u
On the Manual Tune Panel click on Tune/DFTPP Tune
The software automatically adjusts the tune parameters using PFTBA to meet the criteria in Table 4. After the software has completed the tune click on File/Save Tune Values/ and select DFTPP.u and save the new parameters.
Click on View/Instrument Control to start analyzing standards and samples.

Table 4 Acceptance Criteria for DFTPP

Target Mass	Relative to Mass	Lower Limit%	Upper Limit%
51	198	30	80
68	69	0	2
69	198	0	100
70	69	0	2
127	198	25	75
197	198	0	1
198	198	100	100
199	198	5	9
275	198	10	30
365	198	1	100
441	443	0.01	100
442	198	40	110
443	442	15	24

Using the autosampler, inject 1 µL of DFTPP tuning standard solution on to the column. Analyze the solution using the DFTPP method which accelerates the elution of the compounds of interest.

Background subtraction must be straightforward and designed only to eliminate column bleed or instrument background ions. Obtain a background-corrected mass spectrum of DFTPP and confirm that all the key m/z criteria in Table 4 are achieved. Three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction is

required, and must be accomplished using a single scan no more than 20 scans prior to the elution of DFTPP. Do not background subtract part of the DFTPP peak. Option: a single scan with background subtraction can also be used to evaluate the DFTPP spectrum. Note: the tuning file used to obtain and evaluate the DFTPP criteria must also be used to obtain and evaluate the sample data. If the criteria are not passed, the analyst must perform needed maintenance, retune the mass spectrometer and repeat the test until all criteria are achieved.

The GC/MS tuning standard must also be used to assess GC column performance and injection port inertness. Benzidine and pentachlorophenol must be present at their normal responses, and no peak tailing must be visible. If poor chromatography is noted, the injection port may require cleaning. It may also be necessary to cut off an additional 10 to 20 cm of the capillary column.

Note: The 12-hour tune period begins at the start of the DFTPP analysis that is recorded as the data acquisition start time on the data file. The last valid calibration standard in the ICAL must have a data acquisition start time less than 12 hours from the start of the tune period.

13.2 Initial Calibration (ICAL)

13.2.1 Analyze 1 µL of each calibration standard and tabulate the area of the analyte against concentration for each compound. Calculate the response factors (RF's) for each compound in each calibration standard as follows:

$$RF = \frac{A_x * C_{is}}{A_{is} * C_x}$$

where:

A_x = Area of the characteristic ion for the compound being measured.
A_{is} = Area of the characteristic ion for the specific internal standard.
C_{is} = Concentration of the specific internal standard (40 ng/µL for this method)
C_x = Concentration of the compound being measured (ng/µL = µg/mL = mg/L).

13.2.2 Calculate the average response factor ($\overline{RF}$) for each compound as follows:

$$\overline{RF} = (S\ RF_1 \text{ to } RF_n)/n$$

where: RF = RF for each of the calibration levels (i.e., 5)
n = Number of RF values (i.e., 5)

13.2.3 A system performance check must be performed to ensure that minimum average RF's are met before the calibration curve is used. For polynuclear aromatic compounds the System Performance Check Compounds (SPCC's) are all compounds reported by this method. Refer to Attachment 1 for the complete list. The minimum acceptable average RF for these compounds is 0.050. If it is determined that one calibration level has an unacceptable response, that level may be reanalyzed once. If the minimum average RF is still not met, corrective action must be taken

and the calibration sequence repeated. If any major changes are made to the system (e.g. column changed or detector cleaned), recalibration of the system must take place.

Calibration Check Compound (CCC) responses are monitored to check the integrity of the system. The CCCs are all compounds reported by this method. Refer to Attachment 1 for a complete compound list.

Using the RFs from the initial calibration, calculate the percent relative standard deviation (%RSD) for the Calibration Check Compounds (CCC).

To calculate %RSD: $\%RSD = 100\% \times SD/\overline{RF}$

where:

%RSD = % Relative Standard Deviation

$\overline{RF}$ = average of initial RFs for a compound
SD = standard deviation (n-1) of average RFs for a compound

To calculate Standard Deviation (n-1 degrees of freedom)

$$SD = \sqrt{\frac{\sum_{i=1}^{N} (RF_i - \overline{RF})^2}{n-1}}$$

where: RF_i = RF for each of the 5 calibration levels
n = Number of RF values (i.e., 5)

13.2.5 If the %RSD of any CCC compound is > 30%, then the chromatographic system is too reactive for analysis to begin. Clean or replace the injector and/or capillary column, then repeat the calibration procedure beginning with section 13.2.1.

13.2.6 Linearity - If the %RSD of any compound is 15% or less, then the relative response factor is assumed to be constant over the calibration range, and the average relative response factor is used for quantitation. If the %RSD is greater than 15%, first order linear regression is used. The calibration curve must meet the requirements for curve fitting listed in SW-846 8000B and the correlation coefficient is = 0.99. The equation is not forced through the origin.

13.2.7 Retention Times: The Relative Retention Times (RRT) of each compound in each calibration standard should be within ± 0.06 RT units.

13.2.8 Before sample analysis can begin, a Initial Calibration Verification (ICV) (see Sec. 10.9) must be performed. The ICV results must be within the acceptance criteria as established for the CCV compounds (Section 13.3).

NOTES:

1. All calibration curves must have a unique identifier. It is recommended that the calibration date be incorporated into the identifier for easy reference.
2. All initial calibration standards must be analyzed within the 12-hour DFTPP tune window.
3. Calibration must be completed (all standard levels analyzed) within 24 hours or the entire calibration sequence must be repeated. If the calibration was not completed in the first tune window it may continue into a second tune window. Standard calibration levels from either tune window can be used. An exception follows: If DFTPP criteria does not pass criteria for the second tune window and major maintenance was done to the instrument or the Mass Spectrometer tuning parameters were adjusted in order to obtain an acceptable tune for DFTPP, the entire calibration sequence must be repeated.
4. All initial calibration standards must be analyzed as a group. No field sample analyses are allowed during the calibration sequence.
5. Do not add calibration standards and update the curve after the original calibration date.
6. Multiple analyses of the same calibration level are not allowed to be included in the calibration curve.
7. Compound responses cannot be selected from different analyses of the same calibration level (i.e. all compound responses for level 1 must come from the same data file).
8. If more than five calibration levels are analyzed, it is permissible to either drop the low compound concentration (poor response) or the high compound concentration (detector saturation). It is not allowed to drop a point in the middle of the curve.
9. If more than five calibration levels are analyzed, it is permissible to drop an entire level if the analyst can document a specific reason or reasons why that level should be excluded. Mechanical failure, significant loss of all analyte responses possibly due to poor technique in standard preparation, or software malfunction during data acquisition (system did not acquire all compound data) are plausible reasons. The reason must be justified and documented. The supervisor should review this situation and approve the analyst's decision.
10. The need to analyze more than two analyses of the same calibration level indicates a potential problem with the secondary stock solution. Prepare a fresh secondary stock solution and repeat all calibration levels. It is recommended that all calibration standard levels come from the same secondary stock solution.
11. Manual integration must only be used if the software fails to properly integrate the peak. If manual integration is used for a particular compound, all levels of that compound do not have to be manually integrated, but all levels must be integrated in a similar manner. Example: the computer generated integration of a compound in the low level standard is not technically sound. A manual integration of the compound is performed (due to baseline noise, etc) in order to achieve a technically sound integration. Other levels of the compound are integrated correctly by the computer. The manual integration of the low level must match, as best as possible, the computer generated integrations for all other levels. See SOP 1255 Manual Integration.
12. If any compound in the mid-point level is manually integrated, the integration of this compound must be reviewed for every continuing calibration standard and QC check solution (i.e. LCS,

and Matrix Spike) to ensure that the integration is the same as the manual integration performed in the initial calibration (ICAL) mid-point. A consistent manner of integration must be achieved.

13. All manual integrations must be reviewed and approved at the supervisory level per SOP 1255 Manual Integration and SOP 1250 Data Review.

13.3 Continuing Calibration Verification (CCV)

13.3.1 The mass spectrometer must pass tune criteria (see Section 13.1) every 12 hours during analysis of samples.

13.3.2 A continuing calibration verification (CCV) sample is analyzed every 12 hours during analysis of samples. Different standards are analyzed for the CCV such that a wider range of the calibration curve is verified. For example: on successive days analyze the 1 µg/mL, then the 5 µg/mL and on the third day, the 7.5 µg/mL standard solution. Compare the response factors, of the SPCC's and the CCC's, and the internal standards from the CCV with the following criteria.

13.3.3 The SPCC compounds must have an RF = 0.05.

13.3.4 Control limits for the CCC compounds are ± 20% difference from the ICAL Response Factor (RF) if the average RF is used for quantitation, or ± 20% drift from the true concentration of the CCV compound if linear regression is used.

13.3.5 The areas of the internal standards in the CCV must be between –50% and +100% of the respective areas of the internal standards in the ICAL mid-point calibration standard.

13.3.6 The retention times of the internal standards in the CCV must be within ± 30 seconds of the respective retention times of the internal standards in the ICAL mid-point calibration standard.

13.3.7 If the CCV results obtained are outside the acceptance criteria, corrective actions must be performed. If routine corrective actions fail to produce an acceptable second consecutive (immediate) CCV, then either the lab has to demonstrate performance after corrective action with two consecutive successful CCVs, or a new ICAL must be performed. If the instrument has not demonstrated acceptable performance, sample analyses cannot continue until a new ICAL is established and verified with an ICV. However, sample data associated with an unacceptable CCV may be reported as qualified data under the following special conditions:

13.3.7.1 When the acceptance criteria for CCV are exceeded high, i.e., high bias, and there are associated samples that are non-detects, then those non-detects may be reported. Otherwise the samples affected by the unacceptable calibration verification must be reanalyzed after a new ICAL has been established, evaluated and accepted.

13.3.7.2 When the acceptance criteria for the CCV are exceeded low, i.e., low bias, those sample results may be reported if they exceed a maximum regulatory limit/decision level. Otherwise the samples affected by the unacceptable verification must be reanalyzed after a new ICAL is established and verified with an ICV.

13.3.7.3 When the acceptance criteria for the CCV are exceeded and it is not possible to reanalyze the sample due to limited sample quantity AND the laboratory cannot obtain a new sample, the data may be reported with the appropriate data qualifiers if the client has been contacted and agrees, in writing, to accept the qualified data.

13.4 Records: Initial and Continuing Calibration Records will contain, at a minimum, the following:

1) Calibration date
2) Test method
3) Instrument
4) Analysis date
5) Each analyte name
6) Analyst's initials or signature
7) Standard Concentration (appropriate units) and number of standards
8) Response (appropriate units)
9) Calibration curve or response factor
10) Evaluation of and Statistics for ICAL curve fit in order to judge calibration curve acceptance
11) Evaluation of and Acceptance Limits for ICV analysis in order to judge calibration curve acceptance
12) Evaluation of and Acceptance Limits for CCV analysis in order to judge continuing calibration acceptance

13.5 Thermometers - The thermometers in the sample refrigerators and the standards freezer must be checked daily. They must meet performance criteria.

14.0 PROCEDURE

14.1 Sample Preparation

14.1.1 Water, soil, sediment and waste samples must be prepared by SOP 3500 Extractions of Samples for Semi-Volatile Organic Analyses (EPA Methods 3510C, 3520C, 3550B, 3580A) prior to GC/MS analysis.

14.1.2 Extract Cleanup: Extracts may be cleaned up by any of the following methods prior to GC/MS analysis.

Compounds	**SOPs**
Semivolatile hydrocarbons	3330 Silicia Gel Clean-up for Semivolatile Organic Analyses

14.1.3 Direct Injection: In very limited applications direct injection of the sample into the GC/MS system with a 10 µL syringe may be appropriate (see SOP 3500 Extractions of Samples for Semi-Volatile Organic Analyses for preparation). The reporting limit is very high (approximately 100 to 1000 mg/L); therefore, it is only applicable where concentrations in excess of 100 mg/L are expected.

14.1.4 Extract Preparation: Sample extracts and the Internal Standard solution should be at ambient temperature prior to use. Using a 10 µL microliter syringe, inject 10 µL of the Internal Standard solution into the 1 mL sample extract just prior to the start of the analytical batch. Ensure that there is no precipitation in the internal standard mixture. If there is precipitation then gently warm the standard until all is dissolved.

14.2 GC/MS Analysis

14.2.1 Instrument CONDITIONS

The recommended Agilent 6890 GC/MS operating conditions:

EMV	1600 to 2500 (nominal)
Mass range:	35 to 500 amu (see Attachment 2 for ions monitored)
Scan time:	3.15 scans/sec
Initial temperature:	50°C hold for 2 minutes
Ramp 1 temperature program	10.0 °C/min
Final temperature 1:	120 °C hold for 0.0 minutes
Ramp 2 temperature program	20 °C/min
Final temperature 2:	310 °C hold for 10.5 minutes
Injector temperature:	250°C
Source temperature:	310 °C
Sample volume:	1 µL
Carrier gas:	Helium at 1.0 ml/minute
Split flow:	Splitless

The recommended Hewlett Packard 5890 GC/MS operating conditions:

EMV	1600 to 2500 (nominal)
Mass range:	35 to 500 amu (see Attachment 2 for ions monitored)
Scan time:	3.15 scans/sec
Initial temperature:	50°C hold for 0 minutes
Ramp 1 temperature program	10.0 °C/min
Final temperature 1:	310 °C hold for 14.0 minutes
Injector temperature:	250°C
Source temperature:	300 °C
Sample volume:	1 µL
Carrier gas:	Helium at 10 psig head pressure
Split flow:	Splitless

Single Ion Mode (SIM) Parameters:

Group IS 1
Start time: Between solvent peak and 1,4-Dichlorobenzene-d4
Dwell: 30
Ions: 82, 128, 150, 152

Group IS 2
Start time: Between Nitrobenzene-d5 and Naphthalene-d8

Dwell: 30
Ions: 68, 128, 129, 136, 141, 142, 171, 172

Group IS 3
Start time: Between 2-Fluorobiphenyl and Acenaphthylene
Dwell: 30
Ions: 139, 151, 152, 153, 154, 162, 164, 165, 166, 168

Group IS 4
Start time: Between Fluorene and Phenanthrene-d10
Dwell: 30
Ions: 94, 101, 122, 176, 178, 179, 188, 200, 202, 244

Group IS 5
Start time: Between p-Terphenyl-d14 and Chrysene-d12
Dwell: 30
Ions: 120, 226, 228, 229, 240

Group IS 6
Start time: Between Chrysene and Benzo(b)fluoranthene
Dwell: 30
Ions: 138, 139, 252, 253, 260, 264, 276, 278

14.2.2 Access the computer and create a batch sequence file. Refer to section 14.3 for instructions.

14.2.3 Using the autosampler, inject 1 µL of the Tuning Standard (DFTPP) and evaluate using tune acceptance criteria. See Section 13.1

14.2.4 Inject 1 µL of the Continuing Calibration Verification Standard (CCV) and evaluate using CCV acceptance criteria. See Section 13.3.

14.2.5 If all criteria are met, continue with sample analysis, injecting 1 µL of each extract, as outlined below.

14.2.6 If the response for any quantitation ion exceeds the initial calibration curve range of the GC/MS system, extract dilution is an option. If extract dilution is required, additional internal standard must be added to the diluted extract to maintain the required 40 ng/µL of each internal standard in the extracted volume. Then the diluted extract is analyzed.

DILUTION PROCEDURE

1. Clean a 1ml syringe equipped with a luer lock needle with rinse and clean solvent (dichloromethane). Fill syringe with clean solvent such that there is sufficient volume remaining for the dilution volume (see Table 5) and remove the needle. Place the needle on the counter top such that the tip of the syringe is elevated.

2. Clean an appropriate syringe (see Table *5*) with rinse and clean solvent. Expel excess solvent by pumping plunger several times. Puncture the sample vial with the syringe needle and withdraw the sample into the syringe.

3. Remove the syringe from the sample vial and insert the needle into the barrel of the 1ml syringe. Inject the sample into the clean solvent. Hold the 1ml syringe so that the tip is up and gently push up on the plunger to remove excess air from the barrel.

4. Replace the needle on the 1ml syringe and add sufficient clean solvent to a final volume of 1ml. Transfer the entire contents of the syringe into a labeled sample vial. Add an appropriate amount of internal standard (see Table *5*) if necessary. Cap vial.

Table 5 STANDARD DILUTIONS

Dilution	Sample Volume mL	Total Volume µL	Amount of Internal Standard added µL
1:5	200	1000	8.0
1:10	100	1000	9.0
1:20	50	1000	9.5
1:50	20	1000	9.8
1:100	10	1000	9.9

14.2.7 Perform all qualitative and quantitative measurements as described in Sections 14.4 and 14.5. After analysis, store the extracts in the dark at 0.1- 6°C.

14.3 Analytical Sequence

START CHEMSTATION SOFTWARE:

From Desktop: Start/Programs/MSD ChemStation/Instrument #1/Instrument #1

The software will locate the instrument and all peripheral equipment. Once the software is fully loaded there will be two windows visible. Window one is the instrument control window. Instrument parameters are readily viewed from this window. The second window is the sequence control window. No instrument parameters are viewable from this window.

SEQUENCE SETUP

From menu: Sequence/Run

1. Set current date in Data File Directory space (i.e., C:\MSDCHEM\1\DATA\060702\)
2. OK (to save changes)

From menu: Sequence/Edit Sample Log Table

1. Set data file name using current date using the following format MMDDYY## (i.e., 06070201)
2. Set up sequence order using the following format:

NOTE: Tune and CCV must always run first

VIAL	METHOD	SAMPLE NAME
1	DFTPP	TUNE STUNE001
2	PNA0610	CCV SSTD005-1
3	PNA0610	MBLK MB-1234-PNA
4	PNA0610	LCS LCS-1234-PNA
5	PNA0610	SAMP 0206001-001A
…	…	…
21	PNA0610	SAMP 0206001-010A
1	DFTPP	TUNE STUNE002
2	PNA0610	CCV SSTD050-2
22	PNA0610	SAMP 0206001-011A

NOTE: The number of samples, including tune and CCV that can be analyzed within the 12-hour window varies with each analysis. Use this list as a guide but always check that the samples were analyzed within 12 hours of the DFTPP injection.

PNA (SIM) = 21 total samples

3. OK (to save changes)

From menu: Method/Set New Default Paths

1. Update the method and data file paths using the current date (i.e., C:\MSDCHEM\1\DATA\060702\)
2. OK (to save changes)

Use Windows Explorer to copy all of the method files from the previous day's folder into the current day's folder.

TO START SEQUENCE:

From menu: Sequence/Run/Run Sequence

Start of the 12 hour sequence (as documented as the date/time stamp on the data file for the Tune Standard):

The analytical sequence for Initial Calibration is:

DFTPP (Tune Standard)
Calibration standard (S1)
Calibration standard (S2)
Calibration standard (S3)
Calibration standard (S4)
Calibration standard (S5)
Calibration standard (S6)
Calibration standard (S7) optional
Initial Calibration Verification Standard (ICV)

The analytical sequence for Sample Analysis is:

DFTPP
Continuing Calibration Verification Standard (CCV)
Method Blank (MB)
LCS
LCS Duplicate (if applicable)
Sample #1
Sample #1 Matrix Spike (MS)
Sample #1 Matrix Spike Duplicate (MSD)
Sample #1 Laboratory Duplicate (if applicable)
Samples #2, #3, etc. until the end of 12 hour tune period

DFTPP
CCV
Samples up to #20
Method Blank (MB) #2
LCS #2
LCSD #2 (if applicable)
Sample #21
Sample #21 Matrix Spike (MS)
Sample #21 Matrix Spike Duplicate (MSD)
Sample #21 Laboratory Duplicate (if applicable)
Samples #22, #23, etc. until the end of 12 hour tune period

14.4 Data Interpretation - Qualitative Analysis

14.4.1 An analyte is identified based upon Relative Retention Time (RRT) and by comparison of the sample mass ions with the mass ions of a standard of the suspected compound (standard reference ions). The reference mass ion ratio must be generated by the laboratory using the conditions of this method. The characteristic ions from the reference mass ion are defined to be the ions of greatest relative intensity. See Attachment 2 for the ions to be monitored. Two criteria must be satisfied to verify identification:
(1) elution of sample component at the same GC relative retention time (RRT) as those of the standard component; and (2) correspondence of the sample component and the standard component mass ions. Intensities of the characteristic ions must maximize in the same scan or within one scan of each other.

14.4.2 The RRT of the sample component is within ± 0.06 RRT units of the RRT of the standard component.

14.4.3 The relative intensities of the characteristic ions should agree within 30% of the relative intensities of these ions in the reference spectrum. (Example: For an ion abundance of 50% in the reference, the corresponding abundance in a sample spectrum can range between 20% and 80%.)

14.4.4 Structural isomers that produce very similar mass spectra must be identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs. An exception to this guidance occurs for the compounds Benzo(b)fluoranthene and Benzo(k)fluoranthene. Although the GC resolution may be minimal between the two, they are routinely reported as individual compounds. The Manual Integration SOP 1255 is used for guidance in the integration of these two peaks and for other situations that may require analyst efforts to correct computer generated integrations that are not technically sound.

14.4.5 Identification is hampered when sample components are not resolved chromatographically or coelute and produce mass spectra containing ions contributed by more than one analyte. When gas chromatographic peaks obviously represent more than one sample component (i.e., a broadened peak with shoulder(s) or a valley between two or more maxima), appropriate selection of analyte spectra and background spectra is important. Examination of extracted ion current profiles of appropriate ions can aid in the selection of spectra, and in qualitative identification of compounds, but each analyte spectrum will contain extraneous ions contributed by the coeluting compound.

14.4.6 For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. Because this method only scans for selective ions, an accurate library search can only be accomplished after analyzing the extract by SOP 4020 SVOCs by GC/MS (EPA Method 8270). See Section 14.6 of SOP 4020 for the tentative identification compound procedure.

14.5 Data Interpretation - Quantitative Analysis

14.5.1 Once a compound has been identified, the quantitation of that compound must be based on the integrated abundance from the EICP of the primary characteristic ion. The internal standard used shall be the one nearest the retention time of that of a given analyte.

14.5.2 If the RSD of a compound's response factor is 15% or less, then the concentration in the extract is determined using the average response factor (RF) from initial calibration data (13.2). See Method 8000, Sec. 7.0, for the equations describing internal standard calibration and either linear or non-linear calibrations.

14.5.3 Where applicable or required, the concentration of any non-target analytes (TIC's) identified in the sample are estimated. The same formulae must be used with the following modifications: The areas A_x and A_{is} must be from the total ion chromatograms, and the RF for the compound must be assumed to be 1. The resulting concentration must be reported indicating: (1) that the value is an estimate, and (2) which internal standard was used to determine concentration. Use the nearest internal standard free of interferences.

14.6 Record the following information in the appropriate logbook or data file. Include any deviations from this procedure. Analyst initials, date of analysis, sample number or ID, initial sample volume or weight processed, final extract volume, calibration standard sample or solution identifier, QC sample or solution identifier, surrogate solution identifier, internal standard solution identifier, any dilution information, readings from support equipment, data file name, instrument method name, visual observations, and any other information as deemed necessary.

14.7 Troubleshooting

The experience of the analyst performing GC/MS analyses is invaluable to the success of the methods. Each day that the analysis is performed, the daily calibration standard (CCV) must be evaluated to determine if the chromatographic system is operating properly. Questions that must be asked: Do the peaks look normal? Is the response obtained comparable to the response from previous calibrations? Careful examination of the standard chromatogram can indicate whether the column is still good the injector is leaking, the injector septum needs replacing, etc. If any major changes are made to the system (e.g. column changed or detector cleaned), recalibration of the system must take place.

14.8 Routine Maintenance - Record all maintenance

14.8.1 Daily, or as needed according to sample throughput, change the septum and or the injection port liner. Trim a short section from the analytical column as necessary. Alternatively, the use of a guard column helps to protect the analytical column from residue buildup. A short section, 10 to 20 cm, of the guard column may be trimmed as to improve column performance. Replace the column on an as needed basis (loss of resolution).

14.8.2 Clean the source on an as needed basis (loss of sensitivity).

14.8.3 Inspect the autosampler syringe for wear; replace as necessary.

14.8.4 Check the carrier gas supply; replace as necessary.

15.0 DATA REDUCTIONS, CALCULATIONS, AND LOADING

15.1 The data system performs the calculations.

15.1.1 If the %RSD of a compound's relative response factor is 15% or less, then the concentration in the extract may be determined using the average response factor (RF) from the initial calibration data (13.2) and the following equation:

$$C_{ex}(mg/L) = \frac{A_x \times C_{is}}{A_{is} \times RF}$$

where C_{ex} is the concentration of the compound in the extract, and the other terms are defined in Sec. 13.2.

15.1.2 Alternatively, linear regression (Sec. 13.2) may be used for determination of the extract concentration.

15.2 Compute the concentration of the analyte in the sample using the equations in Secs. 15.2.1 and 15.2.2.

15.2.1 The concentration of the analyte in the liquid samples is calculated using the concentration of the analyte in the extract and the volume of liquid extracted, as follows:

$$\text{Concentration in liquid (mg/L)} = \frac{C_{ex} * V_f}{V_i}$$

or

$$\text{Concentration in liquid (µg/L)} = \frac{C_{ex} * V_f * 1000}{V_i}$$

where:

V_f = final extract volume in mL (includes any dilution volumes)
V_i = initial volume of liquid extracted, in mL.

15.2.2 The concentration of the analyte in the solid sample is calculated using the concentration of the analyte in the extract and the weight of the solid extracted, as follows:

$$\text{Concentration in solid (mg/Kg)} = \frac{C_{ex} * V_f}{W_i}$$

or

$$\text{Concentration in solid (µg/Kg)} = \frac{C_{ex} * V_f * 1000}{W_i}$$

where:

V_f = final extract volume in mL (includes any dilution volumes)
W_i = initial sample weight, in g.

For soil samples reported on dry weight basis, divide the Concentration by the decimal equivalent of the Percent Solids. For example: a sample contains 90% solids, thus

$$\text{Concentration in solid (mg/Kg) dry weight} = \frac{C_{ex} * V_f}{W_i * 0.90}$$

15.3 See Section 14.10 of SOP 1040 Good Laboratory Practices for general calculations.

16.0 METHOD PERFORMANCE

Demonstration of Capability (DOC)

All parameters of interest must meet the method acceptance criteria before actual sample analysis begins. See SOP 1230 Training for the procedure to perform and document the DOC. The DOCs for the analysts performing this method are located in the analysts' training form folders located in the QA office files.

A quality control (QC) reference concentrate is required containing each analyte at a concentration of 5 µg/mL in acetone. The QC reference sample used is the PNA ICV (refer to Section 10.9 for composition). The QC reference sample is made using stock standards prepared independently from those used for calibration.

For each analyte calculate the mean recovery (x) and standard deviation (s) and the average % Recovery (%R). Compare X and s and %R with the corresponding acceptance criteria for accuracy and precision, respectively. Note: x must be within 1.5 and 7.5 µg/mL and s must be less than 2.5 µg/mL and %R must be within 30 % to 150 %. If x and s and %R for all analytes meet the acceptance criteria, the system performance is acceptable and analysis of actual samples can begin. If any individual x or %R falls outside the range for accuracy or any individual s exceeds the precision limit, then the system performance is unacceptable for that analyte and corrective action must be taken.

Locate and correct the source of the problem and repeat the test only for those analytes that failed to meet criteria. Repeated failure, however, will confirm a general problem with the measurement system. If this occurs, locate and correct the source of the problem and repeat the test for all compounds of interest.

Comparison to Reference Method Data

EPA Method 8000B provides guidance for the establishment of control limits for the LCS and MS QC samples. Recovery limits of 70% to 130% are provided as initial benchmarks for performance (8000B Section 8.5.4). These limits are designed for a wide variety of organic test methods. Individual analyte performance may vary. The control limits stated in Section 18 of this SOP are referenced from the CLP Statement of Work (SOW) for Organic Analyses Revision OLM04.2 May 1999 and in-house recovery data.

In-House Control Limits

Method performance data is on file in the laboratory QC department. Comparison of method performance data for the laboratory to the reference method criteria occurs when laboratory in-house acceptance limits are generated. In-house generated data is compared to the specifications of the reference method. If the in-house limits are within the specifications of the reference method, the control limits are updated in LIMS. If the in-house limits are not within specifications, an investigation is performed to determine the cause(s) of the problem and a corrective action is completed. The analysis may continue until enough data points are collected to regenerate new control limits. Any QC data generated outside of reference method limits during that time frame is flagged.

The laboratory maintains performance records to document the quality of data that is generated. Method accuracy for samples is assessed and records maintained. After the analysis of 20 laboratory control samples and surrogates, calculate the average percent recovery (R) and the standard deviation of the percent recovery (S).

Control limits for the method parameters are generated by the QC staff and distributed to the analysts via updates to the LIMS control charts. The control limits are calculated based on in-house performance data. At a minimum, these limits are reviewed annually.

17.0 POLLUTION PREVENTION

The preparation of excessive volumes of laboratory reagents and standards shall be avoided so that waste and potential for pollution are minimized. Samples, reagents and standards shall be disposed in compliance with the lab waste disposal program, SOP 1130 Waste Disposal. With the consent of the client, the samples may be returned to their origin for treatment.

Uncontaminated paper waste, glass and cans should be separated for recycling. Laboratory staff are required to protect the laboratory's and our clients' business information when disposing recycled paper or waste from the facility.

18.0 DATA ASSESSMENT AND CRITERIA FOR QUALITY CONTROL MEASURES

Data assessment includes review of: proper sample condition, preservation, and storage; analysis within holding time limitations; deviations from the SOP, evaluation of performance based or in-house control limits, reference method limits or project specific limits.

The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When results of sample spikes indicate atypical method performance, calibration verification standard is used to confirm the measurements were performed in an in-control mode of operation. The data review is conducted according to SOP 1250 Data Review.

18.1 Blanks

If the blank exceeds the RL (usually the lowest calibration standard or specifically defined in this test method SOP), the source of contamination must be investigated and corrective actions taken. The compound concentrations in the method blank of an extraction batch must be less than the RL's listed in Attachment 1. If this criteria is exceeded, re-analyze the method blank. If after re-analysis, the blank criteria is still exceeded, then the entire extraction batch must be re-extracted. Always refer to a client specific QAPP for additional guidance.

If the surrogate recovery is outside the QA limits as defined in this test method the source of the nonconformance must be investigated and corrective actions taken. If this criteria is exceeded, re-analyze the method blank. If after re-analysis, the blank criteria is still exceeded, then the entire extraction batch must be re-extracted. Always refer to a client specific QAPP for additional guidance.

Affected samples must be reprocessed and reanalyzed **or** Data must be appropriately qualified if:

1) The concentration of a targeted analyte in the blank is at or above the reporting limit as established by the SOP or by regulation, AND is greater than 1/10 of the amount measured in any sample.

2) The blank contamination otherwise affects the sample results as per the test method requirements or the individual project data quality objectives.

18.2 Laboratory Control Samples (LCS)

The results of the individual batch LCS are calculated in percent recovery (%R) and compared to established acceptance criteria from in house analyses. If the LCS is outside the acceptance criteria, see Table 6 in Attachment 3 for current acceptance criteria, the analytical system is "out-of-control." Any affected samples associated with an out-of-control LCS must be reprocessed and reanalyzed or the results reported with appropriate data qualifiers. If after re-analysis the control criteria has not been met, the entire extraction batch must be re-extracted. Always refer to a client specific QAPP for additional guidance.

18.3 Surrogates

18.3.1 The results of the individual Surrogate compounds are calculated in percent recovery (%R) and are compared to established acceptance criteria from the CLP Statement of Work (SOW) for Organic Analyses Revision OLM04.2 May 1999. Surrogates outside the acceptance criteria, see Table 7 in Attachment 3 for current acceptance criteria, must be evaluated for the effect indicated for the individual sample results.

If surrogate recoveries are not within the established acceptance criteria, proceed as follows (SW-846 8000B):

1) Check to be sure that there are no errors in the calculations, surrogate solutions or internal standards. If errors are found, recalculate the data accordingly. Examine chromatograms for interfering peaks and integrated peak areas.

2) Check instrument performance. If an instrument performance problem is identified, correct the problem and re-analyze the extract (or re-analyze the sample for volatiles).

3) Some samples may require dilution in order to bring one or more target analytes within the calibration range or to overcome significant interferences with some analytes. This may result in the dilution of the surrogate responses to the point that the recoveries cannot be measured. If the surrogate recoveries are available from a less diluted or undiluted aliquot of the sample or sample

extract, those recoveries may be used to demonstrate that the surrogates were within the QC limits, and no further action is required. However, the results of both the diluted and undiluted (or less-diluted) analyses should be provided to the data user.

4) If no instrument problem is found and if sufficient sample is available, the sample should be re-extracted and re-analyzed.

18.3.2 If, upon re-analysis (in either 2 or 4 above), the recovery is again not within limits, report the data as an "estimated concentration." If the recovery is within the limits in the re-analysis, provide the re-analysis data to the data user. If the holding time for the method has expired prior to the re-analysis, provide both the original and reanalysis results to the data user, and note the holding time problem.

18.4 Duplicates

The results from laboratory duplicates are designed to assess the precision of analytical results in a given matrix and are expressed as relative percent difference (RPD). See the STAT Quality Assurance Manual, Section 5.4 for the calculation for RPD. Results are compared to established acceptance criteria as listed in the MS/MSD Tables 8 and 9 in Attachment 3. For duplicates results outside established criteria, corrective action must be documented or the data reported with appropriate data qualifying codes.

For this test method, the analysis of the MS/MSD pair is used for determination of method precision. For cases where the sample cannot be divided (e.g., wipes, air samples, not enough sample provided by customer) and thus a MS/MSD pair is cannot be prepared in the preparation batch, an LCS/LCSD pair is prepared and analyzed to measure precision. Precision data from Tables 8 and 9 in Attachment 3 will be used for RPD acceptance criteria for LCS/LCSD.

18.5 Matrix Spikes

18.5.1 The results from MS/MSD are primarily designed to assess the precision and accuracy of analytical results in a given matrix and are expressed as percent recovery (%R) and relative percent difference (RPD). See the STAT Quality Assurance Manual, Section 5.4 for the calculation for RPD. Results are compared to established acceptance criteria from the CLP Statement of Work (SOW) for Organic Analyses Revision OLM04.2 May 1999. For matrix spike results outside established criteria corrective action must be documented or the data reported with appropriate data qualifying codes.

18.5.2 Tables 8 and 9 in Attachment 3 show the compounds spiked, the levels and the current QC criteria for soils and water samples.

18.6 Internal Standards

The results of the individual Internal Standard compounds on all samples, blanks, and spikes are calculated in percent recovery (%R*) and are compared to established acceptance criteria. If the Internal Standard recovery is outside the acceptance criteria, see Table 10, corrective action should be taken. Note: the recovery of internal standards in these samples within the stated limits is not mandatory per the reference method, 8270C. It can be a useful diagnostic tool. Client specific project criteria may require the adherence to these limits. If so, then corrective action must be documented or the data reported with appropriate data qualifying codes.

Table 10 Internal Standards

INTERNAL STD COMPOUND	CRITERIA (%R*)
1,4-Dichlorobenzene-d_4	-50 to +100
Naphthalene-d_8	-50 to +100
Acenaphthene-d_{10}	-50 to +100
Phenathrene-d_{10}	-50 to +100
Chrysene-d_{12}	-50 to +100
Perylene-d_{12}	-50 to +100

* Internal Standard Response of CCV or midpoint calibration Level

18.7 Other

The laboratory will analyze standard reference materials and participate in relevant performance evaluation studies quarterly.

19.0 CORRECTIVE ACTIONS FOR OUT-OF-CONTROL DATA

The process for handling unacceptable and out-of-control data is found in SOP 230 Corrective Action.

If the CCV, MB, LCS/LCSD, MS/MSD, lab duplicate, surrogate, internal standard, or recovery of any parameter falls outside the designated acceptance range, the laboratory performance for that parameter is judged to be out-of-control, and the problem must be immediately identified and corrected. The analytical result for that parameter in the samples is suspect and is only reported for regulatory compliance purposes with the appropriate corrective action form. Immediate corrective action includes reanalyzing all affected samples by using any retained sample before the expiration of the holding time. Final data results must be qualified in the client report for reported results not meeting the laboratory-defined criteria.

1) Review standards preparation logbooks. Check all calculations and ensure dilution factors are properly recorded.
2) Re-prepare the suspected standard or QC sample to identify possible preparation errors of the standard or QC sample.
3) Re-Analyze the samples when the CCV or LCS is not within acceptable limits.
4) Perform routine preventative maintenance following manufacturer's specification. Record all maintenance in the instrument logbook.

20.0 CONTINGENCIES FOR HANDLING OUT-OF-CONTROL OR UNACCEPTABLE DATA

Every effort is made to prevent problems from occurring. When out-of-control or unacceptable data occurs the first option is to identify the problem and reanalyze the samples within the holding times. When this is not possible, the QA Manager and/or the Laboratory Director reviews data and discusses options

with the client. Reanalysis or reporting the data with qualification are alternatives. Out-of-control or unacceptable data reported to the client must include the data qualifier, flag and discussion on the rationale for reporting.

Holding time exceedence, improper preservation and improper sample condition or storage are noted on the corrective action form and included on the final report.

Review the CCV standard response, LCS result, the surrogate recovery, and internal standard recovery for acceptable performance for each batch of samples. Record any trends or unusual performance on a corrective action form. Final data results must be qualified in the client report for results not meeting the laboratory-defined criteria.

Manual integration must be minimized for standards, reagent blanks and surrogates. Routine manual integration of the same parameters indicates a system performance problem. Correct this problem or note in the instrument analysis logbook the suspected causes for routine manual integration. Sign and date all manually integrated chromatograms.

20.1 The process for handling unacceptable and out-of-control data is found in the Laboratory QAM Section 11. The reporting of data that is out-of-control must be approved and documented by Quality Assurance Manager and either the Technical Manager or the Laboratory Director.

20.2 Client Requested Modifications:

20.2.1 Clients must request modifications from the laboratory SOP in writing to the lab.

20.2.2 The lab director, technical manager and quality assurance manager will evaluate the requested client deviations, determine the feasibly of the deviation and the potential effects on the data.

20.2.3 If it is determined that the lab will perform the requested deviations, lab director, technical manager and quality assurance manager will decide if a method validation study is required.

20.2.4 The designated project manager will retain all documentation concerning the requested deviation, including all correspondence with the client, in the client folder.

20.2.5 The final analytical report must include the statement *"This report has analyses performed using client requested modifications"*.

21.0 WASTE MANAGEMENT

The STAT Analysis Corporation Waste Disposal SOP 1130 identifies proper waste management practices for the chemicals and biological materials used in this procedure. Samples are stored and discarded accordance with SOP 1130 Waste Disposal.

22.0 REFERENCES

22.1 Method 8270C, Revision 3, December 1996; U.S. EPA SW-846 "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods" Update III, December 1996.
22.2 SW-846 8000B Determinative Chromatographic Separation
22.3 "USEPA Contract Laboratory Program Statement of Work for Organic Analysis" Revision OLM04.2 May 1999, U. S. Environmental Protection Agency. Office of Solid Waste, Washington DC 20460.
22.4 NIST Library of Reference Spectra, Edition Number NIST98
22.5 NBS Library of Reference Spectra, Edition Number NBS75K
22.6 SAP QA 003 Chemical Hygiene Plan
22.7 SOP 230 Corrective Action
22.8 SOP 1000 Control and Use of Laboratory Notebooks
22.9 SOP 1010 Analytical Standards and Reagent Receipt and Preparation
22.10 SOP 1040 General Laboratory Practices
22.11 SOP 1130 Waste Disposal
22.12 SOP 1210 Method Detections Limits
22.13 SOP 1230 Training
22.14 SOP 1250 Data Review
22.15 SOP 1255 Manual Integration
22.16 SOP 1400 LIMS
22.17 SOP 3330 Silica Gel Cleanup for Semi-Volatile Organics (EPA Method 3630C)
22.18 SOP 3500 Extraction of Samples for Semi-Volatile Organic Analyses (EPA 3510C, 3520C, 3550B, 3580A)
22.19 Manufacturers' Equipment Instruction Manuals

23.0 FORMS, FIGURES, TABLES, DIAGRAMS, FLOWCHARTS, ATTACHMENTS OR VALIDATION DATA

Attachment 1 MDL's and Reporting Limits for Semivolatile Compounds
Attachment 2 Characteristic Ions for Semivolatile Compounds
Attachment 3 LCS, Surrogate and MS/MSD Criteria

Attachment 1:
MDL's and REPORTING LIMITS FOR POLYNUCLEAR AROMATIC COMPOUNDS

CASN	Compounds	MDL (µg/L)	RL (µg/L)	RL (mg/L)	MDL (µg/Kg)	RL (µg/Kg)	RL (mg/Kg)
83-32-9	Acenaphthene	0.13	2	0.002	2.5	25	0.025
208-96-8	Acenaphthylene	0.05	2	0.002	2.9	25	0.025
120-12-7	Anthracene	0.03	2	0.002	2.0	25	0.025
56-55-3	Benzo(a)anthracene	0.04	0.13	0.00013	3.2	25	0.025
205-99-2	Benzo(b)fluoranthene	0.06	0.18	0.00018	2.3	25	0.025
207-08-9	Benzo(k)fluoranthene	0.06	0.17	0.00017	2.5	25	0.025
191-24-2	Benzo(g,h,i)perylene	0.08	0.1	0.0001	2.4	25	0.025
50-32-8	Benzo(a)pyrene	0.08	0.2	0.0002	1.6	25	0.025
218-01-9	Chrysene	0.05	1	0.001	1.7	25	0.025
53-70-3	Dibenz(a,h)anthracene	0.08	0.1	0.0001	2.9	25	0.025
132-64-9	Dibenzofuran	0.07	0.5	0.0005	2.2	25	0.025
206-44-0	Fluoranthene	0.05	2	0.002	3.1	25	0.025
86-73-7	Fluorene	0.09	2	0.002	2.8	25	0.025
193-39-5	Indeno(1,2,3-cd)pyrene	0.06	0.1	0.0001	2.8	25	0.025
91-20-3	Naphthalene	0.12	1	0.001	2.0	25	0.025
90-12-0	1-Methyl naphthalene	0.08	0.5	0.0005	2.5	25	0.025
91-57-6	2-Methyl naphthalene	0.07	0.5	0.0005	1.6	25	0.025
85-01-8	Phenanthrene	0.15	2	0.002	3.1	25	0.025
129-00-0	Pyrene	0.04	2	0.002	2.3	25	0.025

Attachment 2:
CHARACTERISTIC IONS FOR POLYNUCLEAR AROMATIC COMPOUNDS

#	Compounds	Retention Time (min.)	Primary Ion	Secondary Ion(s)
1	1,4-Dichlorobenzene-d4 (ISTD)	9.21	152	150
2	1,2-Dichlorobenzene-d4 (SURR)	9.60	152	150
3	Nitrobenzene-d5 (SURR)	10.34	82	128
4	Naphthalene-d8 (ISTD)	11.55	136	68
5	Naphthalene	11.58	128	129
6	2-Methylnaphthalene	12.64	142	141
7	1-Methylnaphthalene	12.80	142	141
8	2-Fluorobiphenyl (SURR)	13.19	172	171
9	Acenaphthylene	13.93	152	151
10	Acenaphthene-d10 (ISTD)	14.14	164	162
11	Acenaphthene	14.17	154	153
12	Dibenzofuran	14.39	168	139
13	Fluorene	14.84	166	165
14	Phenanthrene-d10 (ISTD)	16.06	188	94
15	Phenanthrene	16.09	178	179
16	Anthracene	16.15	178	176
17	Fluoranthene	17.61	202	101
18	Pyrene	17.90	202	200
19	p-Terphenyl-d14 (SURR)	18.05	244	122
20	Chrysene-d12 (ISTD)	19.52	240	120
21	Benzo(a)anthracene	19.49	228	229
22	Chrysene	19.56	228	226
23	Benzo(b)fluoranthene	21.53	252	253
24	Benzo(k)fluoranthene	21.59	252	253
25	Benzo(a)pyrene	22.33	252	253
26	Perylene-d12 (ISTD)	22.47	264	260
27	Indeno(1,2,3-cd)pyrene	25.87	276	138
28	Dibenz(a,h)anthracene	25.91	278	139
29	Benzo(g,h,i)perylene	26.90	276	138

ISTD = Internal Standard
SURR = Surrogate

Attachment 3:

Table 6 LCS Recovery

Compound	Soil % Recovery	Water % Recovery
Naphthalene	30-130	50-125
Acenaphthylene	30-130	50-125
Acenaphthene	30-130	50-125
Fluorene	30-130	50-125
Phenanthrene	30-130	50-125
Anthracene	30-130	50-125
Fluoranthene	30-130	50-125
Pyrene	30-130	50-125
Benzo(a)anthracene	30-130	50-125
Chrysene	30-130	50-125
Benzo(b)fluoranthene	30-130	50-125
Benzo(k)fluoranthene	30-130	50-125
Benzo(a)pyrene	30-130	50-125
Indeno(1,3,3-cd)pyrene	30-130	50-125
Dibenz(a,h)anthracene	30-130	50-125
Benzo(g,h,i)perylene	30-130	50-125

Table 7 Surrogate Recovery

Surrogate Compound	Soil % Recovery	Water % Recovery
Nitrobenzene-d_5	23-120	35-114
2-Fluorobiphenyl	30-115	43-116
Terphenyl-d_{14}	18-137	33-141
1,2-Dichlorobenzene-d_4	20-130	16-110

Table 8 Matrix Spike – Soil

Compound	Amount added µg/Kg	RPD Limit	% Recovery
Naphthalene	167	50	30-130
Acenaphthylene	167	50	30-130
Acenaphthene	167	50	30-130
Fluorene	167	50	30-130
Phenanthrene	167	50	30-130
Anthracene	167	50	30-130
Fluoranthene	167	50	30-130
Pyrene	167	50	30-130
Benzo(a)anthracene	167	50	30-130
Chrysene	167	50	30-130
Benzo(b)fluoranthene	167	50	30-130
Benzo(k)fluoranthene	167	50	30-130
Benzo(a)pyrene	167	50	30-130
Indeno(1,3,3-cd)pyrene	167	50	30-130
Dibenz(a,h)anthracene	167	50	30-130
Benzo(g,h,i)perylene	167	50	30-130

Table 9 Matrix Spike –Water

Compound	Amount added µg/L	RPD Limit	% Recovery
Naphthalene	5	25	50-125
Acenaphthylene	5	25	50-125
Acenaphthene	5	25	50-125
Fluorene	5	25	50-125
Phenanthrene	5	25	50-125
Anthracene	5	25	50-125
Fluoranthene	5	25	50-125
Pyrene	5	25	50-125
Benzo(a)anthracene	5	25	50-125
Chrysene	5	25	50-125
Benzo(b)fluoranthene	5	25	50-125
Benzo(k)fluoranthene	5	25	50-125
Benzo(a)pyrene	5	25	50-125
Indeno(1,3,3-cd)pyrene	5	25	50-125
Dibenz(a,h)anthracene	5	25	50-125
Benzo (g,h,i)perylene	5	25	50-125

STAT Analysis Corporation:

STANDARD OPERATING PROCEDURE 4510

METALS ANALYSIS BY INDUCTIVELY COUPLED PLASMA - MASS SPECTROMETRY (EPA METHOD 6020 AND EPA METHOD IO-3.5)

Revision 05

Effective Date: May 16, 2005

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1.0 IDENTIFICATION OF TEST METHOD

SOP Title: Metals Analysis by Inductively Coupled Plasma - Mass Spectrometry (EPA Method 6020 and EPA Method IO-3.5) is abbreviated as ICP-MS in the laboratory records.

2.0 APPLICABLE MATRICES

Inductively coupled plasma-mass spectrometry (ICP-MS) is applicable to the determination of µg/L and sub-µg/L concentrations of a large number of elements in water samples and in waste extracts or digests. When dissolved constituents are required, samples must be filtered and acid-preserved prior to analysis. No digestion is required prior to analysis for dissolved elements in water samples. Acid digestion prior to filtration and analysis is required for aqueous, solids, and air filters for which total (acid-leachable) elements are required.

3.0 DETECTION LIMITS

The lab follows the procedure found in 40CFR Part 136B to determine the MDL for each matrix type on an annual basis. See the STAT Analysis SOP 1210 Method Detection Limits for the MDL procedure, frequency, and acceptance criteria. The MDLs measured by the lab and all supporting documentation are in the laboratory QA files for review.

The laboratory determined method detection limit (MDL) must always be less than the reporting limit (RL). The RLs will usually range from three to ten times the laboratory measured MDLs but this relationship may vary dependent on dilution, reduced sample size to avoid saturation of the detector, matrix interferences, moisture adjustments (in solid samples), or method-specified requirements. Attachment 1 contains the current MDLs and reporting limits (RLs) for soils, waters and air filters.

4.0 SCOPE AND APPLICATION

4.1 Inductively coupled plasma-mass spectrometry (ICP-MS) is applicable to the determination of sub-µg/L concentrations of a large number of elements in water samples and in waste extracts or digests. When dissolved constituents are required, samples must be filtered and acid-preserved prior to analysis. No digestion is required prior to analysis for dissolved elements in water samples. Acid digestion prior to filtration and analysis is required for groundwater, aqueous samples, industrial wastes, soils, sludges, sediments, air filters, wipes, and other solid wastes for which total (acid-leachable) elements are required.

4.2 ICP-MS has been historically applied to the determination of over 60 elements in various matrices. Analytes determined at this laboratory for this method are listed in Attachment 1 (along with the masses used for determination). If Method 6020 is used to determine any analyte not listed in Attachment 1, it is the responsibility of the laboratory to demonstrate the accuracy and precision of this method in the material to be analyzed. The analyst is always

required to monitor potential sources of interferences and take appropriate action to ensure data of known quality (see Section 14.4 Qualitative Analysis).

4.3 This method is restricted to use by or under the supervision of analysts experienced in the use of ICP-MS and knowledgeable in the recognition and correction of spectral, chemical, and physical interferences in ICP-MS. Each analyst must demonstrate the ability to generate acceptable results with this method.

5.0 SUMMARY OF TEST METHOD

5.1 Samples that require total "acid-leachable" values must be digested using appropriate sample preparation methods prior to analysis.

5.2 EPA methods 6020 and IO-3.5 describes the multi-elemental determination of analytes by ICP-MS. The method measures ions produced by a radio frequency inductively coupled plasma. Analyte species originating in a liquid are nebulized and the resulting aerosol transported by argon gas into the plasma. The ions produced are entrained in the plasma gas and introduced, by means of an interface, into a mass spectrometer. The ions are sorted according to their mass-to-charge ratios and quantified with a channel electron multiplier. Interferences must be assessed and valid corrections applied or the data flagged to indicate problems. Interference correction must include compensation for background ions contributed by the plasma gas, reagents, and constituents of the sample matrix. An appropriate internal standard is required for each analyte determined by ICP-MS.

5.3 Method Modifications from Reference – This SOP is based on EPA Method 6020 and incorporates IO-3.5 for TSP/PM10 high-volume filters except that: 1) polypropylene volumetric flasks are used since analysis for boron is occasionally required, 2) the instrument resolution is set for 1 amu peak width at 10% peak height according to 6020 but is less stringent than IO-3.5, 3) samples which fail high or low for one or more internal standards are diluted as needed to bring within range for the internal standard, 4) A matrix spike and matrix spike duplicate are digested and analyzed, since a duplicate sample is not typically analyzed, 5) Dilution test may be performed on aqueous matrices. Non-aqueous matrices are already diluted before analysis 6) reagent water must be at least Type II (ASTM) for all standards, solutions, and sample preparation according to 6020 but is less stringent than IO-3.5, 7) internal standards and tuning solutions cover the entire mass range of analysis, but the elements used vary slightly from IO-3.5, 8) the MDLs are determined annually according to the requirements described in SOP 1210 Method Detection Limits 9) the ICB/CCB acceptance limit is the lower reporting limit and not the MDL per IO-3.5, since we do not report down to the MDL. 10) Germanium instead of yttrium is used as an internal standard, since yttrium is found in environmental samples.

6.0 DEFINITIONS

The STAT Analysis Quality Assurance Manual Section 19.0 contains all the definitions of standard terms used in SOPs.

7.0 INTERFERENCES

7.1 Isobaric elemental interferences in ICP-MS are caused by isotopes of different elements forming atomic ions with the same nominal mass-to-charge ratio (m/z). A data system must be used to correct for these interferences. This involves determining the signal for another isotope of the interfering element and subtracting the appropriate signal from the analyte isotope signal. Since commercial ICP-MS instruments nominally provide unit resolution at 10% of the peak height, very high ion currents at adjacent masses can also contribute to ion signals at the mass of interest. Although this type of interference is uncommon, it is not easily corrected, and samples exhibiting a significant problem of this type could require resolution improvement, matrix separation, or analysis using another verified and documented isotope, or use of another method.

7.2 Isobaric molecular and doubly charged ion interferences in ICP-MS are caused by ions consisting of more than one atom or charge, respectively. Most isobaric interferences that could affect ICP-MS determinations have been identified in the literature. Examples include $ArCl^+$ ions on the ^{75}As signal and MoO^+ ions on the cadmium isotopes. While the approach used to correct for molecular isobaric interferences is demonstrated below using the natural isotope abundances from the literature, the most precise coefficients for an instrument can be determined from the ratio of the net isotope signals observed for a standard solution at a concentration providing suitable (<1 percent) counting statistics. Because the ^{35}Cl natural abundance of 75.77 percent is 3.13 times the ^{37}Cl abundance of 24.23 percent, the chloride correction for arsenic can be calculated (approximately) as follows (where the ^{38}Ar ^{37}Cl contribution at m/z 75 is a negligible 0.06 percent of the ^{40}Ar ^{35}Cl signal): corrected arsenic signal (using natural isotopes abundances for coefficient approximations) = (m/z 75 signal) - (3.13) (m/z 77 signal) + (2.73) (m/z 82 signal), (where the final term adjusts for any selenium contribution at 77 m/z).

NOTE: Arsenic values can be biased high by this type of equation when the net signal at m/z 82 is caused by ions other than $^{82}Se^+$, (e.g., $^{81}BrH^+$ from bromine wastes. Similarly, corrected cadmium signal (using natural isotopes abundances for coefficient approximations) = (m/z 114 signal) - (0.027)(m/z 118 signal) - (1.63)(m/z 108 signal), (where last 2 terms adjust for any tin or MoO^+ contributions at m/z 114).

NOTE: Cadmium values will be biased low by this type of equation when $^{92}ZrO^+$ ions contribute at m/z 108, but use of m/z 111 for Cd is even subject to direct ($^{94}ZrOH^+$) and indirect ($^{90}ZrO^+$) additive interferences when Zr is present.

NOTE: As for the arsenic equation above, the coefficients in the Cd equation are **ONLY** illustrative. The most appropriate coefficients for an instrument can be determined from the ratio of the net isotope signals observed for a standard solution at a concentration providing suitable (<1 percent) counting precision. The accuracy of these types of equations is based upon the constancy of the OBSERVED isotopic ratios for the interfering species. Corrections that presume a constant fraction of a molecular ion relative to the "parent" ion have not been found to be reliable, e.g., oxide levels can vary. If a correction for an oxide ion is based upon the ratio of parent-to-oxide ion intensities, the correction must be adjusted for the degree of oxide formation by the use of an appropriate oxide internal standard previously demonstrated to form a similar level of oxide as the interferent. This

type of correction has been reported for oxide-ion corrections using ThO^+ /Th^+ for the determination of rare earth elements. The use of aerosol, desolvation, and/or mixed plasmas has been shown to greatly reduce molecular interferences. These techniques can be used provided that method detection limits, accuracy, and precision requirements for analysis of the samples can be met.

7.3 Physical interferences are associated with the sample nebulization and transport processes as well as with ion-transmission efficiencies. Nebulization and transport processes can be affected if a matrix component causes a change in surface tension or viscosity. Changes in matrix composition can cause significant signal suppression or enhancement. Dissolved solids can deposit on the nebulizer tip of a pneumatic nebulizer and on the interface skimmers (reducing the orifice size and the instrument performance). Total solid levels below 0.2% (2,000 mg/L) have been currently recommended to minimize solid deposition. An internal standard can be used to correct for physical interferences, if it is carefully matched to the analyte so that the two elements are similarly affected by matrix changes. When the intensity level of an internal standard is less than 30 percent or greater than 120 percent of the intensity of the first standard used during calibration, the sample must be reanalyzed after a fivefold (1+4) or greater dilution has been performed.

7.4 Memory interferences can occur when there are large concentration differences between samples or standards which are analyzed sequentially, deposition on the sampler and skimmer cones, spray chamber design, and the type of nebulizer affect the extent of the memory interferences which are observed. The rinse period between samples must be long enough to eliminate significant memory interference. Whenever an unusually concentrated sample is encountered, the sample after it may need to be reanalyzed to check for cross contamination.

8.0 SAFETY

Proper personal protective equipment including safety glasses, gloves and a lab coat are required during different parts of this method. Other safety precautions must be conducted in accordance with the Chemical Hygiene Plan. Other actions can also be applied if deemed necessary. A reference file of Material Safety Data Sheets (MSDS) for all reagents/chemical involved in this method is available to all personnel.

Stock metal standards and acid solutions (strong oxidizers) may pose potential health risks. Extreme care should be utilized when handling these solutions.

9.0 EQUIPMENT AND SUPPLIES

The following apparatus is recommended for performing this procedure. Equivalent items can be used, if with their use, the analytical and QA/QC requirements in this SOP can be met.

9.1 Inductively coupled plasma-mass spectrometer: Aglient 7500i or equivalent.

9.1.1 A system capable of providing resolution, better than or equal to 1.0 amu at 10% peak height is required. The system must have a mass range from at least 6 to 240 amu and

a data system that allows corrections for isobaric interferences and the application of the internal standard technique. Use of a mass-flow controller for the nebulizer argon and a peristaltic pump for the sample solution are recommended.

9.1.2 Chiller - Neslab CT 100 or equivilent

9.1.3 Argon gas supply – high purity grade (99.99%).

9.1.4 Data system - An Agilent Kayak computer system using 3365 Chemstation Version C.00.01 to interpret spectral data is attached to the ICP-MS.

9.1.5 Autosampler – Cetac ASX-450 or equivalent.

9.2 Autopipettes – 0.01 to 0.10 mL, 0.1 to 1.0 mL, 1.0 to 5.0 mL.

9.3 Dispensing pipettes – 1 to 10 mL

9.4 Polypropylene Volumetric Flasks, - 50 mL, 100 mL, 250 mL, and 500 mL with screw caps. See section 14.8 for the procedure of checking the flask volume.

9.5 Plastic Tubes – 14 mL culture tubes and 50-mL graduated with screw caps.

9.6 Plastic bottles – 250 mL, 500 mL and one liter with Teflon screw caps

10.0 REAGENTS AND STANDARDS

The following reagents and standards are required to perform this procedure. When instructions are given on how to prepare a specific volume of a reagent or standard, larger or smaller volumes can be prepared as needed so long as the final concentrations remain the same. Any other deviations from the reagents or standards listed in this SOP could be detrimental to the quality of the data produced. Such deviations would have to be approved and documented (see SOP 230 Corrective Action).

Instructions for labeling and record keeping of reagents and standards are contained in SOP 1010 Analytical Standards and Reagents Receipt and Preparation. All standards solutions and QC solutions are stored at room temperature in plastic bottles.

10.1 Analytical reagent grade chemicals shall be used in all tests. Unless otherwise indicated, all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.

10.2 Reagent water - All references to water in this SOP refers to Type II reagent water (in-house system).

10.3 Calibration Stock Standard - Standard solutions can be prepared from pure standard materials or purchased as certified solutions. The routine laboratory practice is to purchase these standards from approved vendors. These stock standard solutions are purchased or prepared from ultra-high purity grade chemicals or metals (99.99 or greater purity) for most elements. The stock standards for individual elements are usually at concentrations of 1000 or 10,000 mg/L in solution. Custom blend stock standard solutions may also be purchased and used. Stock standard solutions and QC solutions are stored at room temperature in their original containers.

10.3.1 Secondary Calibration Stock Standard – These solutions are made using the individual Stock Standard solutions. Three secondary solutions are prepared by combining and diluting the individual stock standard solutions to levels in the linear range for the instrument in a matrix consisting of 2% (v/v) HNO_3 in reagent water. When preparing the secondary stock standards, each stock solution must be initially verified to determine correct preparation and/or the presence of impurities. Care must be taken when preparing the mixed standards that the elements are compatible and stable. The following amounts of each Stock Standard solution are pipetted into a 250 mL volumetric flask. The solution is brought to volume with 2% nitric acid (HNO_3). The final concentration of each component is listed in Table 1. These Secondary Stock Standard solutions are the source solutions to prepare the calibration standards in Section 10.4. Fresh mixed standards must be prepared as needed with the realization that concentrations can change on aging. Calibration standards must be initially verified using a quality control standard and monitored weekly for stability.

Table 1 Secondary Calibration Stock Standard Solutions

Secondary Stock Solution	Elements	Conc. Stock (mg/L)	Vol. Stock (mL)	Final Volume (mL)	Final Conc. (mg/L)
A	Al, As, B, Ba Be, Cd, Cr, Co, Cu, Pb, Mn, Ni, Se, Tl, V, Zn	1000 each	2.5 mL each	250	10
	Sb, Mo, Sn, Ti		1.25 mL each		5
B	Ag	1000 each	2.5 mL each	250	10
C	Na, Ca, Mg, K, Fe	10,000 each	2.5 mL each	250	100

10.4 Calibration standards - Four calibration standards are prepared. Calibration standards in current use: 1, 10, 100, and 200 mg/L (for all elements except Ca, Fe, K, Mg, Mo, Na, Sb, Sn , and Ti (see Table 2). The following amounts of Secondary Stock Standard Solutions A, B, and C are pipetted into a 50 mL volumetric flask. Each calibration standard solution is brought to volume with 2% nitric acid (HNO_3). The final concentration of each component is listed in Table 2. Level 1 Calibration standard can be prepared by taking 5 mL of level 2 and diluting to 50 mL.

Table 2 Calibration Standards

Level	Volume (µL) Secondary Stock A and B	Volume (µL) Secondary Stock C	Final Volume (mL)	Final Conc. Trace Elements * (µg/L)	Final Conc. of Sb, Mo, Sn, & Ti (µg/L)	Final Conc. Major Elements (µg/L) Na, Ca, Mg, K, Fe
1	5mL of level 2 standard		50	1	0.5	10
2	50	50	50	10	5	100
3	500	500	50	100	50	1000
4	1000	5000	50	200	100	10000

* Except Sb, Mo, Sn, and Ti.

10.5 ICP-MS Internal Standard Stock Solutions: A solution containing 100 µg/mL ^{6}Li, ^{45}Sc, ^{159}Tb, ^{89}Y, ^{115}In and ^{209}Bi. Single element Germanium Standard 1000 mg/L. These solutions are purchased commercially.

10.5.1. Working Internal Standard Solution (1 mg/L): Pipette 1.0 mL of the mixed ICP-MS Internal Standard Stock Solution and 0.10 mL of the Germanium Standard into a 100 mL volumetric flask and bring to volume with 2% nitric acid (HNO_3). The working internal standard solution is added to a reservoir and will be added on-line to each standard, QC sample, and test sample at the time of analysis using a second channel of the peristaltic pump and an appropriate mixing manifold. This will deliver approximately 40 mg/L at the instrument for every sample/standard analyzed. Generally, an internal standard should be no more than 50 amu removed from the analyte.

10.6 ICP-MS Tuning Solution Stock 10 mg/L: Commercially purchased. This solution contains 10 mg/L each of Ce, Tl, Li and Y.

10.6.1. Working ICP-MS Tuning Solution 10 µg/L: Pipette 0.25 mL of the ICP-MS Tuning Stock Solution into a 250 mL volumetric flask and bring to volume with 2% nitric acid (HNO_3).

10.7 Stock 6020 Tune Check Solution: A solution containing elements representing all of the mass regions of interest (10 mg/L each of Li, Co, In, and Tl) must be prepared to verify that the resolution and mass calibration of the instrument are within the required specifications. This solution is also used to verify that the instrument has reached thermal stability. Purchased commercially.

10.7.1. Working 6020 Tune Check Solution 100 µg/L: Pipette 1.0 mL of the Stock 6020 Tune Check Solution into a 100 mL volumetric flask and bring to volume with 2% nitric acid (HNO_3).

10.8 Stock P/A Factor Tuning Solution (10 mg/L): Using multi-element Standards prepare a 10 mg/L Standard in 2% Nitric Acid.

10.8.1. Working P/A Factor Tuning solution 100 µg/L: Pipette 1.0 mL of the Stock 6020 Tune Check Solution into a 100 mL volumetric flask and bring to volume with 2% nitric acid (HNO_3).

NOTE: Working Calibration Standards 1, 2, 3, and 4 may also be used to determine P/A Factors.

10.9 ICP-MS Interference Check Solutions A and AB: Purchased commercially. See Attachment 2 for concentrations.

Working ICS Solutions:

10.9.1. ICS-A: Pipette 20.0 mL of ICP-MS Interference Check Solution A and 2 mL of concentrated Nitric Acid into a 100 mL volumetric flask and bring to volume with reagent water. ICS solution A must be prepared fresh weekly.

10.9.2. ICS-AB: Pipette 20.0 mL of ICP-MS Interference Check Solution AB and 2 mL of concentrated Nitric Acid into a 100 mL volumetric flask and bring to volume with reagent water. ICS solution AB must be prepared fresh weekly. The analyst should be aware that the solution might precipitate silver more quickly.

10.10 Laboratory Control Sample/Matrix Spike Stock - The LCS/matrix spike is prepared from individually purchased elements or custom blend stock standards. The Calibration Verification Stock Standards or Independent Stock Standards may be used to prepare the solution. The LCS/Matrix Spike Stock is prepared according to Table 3 below. Fill a 1000 mL volumetric flask with 400 mL of 2% v/v nitric acid. Pipette the appropriate volume of each analyte into the flask and bring to volume with 2% v/v nitric acid. This solution has a shelf life of six months.

Table 3 Laboratory Control Sample/Matrix Spike Stock

Elements	Conc. Stock (mg/L)	Vol. Stock (mL)	Final Volume (mg/L)	Final Conc. (mg/L)
Al, As, B, Ba Be, Cd, Cr, Co, Cu, Pb, Mn, Ni, Se, Tl, V, Zn	1000 each	25 mL each	1000	25
Sb, Mo, Sn, Ti	1000 each	12.5 mL ea.		12.5
Ag	1000 each	10 mL each		10
Na, Ca, Mg, K, Fe	10,000 each	10 mL each		100

Spike with one milliliter of this stock solution per 50 ml digestate when preparing the LCS, LCSD, MS, MSD. For the Post Digestion Spike (PDS) samples, spike in the ratio of 1 mL per 50 mL digestate.

10.10.1 If ambient air filters are to be analyzed for Barium or Zinc, additional spike will need to be added. The additional spike should have a concentration of 24 mg/L of Barium and 0.5 mg/L of Zinc. Spike with 1 mL of the Barium and Zinc spike. To prepare this solution, add 100 mL of 2% HNO_3 to a 250 mL volumetric flask.

Pipette 6 mL of 1000 mg/L Ba standard and 0.125 mL of 1000 g/mL Zn standard. Dilute to volume.

10.11 Calibration Verification Stock Standard Solutions (ICV/CCV) – The Calibration Verification Stock Standard Solutions A and B are prepared from 1000mg/L single element standards. These solutions are prepared by combining and diluting individual stock standard to levels in the linear range for the instrument in a matrix consisting of 2 percent (v/v) HNO_3 in reagent water. Prior to preparing the calibration verification stock standards, each stock solution must be analyzed to determine correct preparation and/or the presence of impurities. Care must be taken when preparing the mixed standards that the elements are compatible and stable. The following amounts of each Stock Standard solution are pipetted into a 250 mL volumetric flask. The solution is brought to volume with 2 percent (v/v) HNO_3 in reagent water. The final concentration of each component is listed in Table 4. These Calibration Verification Stock Standard Solutions are the source solutions to prepare the Initial Calibration Verification (ICV), and Continuing Calibration Verification (CCV) standards. Fresh mixed standards must be prepared as needed with the realization that concentrations can change on aging. Calibration standards must be initially verified using a quality control standard and monitored for stability.

Table 4. Calibration Verification Stock Standard Solutions (ICV/CCV)

Secondary Stock Solution	Elements	Conc. Stock (mg/L)	Vol. Stock (mL)	Final Volume (mL)	Final Conc. (mg/L)
A	Al, As, B, Ba Be, Cd, Cr, Co, Cu, Pb, Mn, Ni, Se, Tl, V, Zn	1000 each	2.5 mL each	250	10
	Sb, Mo, Sn, Ti	1000 each	1.25	250	5
	Na, Ca, Mg, K, Fe	10,000 each	2.5 mL each	250	100
B	Ag	1000 each	2.5 mL each	250	10

10.11.1 Initial Calibration Verification Standard (ICV) - To a 100-mL volumetric flask add about 80 mL of 2% Nitric Acid (HNO_3). Pipette 0.5 ml of secondary stock solutions A and B into this flask and dilute to the mark with 2 percent (v/v) HNO_3 .

10.11.2 Continuing Calibration Verification Standard (CCV) – To a 250-mL volumetric flask add about 200 mL of 2% Nitric Acid HNO_3). Pipette 2.5 ml of secondary stock solutions A and B into a 250-ml flask and dilute to the mark with 2 percent (v/v) HNO_3.

10.12 Blanks: Three types of blanks are required for the analysis. The calibration blank is used in establishing the calibration curve. The method blank is used to monitor for possible contamination resulting from the sample preparation procedure. The rinse blank is used to flush the system between all samples and standards.

10.12.1 The calibration blank consists of the same concentration(s) of the same acid(s) used to prepare the calibration standard solutions of the analytes (usually 2 % HNO_3in reagent water).

10.12.2 The method (or digestion) blank must be carried through the complete digestion procedure and contain the same volumes of reagents as the sample solutions.

10.12.3 The rinse blank consists of 2% HNO_3 in reagent water. Prepare a sufficient quantity to flush the system between standards and samples.

10.13 Nitric Acid: Acids used in the preparation of standards and for sample processing must be of high purity. Redistilled acids are recommended because of the high sensitivity of ICP-MS. Many more molecular-ion interferences are observed on the analytes when hydrochloric and sulfuric acids are used.

10.13.1 1:1 HNO_3: Cautiously and slowly add 100 mL concentrated HNO_3 to 100 mL of reagent water.

10.13.2 2% v/v HNO_3: Cautiously and slowly add 20 mL concentrated HNO_3 to a 1000 mL volumetric flask and bring to volume with reagent water and mix.

10.14 Argon gas supply: high-purity grade (99.99%).

11.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

11.1 The recommended containers used to collect samples for the determination of metals are polyethylene or fluorocarbon (TFE or PFA): 500 mL for water samples and 4 to 8 oz jars for soil samples.

11.2 Samples may be transported to the laboratory and stored at room temperature. Solid samples may be stored under refrigeration at between 0.1 and 6.0°C until time of digestion. Digestion and analysis must be within 180 days from sampling date. Sample digestates are stored at room temperature.

11.3 Aqueous samples must be preserved with 1:1 HNO_3 to a pH < 2.

11.4 For proper handling and storage of the PM10/SPM filters, see SOP 3115 Extraction of High Volume Filters.

12.0 QUALITY CONTROL

The following details the QC requirements that apply to this analysis. Each Quality Control Indicator (QCI) provides information pertaining to either method or individual sample performance. Our goal is to produce defensible data of known and documented quality. The results of these QCI samples are used to assess the acceptability of data.

12.1 **Blanks**

Method Blank analysis is performed to determine if any contamination is present in the analytical process and is used to evaluate acceptance of the batch of samples. A method blank shall be prepared once per preparation batch of 20 or less samples per matrix type. If more than 20 samples are prepared a second blank shall be prepared after the twentieth sample. The method blank shall be processed through all preparatory steps used for the

samples, including cleanup procedures. The blank shall be analyzed using the same instrument and conditions as the samples.

The Calibration Blank is used to monitor the initial level of contamination in the reagent solutions prior to initial calibration.

The Rinse Blank is used to monitor the ICP-MS system for potential cross-contamination from one sample to another or for residual contamination in the system.

12.2 **Initial Calibration Verification (ICV)**

An Initial Calibration Verification (ICV) standard containing all of the target analytes reported in this method (refer to section 10.11.1) shall be analyzed immediately after the completion of the initial calibration. The ICV shall be purchased from or prepared from second source standards to verify analyte concentrations.

12.3 **Continuing Calibration Verification (CCV)**

A CCV standard containing all of the target analytes reported in this method (refer to section 10.11.2) shall be analyzed after every tenth sample. The CCV standard shall be at a different concentration than the ICV, and shall be used to confirm the system is in calibration.

12.4 **Laboratory Control Sample (LCS)**

The LCS is used to evaluate the performance of the total analytical system, including all preparation and analysis steps. The LCS shall be prepared once per preparation batch of 20 or less samples per matrix type. If more than 20 samples are prepared a second LCS shall be prepared after the twentieth sample. The LCS shall be processed through all preparatory steps used for the samples, including cleanup procedures. The LCS shall be analyzed using the same instrument and conditions as the samples. Refer to section 10.10 for LCS analytes and concentrations.

12.5 **Duplicates**

Duplicates of field samples or of the LCS must be prepared in compliance with the method requirements and client directives. Note: the analysis of the Matrix Spike Duplicate (MSD) is used as a substitute for the laboratory duplicate. In those cases when there is insufficient sample to perform either a duplicate analysis or MSD analysis or the sample cannot be divided (e.g., wipes), the duplicate analysis of the LCS (LCS/LCSD) is used to judge the precision of the analytical results.

12.6 **Matrix Spike and Matrix Spike Duplicate (MS/MSD)**

MS/MSDs indicate the effect of the sample matrix on the precision and accuracy of the results generated using the selected method. This information does not determine the validity of the entire batch. MS/MSDs must be analyzed at a minimum of 1 per 20 samples per matrix per preparation procedure, or as specified by the required test method. If an MS/MSD pair is not analyzed in the preparation batch, an LCS/LCSD pair is analyzed. Samples chosen for matrix spiking are rotated among different clients and/or different client projects. This is accomplished through communication between the Department Manager and the analyst. In addition, designated samples, as indicated by client request or

contract requirement, are matrix spiked. The MS/MSD pair shall be processed through all preparatory steps used for the samples. They shall be analyzed using the same instrument and conditions as the samples. Refer to section 10.10 for MS analytes and concentrations. Some clients may require different spiking levels and/or target analytes. These specific needs are documented on the request for analysis forms.

12.7 **Internal Standards**

The internal standards for this method are used to monitor physical and matrix interferences and they are added to all samples, standards, and blanks. Refer to section 10.5 for preparation and concentration instructions.

12.8 **Interference Check Solutions**

The interference check solution (ICS) is prepared to contain known concentrations of interfering elements that will demonstrate the magnitude of interferences and provide an adequate test of any corrections. Chloride in the ICS provides a means to evaluate software corrections for chloride-related interferences such as $^{35}Cl^{16}O^{+}$ on ^{51}V and $^{40}Ar^{35}Cl^{+}$ on 75As+. Iron is used to demonstrate adequate resolution of the spectrometer for the determination of manganese. Molybdenum serves to indicate oxide effects on cadmium isotopes. The other components are present to evaluate the ability of the measurement system to correct for various molecular-ion isobaric interferences. The ICS is used to verify that the interference levels are corrected by the data system within quality control limits. The ICS pair, solutions A and AB, is analyzed after calibration, every twelve hours of analysis, and at the end of the analytical batch. Refer to Section 10.9 for the preparation of these solutions.

Note: For ambient air filters, the ICS pair is analyzed every eight hours of analysis, and at the end of the analytical batch.

12.9 **Serial Dilutions**

If the analyte concentration is within the linear dynamic range of the instrument and sufficiently high (minimally, a factor of at least 100 times greater than the concentration in the reagent blank, an analysis of a fivefold (1+4) dilution must agree within 10% of the original determination. If not, an interference effect must be suspected. One dilution test may be included for each twenty samples (or less) in a batch.

12.10 **Post-Digestion Spike**

This test may be applied for new or unusual matrices. An analyte spike added to a portion of a prepared sample, or its dilution, should be recovered to within 75 to 125 %R of the known value or within the laboratory derived acceptance criteria. The spike addition should be based on the indigenous concentration of each element of interest in the sample. If the spike is not recovered within the specified limits, the sample must be diluted and reanalyzed to compensate for the matrix effect. Results must agree to within 10% of the original determination. The use of a standard-addition analysis procedure may also be used to compensate for this effect.

13.0 CALIBRATION AND STANDARDIZATION

Calibrate the instrument after tuning to generate an acceptable Tune Report (section 14.2.1), and setting the Pulse/Analog factors for each analyte.

Note: Generating a tune report and setting the Pulse/Analog factors needs to be done only once each day. After calibration the software goes immediately into sample analysis. Step by step instructions to calibrate are listed in the procedure in section 14.

Initial Calibration (ICAL)
In addition to achieving the reference method requirements for the minimum number of calibration standards and the acceptance criteria (statistics) for calibration curve fit, the following ICAL criteria also apply:

13.1 The ICAL must be a minimum of two standards, not including a blank. Flush the system with the rinse blank between each standard solution. Use the average of at least three integrations for both calibration and sample analyses. All masses that could affect data quality should be monitored to determine potential effects from matrix components on the analyte peaks.
13.2 The ICAL must be verified with a second source standard (ICV) prior to the analysis of samples.
13.3 Results of samples not within the linear range of the instrument must be qualified on the final report. Dilute the sample and reanalyze in order to achieve a result within the linear range of the instrument.
13.4 The lowest calibration standard may establish the reporting limit: see Attachment 1 for analyte reporting limits (RL). The RL must be greater than the detection limit.

Initial Calibration Verification (ICV)
In addition to the method requirements, the following ICV criteria also apply:

13.5 Must be a second source standard from the ICAL standards or from a different manufacturer lot number.
13.6 Must be traceable to NIST when available.

13.7 Initial Calibration Blank (ICB): (2% HNO_3) Analyzed immediately after the ICV. Acceptance limits are ± RL.

Continuing Calibration Verification (CCV)
In addition to the method requirements, the following CCV criteria also apply:

13.8 Must be analyzed every 10 samples and at the end of each analytical batch.
13.9 Continuing Calibration Blank (CCB): (2% HNO_3 Analyze immediately after the CCV. Acceptance limits are ± RL.
13.10 If the CCV results obtained are outside the acceptance criteria, corrective actions must be performed. If routine corrective actions fail to produce an acceptable second consecutive CCV, then sample analyses cannot continue until a new ICAL is established and verified with an ICV.
NOTE: For calibration verification purposes, the CCV/CCB is analyzed as a set.

However, sample data associated with an unacceptable CCV may be reported as qualified data under the following special conditions:

13.10.1 When the acceptance criteria for CCV are exceeded high, i.e., high bias, and there are associated samples that are non-detects, then those non-detects may be reported. Otherwise the samples affected by the unacceptable calibration verification must be reanalyzed after a new ICAL has been established, evaluated and accepted.

13.10.2 When the acceptance criteria for the CCV are exceeded low, i.e., low bias, those sample results may be reported if they exceed a maximum regulatory limit/decision level. Otherwise the samples affected by the unacceptable verification must be reanalyzed after a new ICAL is established and verified with an ICV.

13.10.3 When the acceptance criteria for the CCV are exceeded and it is not possible to reanalyze the sample due to limited sample quantity AND a new sample cannot be obtained by the laboratory, the data may be reported with the appropriate data qualifiers if the client has been contacted and agrees, in writing, to accept the qualified data.

13.11 Records: Initial and Continuing Calibration Records will contain, at a minimum, the following:

1. Calibration date
2. Test method
3. Instrument
4. Analysis date
5. Each analyte name
6. Analyst's initials or signature
7. Standard Concentration (appropriate units) and number of standards
8. Response (appropriate units)
9. Calibration curve or response factor
10. Statistics for ICAL curve fit in order to judge calibration curve acceptance
11. Acceptance Limits for ICV analysis in order to judge calibration curve acceptance
12. Acceptance Limits for CCV analysis in order to judge continuing calibration acceptance
13. Calibration Standards and Reagent Solutions ID's

Table 5 Calibration Requirements

QCI	Frequency	Standards	Control Limits	Corrective Action
ICAL	Daily or as needed	Minimum of two standards, see Table 2 for concentrations	r = 0.995	Correct problem then repeat initial calibration
ICV	After each new ICAL	25µg/L, 50 µg/L, 500 µg/L	± 10% of true value	Correct problem then repeat ICV or initial calibration
ICB	After each new ICV	Reagent Blank (2% HNO_3)	< RL	Correct problem then repeat ICB
CCV	Every 10 samples, and end of the batch	50 µg/L, 100 µg/L, 1000 µg/L	± 10% of true value	Correct problem then repeat CCV and associated samples, or repeat initial calibration
CCB	After each CCV	Reagent Blank (2% HNO_3)	< RL	Correct problem then repeat CCB and associated samples

Support Equipment
Autopipettes - Check autopipette to ensure standardization is within control limits (see SOP 1040 General Laboratory Practices for Pipette Calibration).

Dispensing Pipettes Check pipette to ensure standardization is within control limits (see SOP 1040 General Laboratory Practices for Pipette Calibration

14.0 PROCEDURE

14.1 Sample Preparation

14.1.1 Acid Digestion: Samples requiring digestion must be prepared by one of the following methods prior to ICP-MS analysis.

Matrix	SOPs
Water	3005
Soil/sediment/Waste	3110
TSP/PM10 filters	3115

14.1.2 Direct Analysis
For Dissolved Metals Analysis:
Filtering the Sample Through a 0.45 Micron Filter.
Wash the filter paper or filter disk with 5 mL of 2% nitric acid followed by 2-3 mL of sample before filtering the aliquot to be tested. Record this procedure in the comments section of the ICP-MS Preparations logbook. Take a 10 ml aliquot of the filtered sample and acidify with 0.2 mL of concentrated HNO_3. Filter a MB and LCS to be analyzed with the batch.

Also prepare a MS/MSD (if sample amount permits, otherwise prepare an LCS/LCSD), by spiking 10 mL of the filtered sample with 0.2 mL of LCS/MS stock (section 10.10) and analyze with the samples. Report results as dissolved metals.

For Drinking Water Analysis - Take a 10 ml aliquot of the sample and acidify with 0.4 mL of 1:1 HNO_3. Report results as total metals.

14.2 ICP-MS Analysis

Turn on the argon flow (100 psi minimum) from the Dewar. Turn on the water chiller. Connect all pump tubing. Double click ICP-MS Top icon. A message will appear "Is ISIS power on?" Turn it on if not already on. Click <yes>, <instrument>, <instrument control>, <plasma>, and <plasma on> to ignite the plasma and allow at least 30 minutes for warm up.

14.2.1 TUNING:
Click <ALS> in the instrument control screen, and <Go To>, to move the sipper probe to the tune solution. Put the internal standard tubing into reagent water. Close the Instrument Control Window. Open the tune screen by clicking <Instrument> and <Tune>. The tune window will open. Click <start> to monitor the counts per 0.1 seconds, and give a visual display of the RSD for counts for ^{7}Lithium, ^{89}Yttrium and ^{205}Thallium. The tune screen also displays the settings for

the Plasma Orientation, Gas Flows, Peripump RPMs, Lens settings, Q-Pole settings and Detector Parameters.

Tune the Agilent 7500 for sensitivity to ensure that the instrument produces the best results for the masses being analyzed. Achieve good sensitivity by running a recommended tuning solution of 10 parts per billion (ppb) of Li, Y, Ce and Tl. [ICP-MS Working Tuning Solution, 10.6]. If necessary adjust the tune parameters for maximum sensitivity, reducing Oxide Ions, and Doubly Charged Ions.

Operating conditions: Attachment 4 lists the affects of adjusting the parameters in the tune window on the tune of the instrument. Once you have adjusted the parameters satisfactorily, generate a Tune Report.

NOTE: A Tune Report MUST be generated prior to analyzing samples every day, whether the parameters have been changed or not.

TUNE SPECIFICATIONS:
Sensitivity:
Li > 5,000 cts/0.1sec @10 ppb concentration
Y > 10,000 cts/0.1 sec @ 10 ppb concentration
Tl > 5,000 cts/0.1sec @ 10ppb concentration

Precision:
Li < 15% RSD (0.1 sec integration time)
Y < 10% RSD (0.1 sec integration time)
Tl < 10% RSD (0.1 sec integration time)

Oxides: < 1.2 %

Double Charged: Ce ++/Ce+ < 5.0%

Background:
Li < 30 cps
Y <15 cps
Tl < 15 cps

Mass Resolution: W-10% 0.65 – 0.8 AMU

Mass Axis: nominal mass +/- 0.1 AMU for ^{7}Li, ^{89}Y and ^{205}Tl

After generating an acceptable tune report insert the sample tube for internal standards into the Internal Standard working solution and place the sipper probe for the sample line into 2% v/v HNO_3 rinse solution. Allow the system to rinse out the lines for at least five minutes.

14.2.2 SETTING P/A FACTORS:
ChemStation automatically switches between pulse and analog mode. For linear calibration curves, these two modes should be adjusted by using P/A Factor tuning.

The counts of each element must range from 400,000 to 4,000,000 cps to get accurate P/A Factors. The P/A factor adjustment must be performed everyday to get accurate results in a sample with a wide concentration range where both the pulse and analog mode are used.

Determine the P/A Factors by

1. Moving the sipper probe in the lowest concentration P/A solution.
2. After the solution has rinsed through into the plasma, click <tune> <adjust P/A factors>. 3. Click on <Load masses from acq. method> in the window that pops up.4. Click <run>. After about 20 seconds a message appears saying, "accept current P/A factors?" Check the clipboard window behind the message. Either a number (the P/A factor) or a message that states "sensitivity is too low" appears next to each mass. Click <yes> to accept the P/A factors and close out the clipboard window. If a message appears that states "sensitivity is too high" you can accept the P/A factor but will need to P/A with a lower concentration solution to get the P/A factor for the mass that gave "sensitivity too high."

Repeat steps 1, 2, and 4 for successively higher analyte concentrations until you have P/A factors for all masses of interest. Check the box "Merge in the current data" if not already checked. This will add in successive P/A factors without deleting the P/A factors for the masses, which have P/A factors already.

DO NOT REPEAT STEP 3 (click on <Load masses from acq. method> for each successive solution). This clears out all your P/A factors and should only be clicked on before you first start to P/A.

14.2.3 Load the appropriate method. (IO35.M for ambient airs samples, or 6020G.M for all other analyses.

14.2.4 TUNE CHECK:

Prior to calibration and analysis the tune conditions must be verified by analyzing a Tune Check Solution at least five times with relative standard deviations of < 5% for the analytes contained in the tuning solution.

Conduct mass calibration and resolution checks in the mass regions of interest. The mass calibration and resolution parameters are required criteria, which must be met prior to any samples being analyzed. If the mass calibration differs more than 0.1 amu from the true value, then the mass calibration must be adjusted to the correct value. The resolution must also be verified to be less than 0.9 amu full-width at 10 percent peak height.

14.2.4.1 After tuning and P/A adjustments go to ICPMS top and click on <sequence>, <edit>, in the dropdown box on the left select TUNE, CCV, CALIB, or ICS, to edit the comment section in each of these screens. Enter any new solution preparation numbers for standards, ICV, CCV, ICB, ICS A, etc. in the comment column. Click <OK> at the bottom to save changes.

14.2.4.2 Click on <sequence>, <edit> again and select "SMPL" from the dropdown box to open up the sample sequence table. Edit inserting information under the column headings, VIAL (vial position), METHOD, SAMPLE (sample ID), COMMENT (sample test code), and Dil/Lv (dilution factor) for all samples to be analyzed. Click <print> to print out the list to refer to when placing the sample tubes in the racks and checking the order for correctness before starting analysis. Then click <save> to save the sample table. Samples are analyzed in order as they appear in the sample table.

14.2.4.3 Uncap and place all standards, tune check, and check standards in their proper places in rack #1. Racks #2-4 are for sample tubes.

14.2.4.4 Start the calibration and running of samples by clicking <sequence>, <run>. "Full Method'" and "Overwrite Existing Data Files," should be checked. Enter the instrument ID and your initials in the box for operator name and click <run sequence>. The software will run a blank, tune check, then the calibration followed by samples. After all samples have run the software will analyze a final ICS A, ICS AB, blank, CCV, and CCB. The plasma will then shut off and the ISIS program will stop. If additional samples will be analyzed later it will be necessary to insert blanks into the sample table to keep the instrument running.

14.2.4.5 Verify the Tune Check when complete. RSDs for Li, Co, In, and Tl must be < 5% and the mass calibration for each mass must be within 0.1 AMU of the mass number and <0.9 AMU at 10% peak height. If not abort the run and restart to rerun the Tune Check.

14.2.5 Initial Calibration and Quality Control Checks

14.2.5.1 Check each standard to determine if all internal standard cps are within 20% of the calibration blank's cps. If not abort the run and restart.

14.2.5.2 Check the ICV and ICB to determine if masses of interest are within tolerance. If they are continue with sample analysis. Rinse time before and after the samples are programmed into the method as well as analysis of CCV and CCB after every ten samples.

14.2.5.3 If an internal standard fails for any mass in a sample the system will run a blank before proceeding with analysis.

14.2.5.4 Perform all qualitative and quantitative measurements as described in Sections 14.4 and 14.5. After analysis, store the digests at room temperature.

14.2.6 The analytical sequence for Initial Calibration is:
(Tune Check)
Blank
Calibration Blank
Calibration standard (S1)
Calibration standard (S2)
Calibration standard (S3)
Calibration standard (S4)
Blank
Initial Calibration Verification Standard (ICV)

Initial Calibration Blank (ICB)
Interference Check Solution A (ICS A)
Interference Check Solution AB (ICS AB)
Blank

A typical analytical sequence for Sample Analysis is:
Method Blank (MB)
LCS
(LCS Duplicate optional)
Sample #1
Sample #1 Matrix Spike (MS)
Sample #1 Matrix Spike Duplicate (MSD)
Samples #2, #3, etc. up to 10 analytical samples
CCV
CCB
10 analytical samples (which may include, MB, LCS, MS, MSD, samples)
CCV
CCB
….
ICS A
ICS AB
blank
CCV
CCB

14.3 Data Interpretation - Qualitative Analysis

To obtain analyte data of known quality, it is necessary to measure more than the analytes of interest in order to apply corrections or to determine whether interference corrections are necessary. If the concentrations of interference sources (such as C, Cl, Mo, Zr, W) are such that, at the correction factor, the analyte is less than the limit of quantification and the concentration of interferents are insignificant, then the data may go uncorrected. Note that monitoring the interference sources does not necessarily require monitoring the interferent itself, but that a molecular species may be monitored to indicate the presence of the interferent. When correction equations are used, all QC criteria must also be met. Extensive QC for interference corrections are required at all times. The monitored masses must include those elements whose hydrogen, oxygen, hydroxyl, chlorine, nitrogen, carbon and sulfur molecular ions could impact the analytes of interest. Unsuspected interferences may be detected by adding pure major matrix components to a sample to observe any impact on the analyte signals. When an interference source is present, the sample elements impacted must be flagged to indicate (a) the percentage interference correction applied to the data or (b) an uncorrected interference by virtue of the elemental equation used for quantitation. The isotope proportions for an element or molecular-ion cluster provide information useful for quality assurance.

NOTE: Only isobaric elemental, molecular, and doubly charged interference corrections that use the observed isotopic-response ratios or parent-to-oxide ratios are acceptable corrections for use in this method.

14.4 Data Interpretation - Quantitative Analysis

Calculations including appropriate interference corrections, internal-standard normalization, and the summation of signals at 206, 207, and 208 m/z for lead (to compensate for any differences in the abundances of these isotopes between samples and standards), are performed automatically by the instrument during analysis.

14.5 Records

Record the following information in the appropriate logbook or data file. Include any deviations from this procedure. Analyst initials, date of analysis, sample number or ID, initial sample volume or weight processed, calibration standard, sample, or solution identifier, QC sample or solution identifier, internal standard solution identifier, any dilution information, readings from support equipment, data file name, instrument method name, visual observations, and any other information as deemed necessary.

14.6 Troubleshooting

The sample line tubing and internal standard tubing should be checked for even flow when the instrument is first started by observing and air bubble passing through the line. Adjust the tension on the tubing so that it is just tight enough to allow the air to evenly move through the tubing without any pulsing.

Check for leaks and air bubbles at tubing connections, tee connectors and fittings. The majority of problems you encounter occur somewhere along the sample introduction path.

Ensure that the argon Dewar has enough argon to maintain a pressure of 100 psi throughout the run.

14.7 Routine Maintenance

Record all maintenance in the instrument logbook. For non-routine maintenance record the problem, what was done to correct it and whether the correction solved the problem.

14.7.1 Daily, or as needed according to sample throughput, examine the tubing
14.7.2 Clean the sample and skimmer cones on an as needed basis (loss of sensitivity).
14.7.3 Inspect the pump tubing for wear and replace as necessary. Check the Argon gas supply; replace as necessary.

14.8 Calibration of the Polypropylene Volumetric Flasks

(Yearly, independently check flask volume with reagent water using a balance to monitor weight of water volume: tolerance is stated volume ± 0.1%). Perform this check every year.

14.8.1 Initially check the volume of each flask. Using an analytical balance, record the weight of the empty and dry flask.
14.8.2 Add room temperature de-ionized reagent water.
14.8.3 Fill to mark and re-weigh.
14.8.4 Subtract initial weight from final weight.
14.8.5 Divide the result by the volume of the flask and multiply by 100.
14.8.6 The percent recovery should be ±0.1%.
14.8.7 Record this information and label the flask for reference.

15.0 DATA REDUCTIONS, CALCULATIONS, AND LOADING

15.1 The data system prepares a calibration curve by plotting response versus standard concentration. Sample concentration is calculated from the regression equation.

NOTE: The LIMS program will convert µg/L to the appropriate reporting units.

15.2 Report only those values that fall between the lowest calibration standard and the linear range of the instrument. Samples exceeding the linear range must be diluted and reanalyzed.

15.3 For sample results greater than the linear range, dilute the sample in a 15 mL centrifuge tube using 2% HNO_3. Pipette in the appropriate volume of sample into the tube and dilute to volume with 2% HNO_3. Dilution Factor = (10 mL/ digestate volume analyzed in mL). Use the dilution factor and calculate the concentration in the digestate as follows:

Concentration in mg/L = readout * 0.001 (10 mL/ digestate volume analyzed in mL)

15.4 Air Samples: calculate the concentration as follows:

Conc. in µg/m^3 = readout in µg/L * (10 mL/ initial sample air volume in m^3) * 1 L/1000 mL

NOTE: 1m^3 = 1000 Liters

15.5 TSP/ PM10 Ambient Air Samples

15.5.1 Each filter should have an associated volume of air sampled, average temperature and pressure. This value is corrected to the EPA standard volume using the equation listed below.

$$V_{std} = V_{avg}(P_{avg}/760\text{mm Hg})(298\text{K}/T_{avg})$$

Where:
V_{avg} is the calculated average flow rate during the elapsed sampling time (field data)
P_{avg} is the average barometric pressure in mm Hg during the sample run (field data)
T_{avg} is the average temperature in K during the sample run (field data)

15.5.2 Metals concentration in the air samples can then be calculated as follows:

$$C = [(\mu g\ metal/L) \times (\text{Digestion volume, L/strip})(9) - F_m]/V_{std}$$

where:
C = concentration, µg metal/m3.
µg metal/L =determined metal concentration determined
final extract volume (L)/strip = total sample extraction volume from extraction procedure
9 = Useable filter area, [20 cm x 23 cm (8" x 9")]
Exposed area of one strip, [2.5 cm x 20 cm (1" x 8")].
F_m = average concentration of blank filters, µg.

V_{std} = standard air volume pulled through filter, std. m^3 (@25°C and 760 mm Hg).

15.5.3 When corrected average volume, average pressure and average temperature are NOT provided for a given filter, calculate µg metal/filter using the following equation

µg metal/ filter =[(µg metal/L) x (Digestion volume, L/strip)(9) - F_m]

15.5.4 Reported values should be blank subtracted for filters that STAT Analysis supplies to the client.

15.6 Wipe Samples: calculate the concentration as follows:

Conc. in µg/ft^2 = readout in µg/L * (50 mL/ initial wipe area in ft^2) * 1 L/1000 mL

NOTE: 1 ft^2 = 144 in^2 = 12 in * 12 in

15.7 Aqueous Samples: The concentration readout for aqueous sample digestates is µg/L. It does not need further data reduction unless the initial sample volume was less than 50 mL. If less than 50 mL sample was digested, calculate the concentration as follows:

Concentration in mg /L = readout *0.001 *(50mL/ initial sample volume digested in mL)

15.8 Soil Samples: The concentration readout for soil samples must be multiplied by the following factor: Factor = (50 / sample weight in g). Calculate the concentration in soil samples as follows:

Conc. in mg/Kg = readout * 0.001 (50 mL/ sample weight in g) * 1 L/1000 mL * 1000 g /1 Kg

15.9 Soil samples reported on a dry weight basis: The concentration is divided by the decimal equivalent of the percent residue of the soil after oven drying at 105 °C.

15.10 Report results in the appropriate units.

15.11 The procedure for uploading data into the LIMS system is detailed in SOP 1400 LIMS.

16.0 METHOD PERFORMANCE

Demonstration of Capability (DOC)
All parameters of interest must meet the method acceptance criteria before actual sample analysis begins. See SOP 1230 Training for the procedure to perform and document the DOC. The DOCs for the analysts performing this method are located in the analysts' training form folders located in the QA office files.

A QC reference concentrate is required containing each analyte at a concentration of either 10 or 100 mg/L. The QC reference sample used is a ten-fold dilution of the CCV solution. The QC

reference sample is made using stock standards prepared independently from those used for calibration.

For each analyte calculate the mean recovery (X) and standard deviation (s) and the average % Recovery (%R). Compare X and s and %R with the corresponding acceptance criteria for accuracy and precision, respectively. X must be within 9/90 and 11/110 µg/L, respectively, and s must be less than 1.0/10.0 µg/L, respectively, and %R must be within 100 ± 10%.

These limits are taken from established in-house criteria. If X and s and %R for all analytes meet the acceptance criteria, the system performance is acceptable and analysis of actual samples can begin. If any individual X or %R falls outside the range for accuracy or any individual s exceeds the precision limit, then the system performance is unacceptable for that analyte and corrective action must be taken.

Comparison to Reference Method Data:
EPA Method 6020 Table 4, aqueous samples, provides guidance for the establishment of control limits for the LCS samples.

EPA Method 6020 Table 5, solid samples, provides guidance for the establishment of control limits for the LCS samples.

EPA Method IO-3.5, Table 7, solid samples, provides guidance for the establishment of control limits for the LCS samples.

In-House Control Limits: Method performance data is on file in the laboratory QC department. Comparison of method performance data for the laboratory to the reference method criteria occurs when laboratory in-house acceptance limits are generated. In-house generated data is compared to the specifications of the reference method. If the in-house limits are within the specifications of the reference method, the control limits are updated in LIMS. If the in-house limits are not within specifications, an investigation is performed to determine the cause(s) of the problem and a corrective action is completed. The analysis may continue until enough data points are collected to regenerate new control limits. Any QC data generated outside of reference method limits during that time frame is flagged.

The laboratory maintains performance records to document the quality of data that is generated. Method accuracy for samples is assessed and records maintained.

Control limits for the method parameters are generated by the QC staff and distributed to the analysts via updates to the LIMS control charts. The control limits are calculated based on in-house performance data. At a minimum, these limits are reviewed annually.

17.0 POLLUTION PREVENTION

The preparation of excessive volumes of laboratory reagents and standards shall be avoided so that waste and potential for pollution are minimized. Samples, reagents and standards shall be disposed in compliance with the lab waste disposal program, SOP 1130 Waste Disposal. With the consent of the client, the samples may be returned to their origin for treatment.

Uncontaminated paper waste, glass and cans should be separated for recycling. Laboratory staff is required to protect the laboratory and our clients' business information when disposing of recycled paper or waste from the facility.

18.0 DATA ASSESSMENT AND CRITERIA FOR QUALITY CONTROL MEASURES

Data assessment includes review of: proper sample condition, preservation, and storage; analysis within holding time limitations; deviations from the SOP, evaluation of performance based on in-house control limits, reference method limits or project specific limits.

The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When results of sample spikes indicate atypical method performance, a calibration verification standard is used to confirm the measurements were performed in an in-control mode of operation. The data review is conducted according to SOP 1250 Data Review.

18.1 Blanks

If the Method Blank, ICB or CCB exceeds the RL the source of contamination must be investigated and corrective actions taken. The analyte concentrations in the method blank of a digestion batch must be less than the RLs listed in Attachment 1. If these criteria are exceeded, re-analyze the method blank. If after re-analysis, the blank criteria are still exceeded, then the entire digestion batch must be re-digested or qualified. Always refer to a client specific QAPP for additional guidance.

Affected samples must be reprocessed and reanalyzed or Data must be appropriately qualified if:

1) The concentration of a targeted analyte in the blank is at or above the reporting limit as established by the SOP or by regulation, AND is greater than 1/10 of the amount measured in any sample.
2) The blank contamination otherwise affects the sample results as per the test method requirements or the individual project data quality objectives.

18.2 Laboratory Control Samples (LCS)

The results of the individual batch LCS are calculated in percent recovery (%R). Results are compared to established acceptance criteria: 100 ± 20% for all samples. If the LCS is outside the acceptance criteria the analytical system is "out-of-control." Any affected samples associated with an out of control LCS must be reprocessed and reanalyzed or the results reported with appropriate data qualifiers. If after re-analysis the control criteria have not been met, the entire digestion batch must be redigested for the out of control analytes of interest. Always refer to a client specific QAPP for additional guidance.

18.3 Duplicates

The results from laboratory duplicates are designed to assess the precision of analytical results in a given matrix and are expressed as relative percent difference (RPD). See the STAT QAM, Section 5.4 for the calculation for RPD. Results are compared to established

acceptance criteria as listed in the MS/MSD. For duplicates results outside established criteria corrective action must be documented or the data reported with appropriate data qualifying codes.

For this test method, the analysis of the MS/MSD pair is used for determination of method precision. Duplicate LCS samples will be analyzed for all matrices where it would be impractical to perform a MS/MSD, such as wipe samples. Precision limits of 20% will be used for RPD acceptance criteria for MS/MSD and LCS/LCSD.

18.4 Matrix Spikes

The results from MS/MSD are primarily designed to assess the precision and accuracy of analytical results in a given matrix and are expressed as percent recovery (%R) and relative percent difference (RPD). See the STAT QAM, Section 5.4 for the calculation for RPD. Results are compared to established acceptance criteria: 100 ± 25%R and 20% RPD for all samples. For matrix spike results outside established criteria corrective action must be documented or the data reported with appropriate data qualifying codes. The RPD control limits are for analyte values greater than 100 times the instrumental detection limit. If this limit is exceeded, the reason for the out-of-control situation must be found and corrected.

NOTE: The %R limits will not apply to samples with analyte concentrations that are greater than four times the spike level.

Post Digestion Spike (PDS): This test may be applied for new or unusual matrices. An analyte spike added to a portion of a prepared sample, or its dilution, should be recovered to within 75 to 125 %R of the known value or within the laboratory derived acceptance criteria. The spike addition should be based on the indigenous concentration of each element of interest in the sample. If the spike is not recovered within the specified limits, the sample must be diluted and reanalyzed to compensate for the matrix effect. Results must agree to within 10% of the original determination. The use of a standard-addition analysis procedure may also be used to compensate for this effect.

18.5 Internal Standards

The results of the individual Internal Standard compounds on all samples, blanks, and spikes are calculated in percent recovery (%R) and are compared to established acceptance criteria. For instrument method 6020G.M, if the Internal Standard recovery in the test sample is outside the acceptance criteria, 30 to 120% of the response of the applicable internal standard in the ICAL Blank, corrective action must be taken. For ambient air samples, instrument method IO35.M, this limit is 60-125 %R. A dilution test (1+4) may be performed to minimize the matrix effect. Report the results from the diluted sample if internal standard recovery is acceptable.

NOTE: If the Internal Standard recovery in the calibration standards, ICV, ICB, CCV, or CCB is outside the acceptance criteria, 80 to 120% of the response of the applicable internal standard in the ICAL Blank, corrective action must be taken and affected samples must be reanalyzed.

18.6 Dilution Test

If the analyte concentration is within the linear dynamic range of the instrument and sufficiently high (minimally, a factor of at least 100 times greater than the concentration in the reagent blank, an analysis of a fivefold (1+4) dilution must agree within 10% of the original determination. If not, an interference effect must be suspected. One dilution test may be included for each twenty samples (or less) in a batch.

18.7 ICS

Verify the magnitude of elemental and molecular-ion isobaric interferences and the adequacy of any corrections at the beginning of an analytical run and once every 12 hours for instrument method 6020G.M. For ambient air sample, instrument method IO35.M, the ICS pair is analyzed at the beginning of the analytical run and once every eight hours. The ICS pair is analyzed at the end of the run as well for both methods. Do this by analyzing the interference check solutions A and AB. The analyst should be aware that precipitation from solution AB may occur with some elements, specifically silver. The recovery of each element in the ICS solution should be 100 ± 20%.

18.8 Instrument Detection Limits

IDLs in µg/L can be estimated by calculating the average of the standard deviations of the three runs on three non-consecutive days from the analysis of a reagent blank solution with seven consecutive measurements per day. Each measurement must be performed as though it were a separate analytical sample (i.e., each measurement must be followed by a rinse and/or any other procedure normally performed between the analysis of separate samples). IDLs must be determined at least every three months and kept on file.

19.0 CORRECTIVE ACTIONS FOR OUT-OF-CONTROL DATA

The process for handling unacceptable and out of control data is found in SOP 230 Corrective Action.

If the ICV, ICB, CCV, CCB, MB, LCS/LCSD, MS/MSD, PDS, lab duplicate, or internal standard recovery of any parameter falls outside the designated acceptance range, the laboratory performance for that parameter is judged to be out of control, and the problem must be immediately identified and corrective action taken. The analytical result for that parameter in the samples is suspect and is only reported for regulatory compliance purposes with the appropriate corrective action. Immediate corrective action includes reanalyzing all affected samples by using any retained sample before the expiration of the holding time. Final data results must be qualified in the client report for reported results not meeting the laboratory-defined criteria.

1) Review standards preparation logbooks. Check all calculations and ensure dilution factors are properly recorded.
2) Re-prepare the suspected standard or QC sample to identify possible preparation errors of the standard or QC sample.
3) Re-Analyze the samples when the CCV or LCS is not within acceptable limits.
4) Perform routine preventative maintenance following manufacturer's specification. Record all maintenance in the instrument logbook.

20.0 CONTINGENCIES FOR HANDLING OUT-OF-CONTROL OR UNACCEPTABLE DATA

Every effort is made to prevent problems from occurring. When out of control or unacceptable data occurs the first option is to identify the problem and reanalyze the samples within the holding times. When this is not possible, the QA Manager and/or the Laboratory Director will review data and discuss options with the client. Reanalysis or reporting the data with qualification are alternatives. Out of control or unacceptable data reported to the client must include the data qualifier, flag and discussion on the rationale for reporting.
Holding time exceedence, improper preservation and improper sample condition or storage are noted on the corrective action form and included on the final report.
Review the CCV standard response, LCS result, ICS results, and internal standard recovery for acceptable performance for each batch of samples. Record any trends or unusual performance on a corrective action form. Final data results must be qualified in the client report for results not meeting the laboratory-defined criteria.

20.1 The process for handling unacceptable and out of control data is found in the Laboratory QAM Section 11. The reporting of data that is out of control must be approved and documented by Quality Assurance Manager and either the Technical Manager or the Laboratory Director.

20.2 Client Requested Modifications:

- 20.2.1 Clients must request modifications from the laboratory SOP in writing to the lab.
- 20.2.2 The lab director, technical manager and quality assurance manager will evaluate the requested client deviations, determine the feasibly of the deviation and the potential effects on the data.
- 20.2.3 If it is determined that the lab will perform the requested deviations, lab director, technical manager and quality assurance manager will decide if a method validation study is required.
- 20.2.4 The designated project manager will retain all documentation concerning the requested deviation, including all correspondence with the client, in the client folder.
- 20.2.5 The final analytical report must include the statement “This report has analyses performed using client requested modifications.”

21.0 WASTE MANAGEMENT

The STAT Analysis Corporation Waste Disposal SOP 1130 identifies proper waste management practices for the chemicals and biological materials used in this procedure. Samples are stored and discarded accordance with SOP 1130 Waste Disposal.

22.0 REFERENCES

22.1 Method 6020, Revision 0, December 1996; U.S. EPA SW-846 “Test Methods for Evaluating Solid Waste, Physical/Chemical Methods” Update III, December 1996

22.2 Compendium Method IO-3.5 Compendium of Methods for the Determination of Inorganic Compounds in Ambient Air: Determination of Metals in Ambient Particulate Matter Using Inductively Coupled Plasma/ Mass Spectrometry (ICP/MS), U.S. EPA, June 1999.

22.3 STAT Analysis Corporation Quality Assurance Manual
22.4 STAT SAP 003 Chemical Hygiene Plan
22.5 STAT SOP 230 Corrective Actions
22.6 STAT SOP 1000 Control and Use of Laboratory Notebooks
22.7 STAT SOP 1010 Standard and Reagent Preparation
22.8 STAT SOP 1040 General Laboratory Procedures
22.9 STAT SOP 1130 Waste Disposal
22.10 STAT SOP 1210 Method Detection Limits (MDLs)
22.11 STAT SOP 1230 Training
22.12 STAT SOP 1250 Data Review
22.13 STAT SOP 1400 LIMS
22.14 STAT SOP 3005 SW846 3005A Acid Digestion of Waters for Total Recoverable or Dissolved Metals for Analysis by FLAA, ICP, or ICP-MS
22.15 STAT SOP 3110 SW846 3050B Acid Digestion of Sediments, Sludges, and Soils for Metals Analysis by FLAA, ICP, or ICP-MS
22.16 STAT SOP 3115 Acid Digestion of High Volume Filters
22.17 Manufacturers' Equipment Instruction Manuals

23.0 FORMS, FIGURES, TABLES, DIAGRAMS, FLOWCHARTS, ATTACHMENTS OR VALIDATION DATA

Attachment 1: MDLs and Reporting Limits
Attachment 2: Concentrations of ICS Solutions
Attachment 3: Concentrations of Spike Solutions
Attachment 4: Tune adjustment Parameters

ATTACHMENT 1: MDLs and REPORTING LIMITS FOR ELEMENTS

				Aqueous		Soil		Air	
CAS #	**Element**	**Mass (Isotope) *, ****	**IDL (mg/L)**	**MDL (mg/L)**	**RL (mg/L)**	**MDL (mg/Kg)**	**RL (mg/Kg)**	**MDL (µg/ filter)**	**RL (µg/ filter)**
7429-90-5	Aluminum	27	0.235	0.00309	0.02	0.3271	2	NA	NA
7440-36-0	Antimony	**121***, 123	0.606	0.00249	0.003	0.1099	0.2	0.75	5
7440-38-2	Arsenic	75	0.063	0.00097	0.002	0.0429	0.1	0.69	5
7440-39-3	Barium	135, **137***	0.007	0.00140	0.002	0.0260	0.1	27	200
7440-41-7	Beryllium	9	0.004	0.00027	0.001	0.0074	0.05	0.25	5
7440-43-9	Cadmium	**111***, 114	0.015	0.00021	0.001	0.0078	0.05	0.20	5
7440-47-3	Chromium	**52*,** 53	0.027	0.00054	0.002	0.0260	0.1	1.4	10
7440-48-4	Cobalt	59	0.019	0.00011	0.002	0.0051	0.1	0.18	5
7440-50-8	Copper	**63***, 65	0.080	0.00158	0.005	0.0404	0.25	0.52	5
7439-92-1	Lead	**206,207, 208****	0.019	0.00059	0.001	0.0065	0.05	0.40	5
7439-96-5	Manganese	55	0.020	0.00029	0.002	0.0114	0.1	0.82	10
7440-02-0	Nickel	**60***, 62	0.186	0.00107	0.002	0.0434	0.1	0.54	10
7782-49-2	Selenium	82	0.210	0.00172	0.002	0.0646	0.1	0.44	5
7440-22-4	Silver	**107***, 109	0.050	0.00079	0.002	0.0278	0.1	0.071	5
7440-28-0	Thallium	205, **203***	0.096	0.00026	0.002	0.0080	0.1	0.17	5
7440-32-6	Titanium	46, 47*		0.00057	0.005	.0261	0.25	1.1	10
7440-66-6	Zinc	**66***, 67, 68	0.080	0.00160	0.01	0.1157	0.5	2.2	25
7440-23-5	Sodium	23	0.671	0.07706	0.15	1.0965	6	NA	NA
7439-95-4	Magnesium	**24***, 25	0.193	0.00832	0.05	0.4429	3	NA	NA
7440-09-7	Potassium	39	0.585	0.03922	0.05	0.7043	3	NA	NA
7440-70-2	Calcium	44	2.698	0.07448	0.10	6.3708	6	NA	NA
7440-62-2	Vanadium	51	0.009	0.00087	0.002	0.0959	0.1	0.52	5
7439-89-6	Iron	**57***, (54)	0.611	0.01154	0.05	0.6888	3	4.6	50
7439-98-7	Molybdenum	92,94,96,97, **98***	0.020	0.00033	0.005	0.0405	0.5	0.37	5
7440-31-5	Tin	**120***, 118	0.026	0.00054	0.01	0.0772	0.5	0.24	5
7440-42-8	Boron	**11***, 10	.332	0.00551	0.02	0.2322	1	NA	NA

NOTES:

* Primary mass used for quantitation. Other masses are optionally used if proper instrument QC is available.

** The summation of all three lead masses is used for quantitation.

NA = not applicable

ATTACHMENT 2: CONCENTRATIONS of ICS SOLUTIONS

Solution A: Concentration in mg/L

Element	Stock	Working
Al	500	100
C	1000	200
Ca	500	100
Cl	3600	720
Fe	500	100
K	500	100
Mg	500	100
Mo	10	2
Na	500	100
P	500	100
S	500	100
Ti	10	2

Solution AB: Concentration in mg/L

Element	Stock	Working		Element	Stock	Working
Al	500	100		Ag	0.100	0.020
C	1000	200		As	0.100	0.020
Ca	500	100		Cd	0.050	0.010
Cl	3600	720		Co	0.200	0.040
Fe	500	100		Cr	0.100	0.020
K	500	100		Cu	0.100	0.020
Mg	500	100		Mn	0.100	0.020
Mo	10	2		Ni	0.200	0.040
Na	500	100		Se	0.100	0.020
P	500	100		V	0.200	0.040
S	500	100		Zn	0.100	0.020
Ti	10	2				

ATTACHMENT 3: CONCENTRATIONS OF LCS/MS SPIKING SOLUTION

Element	Concentration (mg/L)
Aluminum	25
Antimony	12.5
Arsenic	25
Barium	25
Beryllium	25
Boron	25
Cadmium	25
Chromium	25
Cobalt	25
Copper	25
Lead	25
Manganese	25
Molybdenum	12.5
Nickel	25
Selenium	25
Silver	10
Thallium	25
Titanium	12.5
Tin	12.5
Vanadium	25
Zinc	25
Calcium	100
Iron	100
Magnesium	100
Potassium	100
Sodium	100

ATTACHMENT 4: Tune Adjustment Parameters

Plasma conditions:
Higher RF Power generally increases the sensitivity.

Sample Depth
Shortening sample depth increases sensitivity and raises oxide levels.

To reduce Oxide Ions <1.2%

- Increase the sampling depth
- Decrease the carrier gas flow
- Increase the RF power
- Decrease the sample flow rate

To Reduce the Doubly Charged Ions < 5%

- Increase the sampling depth
- Decrease the carrier gas flow
- Increase the RF power
- Decrease the sample flow rate

Resolution and Mass Axis
Peak width at 10 % should be 0.65 – 0.8 AMU
Mass Axis should be within +/- 0.1 AMU of the selected mass

AMU Gain - Adjusts the peak width. The higher the value the narrower the peak width for heaver masses

AMU Offset - Adjusts the peak width. The higher the value the narrower the peak width for ALL masses

Axis Gain - Adjusts mass calibration. Higher value shifts the peak of heavier masses towards higher mass

Axis Offset - Adjusts mass calibration. Higher value shifts the peak of ALL masses towards higher mass

QP Bias - Controls the speed of ions as they pass through the Q-Pole.

SOP ADDENDUM

SOP No. & TITLE: No. 4510. Metals analysis by ICP-MS.

Revision Effective Date: 05. May 16, 2005.

Issued by Pinaki Banerjee, QA Director

Approved by: Dennis Jachim, Technical Manager

Date of Issue: August 6, 2007

Section (additions are *italicized*, ~~deletions are strikethroughs~~)

14.2.1

TUNE SPECIFICATIONS:
Sensitivity:
Li > 5,000 cts/0.1sec @10 ppb concentration
Y > 10,000 cts/0.1 sec @ 10 ppb concentration
Tl > 5,000 cts/0.1sec @ 10ppb concentration

Precision:
Li < 15% RSD (0.1 sec integration time)
Y < 10% RSD (0.1 sec integration time)
Tl < 10% RSD (0.1 sec integration time)

Oxides: < 1.2 % *(Babington Nebulizer)*
< 2 % *(Concentric Nebulizer)*

Double Charged: Ce ++/Ce+ < 5.0%

Attachment 4

Plasma conditions:
Higher RF Power generally increases the sensitivity.

Sample Depth
Shortening sample depth increases sensitivity and raises oxide levels.

To reduce Oxide Ions <1.2% *(< 2% for concentric nebulizer)*

- Increase the sampling depth
- Decrease the carrier gas flow
- Increase the RF power
- Decrease the sample flow rate

SOP ADDENDUM

SOP No. & TITLE: ~~4~~510, Metals Analysis by ICP

Revision 05; Effective Date: May 16, 2005.

Issued by : Pinaki Banerjee, QA Director

Approved by: Dennis Jachim, Technical Manager

Date of Issue: March 14, 2008

Section (additions are *italicized*, ~~deletions are strikethroughs~~)

5.3 Method Modifications from Reference – This SOP is based on EPA Method 6020 and incorporates IO-3.5 for TSP/PM10 high-volume filters except that: 1) polypropylene volumetric flasks are used since analysis for boron is occasionally required, 2) the instrument resolution is set for 1 amu peak width at 10% peak height according to 6020 but is less stringent than IO-3.5, 3) samples which fail high or low for one or more internal standards are diluted as needed to bring within range for the internal standard, 4) A matrix spike and matrix spike duplicate are digested and analyzed, since a duplicate sample is not typically analyzed, 5) ~~Dilution test may be performed on aqueous matrices. Non-aqueous matrices are already diluted before analysis~~ *The dilution test will be applied to preparation batches /matrices in which analyte concentration is at least 10 times greater than the reporting limit.* 6) reagent water must be at least Type II (ASTM) for all standards, solutions, and sample preparation according to 6020 but is less stringent than IO-3.5, 7) internal standards and tuning solutions cover the entire mass range of analysis, but the elements used vary slightly from IO-3.5, 8) the MDLs are determined annually according to the requirements described in SOP 1210 Method Detection Limits ~~and not every six months according to IO-3.5,~~ 9) the ICB/CCB acceptance limit is the ~~lower~~ reporting limit and not the MDL per IO-3.5, since we do not report down to the MDL. 10) Germanium, instead of yttrium, is used as an internal standard, since yttrium is found in environmental samples.

12.9 **Serial Dilutions**

If the analyte concentration is within the linear dynamic range of the instrument and sufficiently high (minimally, a factor of at least 10 ~~100~~ times greater than the ~~concentration in the~~ *reporting limit* ~~reagent blank~~, an analysis of a fivefold (1+4) dilution must agree within 10% of the original determination. If not, an interference effect must be suspected. ~~One dilution test may be included for each twenty samples (or less) in a batch.~~

18.6 **Dilution Test**

If the analyte concentration is within the linear dynamic range of the instrument and sufficiently high (minimally, a factor of at least ~~100~~ 10 times greater than the ~~concentration in the reagent blank~~ *reporting limit*, an analysis of a fivefold (1+4) dilution must agree within 10% of the original determination. If not, an interference effect must be suspected. One dilution test ~~may~~ *must* be included for each twenty samples (or less) in a batch.

STAT Analysis Corporation

Standard Operating Procedure 4530:

Mercury In Water, Solid Or Semisolid Water (Manual Digestion/Automated Analysis Cold-Vapor Technique)

(EPA METHODS 7470A & 7471A)

Revision 03
Effective Date: January 9, 2003

Authors: **Dennis Jachim**

Printed Name	**Signature/Date**
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This Standard Operating Procedure has been prepared for the sole use of STAT Analysis Corporation.

Copy Number: _____

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1.0 Identification of Test Method

Mercury In Water, Solid Or Semisolid Water (Manual Digestion/Automated Analysis Cold-Vapor Technique) - EPA METHODS 7470A & 7471A

2.0 Applicable Matrix or Matrices

This method is applicable to the following matrices: non-potable water, solid and chemical waste.

3.0 Detection Limits

The lab follows the procedure found in 40CFR Part 136B to determine the MDL for each matrix type on an annual basis. See the STAT Analysis SOP 1210 for the MDL Procedure, frequency and acceptance criteria. The MDLs measured by the laboratory and all supporting documentation are in the laboratory QA files for review.

The laboratory determined MDL must always be less than the reporting limit (RL). The RLs will usually range from three to ten times the laboratory measured MDLs, but this relationship may vary dependent on dilution of sample aliquots, matrix interferences, moisture adjustments (in solid samples), or method specific requirements.

The reporting limits for this method is 0.00025 mg/L for waters and 0.025 mg/kg for soils. The method detection limits for these methods are 0.000015 mg/L for waters and 0.0022 mg/kg for soils. Reporting limits are based upon the lowest calibration standard

4.0 Scope and Application

This method is a cold-vapor atomic absorption procedure for determining the concentration of mercury in mobility-procedure extracts, aqueous wastes, and ground waters (EPA Method 7470A) as well as measuring total mercury (organic and inorganic) in soils, sediments, bottom deposits, and sludge-type materials (EPA Method 7471A). All samples must be subjected to an appropriate dissolution step prior to analysis. If this dissolution procedure is not sufficient to dissolve a specific matrix type or sample, then this method is not applicable for that matrix.

NOTE: Each analyst must demonstrate the ability to generate acceptable results with this method.

5.0 Summary of Test Method

5.1 Prior to analysis, the liquid samples and the solid or semi-solid samples must be prepared according to the procedures discussed in this method.

5.2 The cold-vapor absorption method is based on the absorption of radiation at the 253.7-nm wavelength by mercury vapor. The mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path

of an atomic absorption spectrophotometer. Absorbance (peak height) is measured as a function of mercury concentration.

5.3 **Method modifications from Reference** - This procedure utilizes an automated cold-vapor technique, mixing stannous chloride with an aliquot of the sample digestion at the instrument. Digestions take place in graduated 50-ml tubes.

6.0 Definitions

The STAT Analysis Corporation Quality Assurance Manual (QAM) contains the definitions of standard terms used in this SOP.

7.0 Interferences

7.1 Potassium permanganate is added to eliminate possible interference from sulfide. Concentrations as high as 20 ppm of sulfide as sodium sulfide do not interfere with the recovery of added inorganic mercury from reagent water.

7.2 Copper has also been reported to interfere; however, copper concentrations as high as 10 ppm had no effect on recovery of mercury from spiked samples.

7.3 For liquid analysis: seawaters, brines, and industrial effluents high in chlorides require additional permanganate (as much as 25 mL) because, during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation of 253 nm. Care must therefore be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine hydrochloride reagent. Both inorganic and organic mercury spikes have been quantitatively recovered from seawater by using this technique.

7.4 For solid analysis: samples high in chlorides require additional permanganate (as much as 25 mL) because, during the oxidations step, chlorides are converted to free chlorine, which also absorbs radiation of 253 nm. Care must therefore be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine sulfate reagent (25 mL). In addition, the dead air space in the digestion vessel must be purged before adding stannous chloride.

7.5 Certain volatile organic materials that absorb at this wavelength may also cause interference. A preliminary run without reagents should determine if this type of interference is present.

8.0 Safety

8.1 General laboratory protection (safety glasses, lab coat, disposal latex/nitrile gloves) should be worn at all times when handling samples or reagents.

8.2 The digestion, and all reagent additions, must be performed in a fume hood.

8.3 The potential health hazards from the samples cannot be determined. Therefore, exposure to the samples should be minimized to the extent possible. Other safety precautions must be conducted in accordance with the Chemical Hygiene Plan. Other actions can also be applied if deemed necessary.

8.4 A reference file of material safety data sheets (MSDS) is available in each room for personnel involved in an analysis using chemicals.

9.0 Equipment and Supplies

The following apparatus is recommended for performing this procedure. Equivalent items can be used, if with their use, the analytical and QA/QC requirements in this SOP can be met.

9.1 Cetac M-6000A Mercury Analyzer with ASX-500 autosampler. This instrument utilizes cold vapor atomic absorption to measure mercury concentration. Manufacturer recommended settings are used during operation.

9.2 Water Bath or Hot plate – adjustable and capable of maintaining a temperature of 90-95°C.

9.3 Analytical balance, capable of measuring 0.001 g.

9.4 Argon gas supply: high-purity grade (99.99%).

9.5 Graduated 50 mL centrifuge tubes, with screw caps

9.6 Thermometer capable of measuring 90-100 °C with suitable precision and accuracy.

9.7 Disposable tubes, approximately 14 mL

9.8 Autopipettor: 0.010 to 0.10 mL, 0.10 to 1.0 mL, 1.0 to 5.0 mL

9.9 Dispensing pipets: 1-5 mL, 1-10 mL, 1-20 mL

10.0 Reagents and Standards

The following reagents and standards are required to perform this procedure. When instructions are given on how to prepare a specific volume of a reagent or standard, larger or smaller volumes can be prepared as needed so long as the final concentrations remain the same. Any other deviations from the reagents or standards listed in this SOP could be detrimental to the quality of the data produced. Such deviations would have to be approved and documented.

10.1 Instructions for labeling and record keeping of reagents and standards are contained in SOP 1010 Standard and Reagent Preparation.

10.2 Reagents – In methods where the purity of reagents is not specified, analytical reagent grade shall be used. Reagents of lesser purity than those specified by the test method shall not be used.

10.3 Standards

10.3.1 At least one of the standards must be traceable to a NIST traceable source when available. The manufacturer should include a certificate of analysis for each standard. If one is not provided, contact the manufacturer. Retain all certificates in the designated binder (see SOP 1010 Reagent Receiving).

10.3.2 Intermediate and Working standards (Sections 10.20 – 10.23) must be prepared volumetrically using class A volumetric glassware, calibrated micro-pipettes, or gas tight syringes. Do not use disposable pipettes to prepare standards.

10.3.3 The use of alternative standards will be allowed as long as the analytical and quality objectives of the SOP can be met.

10.4 Reagent Water: Reagent water will be interference free. All references to water in this method will refer to reagent water unless otherwise specified.

10.5 Sulfuric acid (H_2SO_4), concentrated: Trace Metal grade.

10.6 Hydrochloric Acid (HCl), concentrated: Trace Metal grade.

10.7 Nitric Acid (HNO_3), concentrated: Trace Metal grade.

10.8 Aqua Regia: Prepare immediately before use by carefully adding three volumes of concentrated HCl to one volume of concentrated HNO_3.

10.9 Stannous Chloride, Dihydrate ($SnCl_2 \cdot 2H_2O$): Reagent Grade

10.10 Stannous chloride, 10% solution (w/v): Dissolve 100 g of $SnCl_2$ in 70 mL of concentrated HCl and dilute to 1 liter with reagent water.

10.11 Sodium Chloride (NaCl): Reagent Grade.

10.12 Hydroxylamine Hydrochloride: Reagent Grade, "Suitable for Mercury Determination".

10.13 Sodium chloride – hydroxylamine hydrochloride solution: dissolve 120 g of sodium chloride and 120 g of hydroxylamine hydrochloride in reagent water and dilute to 1 liter.

10.14 Potassium Permanganate ($KMnO_4$): Reagent Grade, "Suitable for Mercury Determination".

10.15 Potassium permanganate ($KMnO_4$), 5% solution (w/v): Dissolve 50 g of $KMnO_4$ in 1 liter of reagent water.

10.16 Potassium persulfate ($K_2S_2O_8$): Reagent Grade.

10.17 Potassium persulfate ($K_2S_2O_8$), 5% solution (w/v): Dissolve 50 g of $K_2S_2O_8$ in 1 liter of reagent water.

10.18 2%HNO_3/2%HCl rinse: Add 40mL of concentrated HNO_3 and 40 mL of concentrated HCl in reagent water and dilute to 2 liters.

10.19 Ottawa Sand

10.20 Stock Standard Solutions: 1000 mg/L mercury standards are purchased commercially. Standards from two separate sources are purchased, one to be used for calibration and the second to be used for calibration verification.

10.21 Intermediate Calibration Standard Solution: (CAL STD 10 mg/L) Add approximately 80 mL of reagent water to a 100 mL volumetric flask, add 0.500 mL of Nitric Acid, add 1.00 mL of Stock Standard Solution (1000 mg/L), dilute to final volume. Prepare fresh every 28 Days.

10.22 Intermediate Calibration Verification Standard Solution: (ICV/CCV 10 mg/L) Add approximately 80 mL of reagent water to a 100 mL volumetric flask, add 0.500 mL of Nitric Acid, add 1.00 mL of the second source Stock Standard Solution (1000 mg/L), dilute to final volume. Prepare fresh every 28 Days.

10.23 Working Calibration Standard Solution: (100.0 µg/L) Add approximately 80 mL of reagent water to a 100 mL volumetric flask, add 0.500 mL of Nitric Acid, add 1.00 mL of Intermediate Calibration Standard Solution (10.0 mg/L, Section 10.20), dilute to final volume. Prepare fresh weekly (Expires in 7 days).

10.24 Working Calibration Verification Standard Solution: (ICV/CCV 100.0 µg/L) Add approximately 80 mL of reagent water to a 100 mL volumetric flask, add 0.500 mL of Nitric Acid, add 1.00 mL of Intermediate Calibration Verification Standard Solution (10.0 mg/L, Section 10.21), dilute to final volume. Prepare fresh weekly (Expires in 7 days).

10.25 ICV Standard: Into a 50.0 mL centrifuge tube spike 0.30 mL of Working Calibration Verification Standard Solution: (ICV/CCV 100 µg/L, Section 10.23). Dilute to 30 mL with reagent water, **TV= 1.0 mg/L**.

10.26 CCV Standard: Into a 50.0 mL centrifuge tube spike 0.750 mL of Working Calibration Verification Standard Solution: (ICV/CCV 100 µg/L, Section 10.23). Dilute to 30 mL with reagent water, **TV= 2.50 mg/L**.

10.27 LCS/MS/MSD Spiking Solution: Spike 0.750 mL of Working Calibration Verification Standard Solution: (ICV/CCV 100 µg/L, Section 10.23) per sample.

10.28 Prepare Calibration Standards in 50.0 mL centrifuge tubes from the Working Calibration Standard Solution (100 µg/L Section 10.21) by dilution to 30.0 mL as follows:

Table 1 Mercury Calibration Standards

Calibration Standard Concentration, µg/L	Amount of solution to add to graduated tube, mL	Concentration of solution added to graduated tube, µg/mL	Final Volume, mL	µg Hg per 30 mL
7.00	2.10	100	30	0.21
5.00	1.50	100	30	0.15
2.50	0.75	100	30	0.075
1.00	0.30	100	30	0.03
0.50	0.15	100	30	0.015
0.25	0.075	100	30	0.075

11.0 Sample Collection, Preservation, Shipment and Storage

11.1 All samples are stored away from all standards, reagents, food, and other potentially contaminating sources in order to prevent cross contamination.

11.2 The following table summarizes the requirements for proper sample collection, preservation, shipment and storage.

Matrix	**Bottle Type**	**Preservation**	**Shipping & Storage**	**Minimum Sample Amount**	**Prep/Analysis Hold Time**
Solid	P, G	Chill to 4°C	Chill to 4°C	4 Oz.	28 days
Liquid	P, G	Acidify with HNO_3 to pH < 2		250 mL	28 days

[P= Polyethylene, G = Glass, AG = Amber Glass, etc.].

11.3 All sample containers should be pre-washed with detergents, acids, and reagent water. Plastic and glass containers are both suitable.

11.4 Aqueous samples must be acidified to a pH < 2 with HNO_3.

11.5 The maximum holding time for mercury is 28 days.

11.6 Non-aqueous samples shall be refrigerated, when possible, and analyzed as soon as possible.

11.7 It can be difficult to obtain a representative sample with wet or damp materials. Wet samples may be dried, crushed, and ground to reduce sub-sample variability as long as drying does not affect the extraction of the analytes of interest in the sample.

11.8 Sample Storage

11.8.1 Non-aqueous samples must be chilled to 4°C.

12.0 Quality Control

The following details the QC requirements that apply to this analysis. Each Quality Control Indicator (QCI) provides information pertaining to either method or individual sample performance. Our goal is to produce defensible data of known and documented quality.

The results of these QCI samples are used to assess the acceptability of data.

12.1 Blanks

The Method Blank analysis is performed to determine if any contamination is present in the analytical process and is used to evaluate acceptance of the batch of samples. The method blank must be processed along and under the same conditions as the associated samples, including cleanup procedures. The method blank must be analyzed at a minimum of 1 per preparation batch (see Section 8 for definition of a prep batch). The method blank is of a similar matrix (e.g., reagent water, Ottawa sand, glass beads, etc.) to the associated samples and is known to be free of the analytes of interest.

12.2 Laboratory Control Sample (LCS)

The LCS is used to evaluate the performance of the total analytical system, including all preparation and analysis steps. The LCS is a controlled matrix (e.g., reagent water, Ottawa sand, glass beads, etc.), known to be free of analytes of interest, spiked with known and verified concentrations of analytes. Alternatively the LCS may consist of a media containing known and verified concentrations of analytes or as Certified Reference Material (CRM). All LCS analyte concentrations must be within the calibration range. The LCS must be analyzed at a minimum of 1 per preparation batch (see Section 8 for definition of a prep batch).

12.3 Matrix Spike and Matrix Spike Duplicate (MS/MSD)

MS/MSDs indicate the effect of the sample matrix on the precision and accuracy of the results generated using the selected method. This information does not determine the validity of the entire batch. MS/MSDs must be analyzed at a minimum of 1 per 20 samples per matrix per preparation procedure, or as specified by the required test method. If an MS/MSD pair is not analyzed in the preparation batch, an LCS/LCSD pair is analyzed.

Samples chosen for matrix spiking are rotated among different clients and/or different client projects. This is accomplished through communication between the Department Manager and the analyst. In addition, designated samples, as indicated by client request or contract requirement, are matrix spiked.

12.4 Duplicates

Duplicates are defined as replicate aliquots of the same sample taken through the entire analytical procedure. The results from this analysis indicate the precision of the results for the specific sample using the selected method. The duplicate provides a usable measure of precision only when target analytes are found in the sample chosen for duplication. Duplicates are performed on replicate aliquots of actual samples. The duplicate analysis may be analyzed at a frequency of 1 per 20 samples per matrix per preparation procedure.

Samples chosen for duplicate analyses are rotated among different clients and/or different client projects. This is accomplished through communication between the Department Manager and the analyst.

Note: For this test method, the analysis of the Matrix Spike Duplicate (MSD) is used as a substitute for the laboratory duplicate. In those cases when there is insufficient sample to perform a MS and MSD analysis, the duplicate analysis is used to judge the precision of the analytical results. In those cases when there is insufficient sample to perform either a duplicate analysis or MSD analysis, the duplicate analysis of the LCS (LCS/LCSD) is used to judge the precision of the analytical results.

12.5 Post Digestion Spikes (PDS)

Post Digestion Spikes are used to check for matrix interference on a given matrix. Added after sample preparation, they provide a measure of recovery for every sample matrix. They may be analyzed at a frequency of 1 per 20 samples per matrix per preparation procedure.

13.0 Calibration and Standardization

Initial Calibration (ICAL)

In addition to achieving the reference method requirements for the minimum number of calibration standards and the acceptance criteria (statistics) for calibration curve fit, the following ICAL criteria also apply:

13.1 The ICAL must be a minimum of 5 standards, not including a blank.

13.2 The ICAL must be verified with a second source standard (ICV) prior to the analysis of samples.

13.3 Results of samples not bracketed by the ICAL range must be qualified on the final report. If possible, dilute the sample or extract and reanalyze in order to achieve a result within the calibrated range of the instrument.

13.4 The lowest calibration standard may establish the reporting limit. The reporting limit may also be based upon another point in the calibration curve. It must be greater than the detection limit.

13.5 The ICAL is digested weekly, and analyzed daily with the preparation batch. The digested standards are stored near the instrument and are labeled with the standard concentration, the matrix (S or W), and the date the standard was digested.

Initial Calibration Verification (ICV)

In addition to the method requirements, the following ICV criteria also apply:

13.6 Must be a second source standard from the ICAL standards or from a different manufacturer lot number.

13.7 Must be traceable to NIST when available.

13.8 Must be digested/analyzed every day a preparation batch is performed.

Continuing Calibration Verification (CCV)

In addition to the method requirements, the following CCV criteria also apply:

13.9 Must be digested/analyzed every day a preparation batch is performed.

13.10 Must be analyzed after every 10 samples and at the end of each analytical batch.

13.11 If the CCV results obtained are outside the acceptance criteria, corrective actions must be performed. If routine corrective actions fail to produce an acceptable *second consecutive (immediate)* CCV, then either the lab has to demonstrate performance after corrective action with two consecutive successful CCVs, or a new ICAL must be performed. If the instrument has not demonstrated acceptable performance, sample analyses cannot continue until a new ICAL is established and verified with an ICV. However, sample data associated with an unacceptable CCV may be reported as qualified data under the following special conditions:

13.11.1 When the acceptance criteria for CCV are exceeded high, i.e., high bias, and there are associated samples that are non-detects, then those non-detects may be reported. Otherwise the samples affected by the unacceptable calibration verification must be reanalyzed after a new ICAL has been established, evaluated and accepted.

13.11.2 When the acceptance criteria for the CCV are exceeded low, i.e., low bias, those sample results may be reported if they exceed a maximum regulatory limit/decision level. Otherwise the samples affected by the unacceptable verification must be reanalyzed after a new ICAL is established and verified with an ICV.

13.11.3 When the acceptance criteria for the CCV are exceeded and it is not possible to reanalyze the sample due to limited sample quantity AND a new sample cannot be obtained by the laboratory, the data may be reported with the appropriate data qualifiers if the client has been contacted and agrees, in writing, to accept the qualified data.

13.12 Records: Initial and Continuing Calibration Records will contain, at a minimum, the following:

Calibration date
Instrument
Analysis date
Analyst's initials or signature
Standard Concentration (appropriate units) and number of standards
Response (appropriate units)
Calibration curve
Evaluation of and Statistics for ICAL curve fit in order to judge calibration curve acceptance

Initial/Continuing Calibration Blank (ICB/CCB – Reagent Blank)

In addition to the method requirements, the following ICB/CCB criteria also apply:

13.13 Must be digested/analyzed every day a preparation batch is performed.

Note: For aqueous digestions, the Method Blank may act as the ICB/CCB.

13.14 Must be analyzed after Initial Calibration Verification (ICV).

13.15 Must be analyzed after every Continuing Calibration Verification (CCV).

Calibration Acceptance Summary (see Table 2):

Table 2 Quick reference of instrument Calibration Requirements

QCI	Frequency	Standards	Control Limits	Corrective Action
ICAL	Digested weekly, analyzed daily	Minimum 5 standards, see Table 1 for concentrations	r = 0.995	Correct problem then repeat initial calibration
ICV	Digested and analyzed daily	1.00 µg/L	± 10% of true value	Correct problem then repeat ICV or repeat initial calibration
CCV	Digested and analyzed daily	2.50 µg/L	± 20% of true value	Correct problem then repeat CCV or repeat initial calibration
ICB/CCB	Digested daily, and analyzed after each ICV and CCV		< RL	Correct problem then repeat ICB/CCB or repeat initial calibration

Support Equipment

Autopipettes - Check autopipette to ensure standardization is within control limits (see SOP for Pipette Calibration).

Balances - Be sure the balance is checked prior to use and performance criteria are met (see SOP for Calibration of Balances).

Thermometers - Check the thermometer to ensure the calibration is not expired (see SOP for Thermometer Calibration). Check the thermometer during the analysis and record the corrected temperature in the analysis logbook.

14.0 Procedure

14.1 Digestion Procedure for Aqueous Samples (EPA METHOD 7470A)

14.1.1 Measure 30 ml of sample aliquot (or portion of sample diluted to 30 mL) into a 50 ml centrifuge tube. **Addition of all reagents should be done in the hood**.

14.1.2 Add 1.5 ml of concentrated H_2SO_4.

14.1.3 Add 0.75 ml of concentrated HNO_3.

14.1.4 Add 4.5 ml of $KMNO_4$ solution, cap, invert to mix, and let sit for at least 15 minutes. If samples are no longer purple after 15 minutes, (i.e. brown or clear) re-prepare sample at dilution.

14.1.5 Add 2.4 ml of $K_2S_2O_8$ solution, screw cap on tube and invert to mix.

14.1.6 Heat for two hours at 90-95°C in water bath or hot block. Record time in/time out in prep logbook. Record thermometer ID and bath/block temperature in prep logbook.

14.1.7 Cool and add 1.8 ml of Sodium Chloride - Hydroxylamine Hydrochloride solution to reduce excess $KMNO_4$. Invert to mix.

14.1.8 Samples are now ready for analysis on Cetac M-6000A according to method and instrument parameters.

14.1.9 Record all reagents used in prep logbook.

14.2 Digestion Procedure for Solid or Semisolid Samples (EPA METHOD 7471A)

14.2.1 Weigh approximately 0.3 g of sample into a 50 ml centrifuge tube. For Method Blank and LCS, weigh approximately 0.3 g of Ottawa sand.

14.2.2 Add 1.5 ml of DI H_2O

14.2.3 Add 1.5 ml Aqua Regia. **Add Aqua Regia and all other reagents in hood**.

14.2.4 Heat in a water bath or hot block at 90-95 °C for 2 minutes. Record time in/time out in prep logbook. Record thermometer ID and bath/block temperature in prep logbook.

14.2.5 Allow to cool for 5 minutes.

14.2.6 Add 15 ml DI H_2O.

14.2.7 Add 4.5 ml of $KMNO_4$, cap and invert to mix.

14.2.8 Heat in water bath at 90-95°C for 30 minutes. Record time in/time out in prep book.

14.2.9 Allow to cool for 15 minutes.

14.2.10 Add 1.8 ml Sodium Chloride – Hydroxylamine Hydrochloride solution to reduce excess $KMNO_4$.

14.2.11 Add 16.5 ml DI H_2O. Invert to mix.

14.2.12 Samples are now ready for analysis on Cetac M-6000A according to method and instrument parameters.

14.2.13 Standards for soils will be prepared as noted above in section 10.27 (Table 1). Before addition of reagents add 3 ml of DI H_2O to ensure the final volume is the same for samples and standards. Otherwise treat standards in the same manner as samples with regard to reagent addition, except add no additional water (omit steps 14.2.2, 14.2.6 and 14.2.11). Final volume of samples and standards should be 40.8 ml.

14.2.14 Record all reagents used in prep logbook.

14.3 Analysis

14.3.1 Turn on the gas.

14.3.2 Turn on the power to the instrument, the lamp, and the autosampler. Allow the lamp to warm up for at least 20 minutes.

14.3.3 Double click on the **Hg Analysis** icon on the desktop.

14.3.4 The main menu appears. Click on **Worksheet**, click on **Open**, and select an appropriate worksheet for analysis (currently **Daniel**).

14.3.5 Click on the **Filing** tab. Click on **Rename**. Click on **Yes**. Change the analyst, and the ICAL and QC solutions, as appropriate.

14.3.6 Disconnect the outlet gas (top tube) from the gas-liquid separator.

14.3.7 Attach the tubing to the pump – Stannous chloride solution on top, followed by the sample tubing, and finally the drain tubings.

14.3.8 Turn on the pump, and allow stannous chloride and rinse solution to start pumping into the gas-liquid separator. Pinch the drain tubing (or disconnect) to allow the gas-liquid separator to fill with solution. This process "wets" the center post of the gas-liquid separator. Once the center post has been sufficiently wetted, reconnect the drain tubing on the pump, and allow the gas-liquid separator to drain completely. Reattach the outlet gas tubing to the gas-liquid separator.

14.3.9 Click on the **Labels** tab. Type the samples into the table.

14.3.10 Load the samples into the autosampler tray.

14.3.11 Click on the **Analysis** tab. Click on **Instrument** on the menu and click on **Zero**. Click on the **Read** button, click on **Standard**, select **Standard 6**, and click **OK**. The instrument will now analyze the highest standard. Check for adequate response, and reproducibility.

14.3.12 Click on the **Start** button. Check the boxes for calibration (as necessary), instrument zero, and for report printing, and click **OK**.

14.3.13 Dilute and reanalyze any sample that exceeds the highest standard. Reanalyze any detectable sample if the %RSD exceeds 5 %.

14.3.14 After analysis, rinse the gas-liquid separator with an HNO_3 solution. Drain the gas-liquid separator completely. Turn off the gas, pump, autosampler, lamp, and then the instrument.

15.0 Data Reduction, Calculations and Loading

15.1 The data system will then prepare a calibration curve by plotting response versus standard concentration. Sample concentration is calculated from the regression equation.

NOTE: The LIMS program will convert µg/L (part per billion) concentrations from the instrument readout to mg/L or mg/Kg (part per million).

15.2 Report only those values that fall between the lowest and highest calibration standards. Samples exceeding the highest standard must be diluted and reanalyzed.

15.3 Aqueous samples - The concentration readout for aqueous sample distillates is µg Hg/L. It does not need further data reduction unless the initial sample volume was less than 30 mL. If less than 30 mL sample was digested, calculate the concentration as follows:

Concentration in mg Hg/L = readout * 0.001 (30 mL/ initial sample volume analyzed in mL)

15.4 Solid Samples – The concentration readout for soil and solid samples must be multiplied by the following factor: Factor = (30/ sample weight in g). Calculate the concentration of Hg in soil and solid samples as follows:

Concentration in mg Hg/L = readout * 0.001 (30 mL/ initial sample weight in g)

15.5 The procedure for uploading data into the LIMS system is detailed in SOP 1400 LIMS.

16.0 Method Performance

Demonstration of Capability (DOC)

All parameters of interest must meet the method acceptance criteria before actual sample analysis begins. See SOP 1230 Training for the procedure to perform and document the DOC. The DOCs for the analysts performing this method are located in the analysts' training form folders located in the QA office files.

A quality control (QC) reference concentrate is required containing each analyte at a concentration of 0.00025 mg/L for aqueous samples and 0.025 mg/Kg for soil samples using the ICV/CCV solution. The

QC reference sample is made using stock standards prepared independently from those used for calibration.

For each analyte calculate the mean recovery (X) and standard deviation (s) and the average % Recovery (%R). Compare X and s and %R with the corresponding acceptance criteria for accuracy and precision, respectively. Note: For aqueous samples, X must be within 0.00025 ± 0.00005 mg/L and s must be less than 0.00005 mg/L and %R must be within 100 ± 20%. Note: For soil samples, X must be within 0.025 ± 0.005 mg/Kg and s must be less than 0.005 mg/Kg and %R must be within 100 ± 20%. These limits are taken from established in-house criteria. If X and s and %R for all analytes meet the acceptance criteria, the system performance is acceptable and analysis of actual samples can begin. If any individual X or %R falls outside the range for accuracy, or any individual s exceeds the precision limit, then the system performance is unacceptable for that analyte and corrective action must be taken.

The Analyst performing the analysis on the Cetac Mercury Analyzer need only perform one DOC (either the aqueous or the soil DOC) to demonstrate capability in the analysis.

Comparison to Reference Method Data

There is no stated reference method criteria for LCS, Duplicates, or MS/MSD recoveries in EPA Methods 7470A or 7471A. EPA Method 7000 does require the recovery of an independent check standard (ICV) to be within ± 10% of the true value, and that the calibration check standard (CCV) be within ± 20% of the true value. EPA Methods 7470A and 7471A require a blank and 5 standards for the calibration curve. EPA Methods 7470A and 7471A recommend that the standards be digested daily. The laboratory digests the calibration standards weekly, but digests the ICV, CCV, and Reagent Blank with every preparation batch.

In-House Control Limits

Method performance data is on file in the laboratory QC department. Comparison of method performance data for the laboratory to the reference method criteria occurs when laboratory in-house acceptance limits are generated. In-house generated data is compared to the specifications of the reference method. If the in-house limits are within the specifications of the reference method, the control limits are updated in LIMS. If the in-house limits are not within specifications, an investigation is performed to determine the cause(s) of the problem and a corrective action is completed. The analysis may continue until enough data points are collected to regenerate new control limits. Any QC data generated outside of reference method limits during that time frame, is flagged.

The laboratory maintains performance records to document the quality of data that is generated. Method accuracy for samples is assessed and records maintained. After the analysis of 20 laboratory control samples, calculate the average percent recovery (R) and the standard deviation of the percent recovery (S).

Control limits for the method parameters are generated by the QC staff and distributed to the analysts via updates to the LIMS control charts. The control limits are calculated based on in-house performance data. At a minimum, these limits are reviewed annually.

17.0 Pollution Prevention

17.1 The preparation of excessive volumes of laboratory reagents and standards shall be avoided so that waste and potential for pollution are minimized. Samples, reagents and standards shall be disposed in compliance with the laboratory waste disposal program, SOP 1130. With the consent of the client, the samples may be returned to their origin for treatment.

17.2 Uncontaminated paper waste, glass and cans should be separated for recycling. Laboratory staff are required to protect the laboratory's and our clients' business information when disposing of recycling or waste from the facility.

18.0 Data Assessment and Criteria for Quality Control Measures

The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When results of QC samples indicate atypical method performance, a calibration verification standard is used to confirm the measurements were performed in an in-control mode of operation. The data review is conducted according to SOP 1250 Data Review.

Method Blank (MB)

If the blank exceeds the RL (usually the lowest calibration standard), the source of contamination must be investigated and corrective actions taken.

Affected samples must be reprocessed and reanalyzed **or** Data must be appropriately qualified if:

1) The concentration of a targeted analyte in the blank is at or above the reporting limit as established by the SOP or by regulation, AND is greater than 1/10 of the amount measured in any sample.

2) The blank contamination otherwise affects the sample results as per the test method requirements or the individual project data quality objectives.

Laboratory Control Sample (LCS)

The results of the individual batch LCS are calculated in percent recovery (%R) and compared to established acceptance criteria (in-house limits). LCS %R limits are 100 ± 20% for both aqueous and soil samples. If the LCS is outside the acceptance criteria, the analytical system is "out of control". Any affected samples associated with an out of control LCS must be reprocessed and reanalyzed or the results reported with appropriate data qualifiers.

Note: An LCS consisting of a media containing known and verified concentrations, or a Certified Reference Material (CRM) may have limits different from the limits listed above.

Matrix Spikes

The results from MS/MSD are primarily designed to assess the precision and accuracy of analytical results in a given matrix and are expressed as percent recovery (%R) and relative percent difference (RPD). See the STAT QAM, Section 5.4 for the calculation for RPD. Results are compared to established acceptance criteria (in-house limits). For aqueous and soil samples, MS/MSD %R limits are 100 ± 25% and RPD limits are 20%. For matrix spike results outside established criteria corrective action must be documented, or the data for the spiked sample is reported with appropriate data qualifying codes.

> Note: If the original sample result is sufficiently high (greater than four times the MS/MSD spike level), then % R limits may not apply.

Duplicates

The results from laboratory Duplicates are designed to assess the precision of analytical results in a given matrix and are expressed as relative percent difference (RPD). See the STAT QAM, Section 5.4 for the calculation for RPD. Results are compared to established acceptance criteria (in-house limits). RPD limits are 20 %. For duplicates results outside established criteria corrective action must be documented, or the data for the duplicate sample is reported with appropriate data qualifying codes.

Post Digestion Spike

The results from PDS are primarily designed to assess the accuracy of analytical results in a given matrix and are expressed as percent recovery (%R). For aqueous and soil samples, PDS %R limits are 100 ± 15%. For post digestion spike results outside established criteria corrective action must be documented, or the data for the spiked sample is reported with appropriate data qualifying codes.

19.0 Corrective Actions for Out-of-Control Data

The process for handling unacceptable and out of control data is found in SOP 230 Corrective Action.

If the CCV, MB, LCS/LCSD, MS/MSD, lab duplicate, PDS, or some other QC sample recovery of any parameter falls outside the designated acceptance range, the laboratory performance for that parameter is judged to be out of control, and the problem must be immediately identified and corrected. The analytical result for that parameter in the samples is suspect and is only reported for regulatory compliance purposes with the appropriate corrective action form. Immediate corrective action includes reanalyzing all affected samples by using any retained sample before the expiration of the holding time. Final data results must be qualified in the client report for reported results not meeting the laboratory defined criteria.

1) Review standards preparation logbooks. Check all calculations and ensure dilution factors are properly recorded.
2) Re-prepare the suspected standard or QC sample to identify possible preparation errors of the standard or QC sample.
3) Re-Analyze the samples when the CCV or LCS are not within acceptable limits.

4) Perform routine preventative maintenance following manufacturer's specification. Record all maintenance in the instrument logbook.

20.0 Contingencies for Handling Out-of-Control or Unacceptable Data

Every effort is made to prevent problems from occurring. When out of control or unacceptable data occurs the first option is to identify the problem and reanalyze the samples within the holding times. When this is not possible, the QA Manager and/or the Laboratory Director reviews data and discusses options with the client. Reanalysis or reporting the data with qualification are alternatives. Out of control or unacceptable data reported to the client must include the data qualifier, flag and discussion on the rationale for reporting.

Holding time exceedence, or improper preservation are noted on the corrective action form and included on the final report.

20.1 The process for handling unacceptable and out of control data is found in the Laboratory QAM Section 11. The reporting of data that is out of control must be approved and documented by Quality Assurance Manager and either the Technical Manager or the Laboratory Director.

20.2 Client Requested Modifications:

20.2.1 Clients must request modifications from the laboratory SOP in writing to the lab.

20.2.2 The Laboratory Director, Technical Manager and Quality Assurance Manager will evaluate the requested client deviations, determine the feasibly of the deviation and the potential effects on the data.

20.2.3 If it is determined that the laboratory will perform the requested deviations, the Laboratory Director, Technical Manager and Quality Assurance Manager will decide if a method validation study is required.

20.2.4 The designated project manager will retain all documentation concerning the requested deviation, including all correspondence with the client, in the client folder.

20.2.5 The final analytical report must include the statement *"This report has analyses performed using client requested modifications"*.

21.0 Waste Management

The STAT Analysis Corporation Waste Disposal SOP 1130 identifies proper waste management practices for the chemicals and biological materials used in this procedure. Samples are stored and discarded in accordance with SOP 1130 Waste Disposal.

22.0 References

22.1 SW 846 3rd Edition, Method 7471A, Mercury in Solid or Semisolid Waste and 7470A Mercury in Liquid Waste.
22.2 STAT SOPs [sample prep]
22.3 STAT SOPs [support equipment, recordkeeping, MDLs, etc]
22.4 SOP 230 Corrective Actions
22.5 SOP 1010 Standard and Reagent Preparation
22.6 SOP 1400 LIMS
22.7 SOP 1130 Waste Disposal
22.8 SOP 003 Chemical Hygiene Plan
22.9 SOP 1250 Data Review
22.10 Manufacturers' Equipment Instruction Manuals
22.11 SOP 1230 Training
22.12 STAT Analysis Corporation Quality Assurance Manual
22.13 NELAC Chapter 5 Quality Systems, Approved May 25, 2001
22.14 Guidance for the Preparation of Standard Operating Procedures (G-6) EPA/240/B-01/004 March 2001

23.0 Forms, Figures, Tables, Diagrams, Flowcharts, Attachments or Validation Data.

23.1 Appendix A Prep Logbook

Appendix A – Prep Logbook

Mercury Prep LogBook (SOP# 4530)

Matrix: W = Water, S = Soil, T = TCLP

Time in Bath ____________
Time out of Bath ____________
Water Bath Temperature ____________
Thermometer ID ____________

Analyst(s)	Date	Sample ID	Bottle #	Matrix	Sample Wt./ Vol. (g or mls)	Final Volume (mls)	Spike Volume (mls)	Spike Solution ID#	Comments

Digestion Reagents

Potassium Permanganate ____________
Potassium Persulfate ____________
Hydroxylamine Hydrochloride ____________

Sulfuric Acid ____________
Hydrochloric Acid ____________
Nitric Acid ____________

Reviewed by ____________

Page 1 of 200

SOP ADDENDUM

SOP TITLE: SOP 4530 Mercury in Water, Solid or Semisolid
Revision 00, Effective Date: 1/9/03.

Issued by Laurie Fetterman, QA Manager LAF 10/31/03

Approved by: Dennis Jachim, Technical Manager DJ 10/31/03

Date of Issue: October 31, 2003

The following information is added to the SOP:

Section 3 (edit this section, additions are *italicized*)

If the regulatory limit is stated or defined for a particular analysis or test parameter, the laboratory's policy is to perform the analysis using a calibration standard at or below the defined regulatory limit.

Section 5.3 (edit this section, additions are *italicized*)

5.3 **Method modifications from Reference** – This procedure utilizes an automated cold-vapor technique, mixing stannous chloride with an aliquot of the sample digestion at the instrument. Digestions take place in graduated 50-ml tubes. *Typically, a 30-mL (instead of 100- mL) aliquot is digested for water samples, and 0.3 g (instead of 0.6 g) aliquot for solids to minimize mercury waste and waste disposal.*

Section 11.8.1 (edit this section, additions are *italicized*)

11.8.1 *Samples are stored in the sample refrigerators located in the sample receiving area. Samples are stored refrigerated at 0.1 - 6°C. Sample analysis that cannot be performed within holding time is flagged on the report. Digestates are stored at room temperature in the laboratory for a maximum of one month before disposal.*

Section 12.6 (edit this section, additions are *italicized*)

12.6 Method of Standard Additions

STAT Analysis does not routinely analyze Extraction Procedure Toxicity (EP) samples or samples for delisting. However, if the sample is known to be delisting sample or an EP sample, the method of standard additions will be utilized.

The initials/signature of the QA Manager and the Technical Manager indicate that this is a controlled document.

Section 13.4 (edit this section, additions are *italicized*)

13.4 The lowest calibration standard may establish the reporting limit. The reporting limit may also be based upon another point in the calibration curve. It must me greater than the detection limit. *The curve is linear regression generated by the instrument software.*

Section 13.12 (edit this section, additions are *italicized*)

Records: Initial and Continuing Calibration Records will contain, at a minimum, the following:

Calibration
Instrument *Identification*
Analysis Type
Analysis Date *and Time of analysis*
Analyst's initials and signature
Lab sample ID code
Standard Concentration (appropriate units) and number of standards
Response (appropriate units)
Calibration curve
Evaluation of and Statistics for ICAL curve for in order to judge calibration curve acceptance.
All manual calculations

Section 14 (new section, additions are italicized)

14.3 Analysis

14.3.1 Turn on the gas.

14.3.2 Turn on the power to the instrument, the lamp, and the autosampler. Allow the lamp to warm up for at least 20 minutes.

14.3.3 Double click on the **Hg Analysis** icon on the desktop.

Typical parameters include:
4 replicates
30 s sample sip time
40 s rinse time
40.75 s read delay
100 ml/min gas flow rate

14.4 Method of Standard Additions: Single Addition Method
This method will be used on all analyses submitted as part of a delisting petition.

14.4.1 Take two identical aliquots of the sample solution, each of volume V_x, and pipette into 50-mL graduated tubes.

14.4.2 Add a known volume V_s of a standard analyte solution of concentration C_s. Label it "A"

14.4.2.1 Note: V_S and C_s should be chosen so that the spike level is roughly twice the concentration of the unspiked sample.

14.4.2.2 Make the spike pre-digestion.

14.4.3 To the second aliquot (labeled "B"), add the same volume V_s of reagent water.

14.4.4 *Digest and analyze the samples according to section 14.1 through 14.3.*

The initials/signature of the QA Manager and the Technical Manager indicate that this is a controlled document.

Section 15 (new section, additions are *italicized*)

15.1 The data system will then prepare a calibration curve by plotting response versus standard concentration. Sample concentration is calculated from the regression equation *and is generated by the software.*

15.6 *Method of Standard Additions: Single Addition Method Calculation*
Calculate sample concentration C_x:

$$C_x = \frac{SB * V_S * C_s}{(SA-SB) * V_X}$$

where:
SA = analytical signal from the spiked sample
SB = analytical signals from the unspiked sample (blank)
V_S = volume of known standard or solvent
V_x = volume of original sample used in each aliquot
C_s = known concentration of standard added
C_x = Concentration in the analyte in original sample

15.7 *See Section 14.10 of SOP 1040 Good Laboratory Practices for calculations.*

END OF ADDENDUM

SOP ADDENDUM

SOP No. & TITLE: 4530; Mercury by Cold Vapor

Revision 03; Effective Date: January 9, 2003

Issued by : Pinaki Banerjee, QA Director

Approved by: Dennis Jachim, Technical Manager

Date of Issue: April 24, 2009.

Section (additions are *italicized*, ~~deletions are strikethroughs~~)

15.4 Solid Samples – The concentration readout for soil and solid samples must be multiplied by the following factor: Factor = (30/ sample weight in g). Calculate the concentration of Hg in soil and solid samples as follows:

Concentration in mg Hg/*Kg*~~L~~ = readout * 0.001 (30 mL/ initial sample weight in g)

To report results on a dry weight basis, a separate aliquot of sample should be analyzed for Percent Solids (or Percent Moisture). The results can then be used to correct the wet weight Mercury results to a dry weight basis. For soil samples reported on dry weight basis, divide the concentration by the decimal equivalent of the Percent Solids. For example: a sample contains 90% solids, thus

$$\textit{Concentration (µg/Kg or mg/Kg) dry weight} = \frac{\textit{Conc (µg/Kg or mg/Kg)}}{0.90}$$

Standard Operating Procedure 4630:

Total Organic Carbon by EPA 415.1

Revision 00
Effective Date: October 13, 2005

Authors: Pinaki Banerjee and Yelena Zavadyak

Printed Name	Signature/Date
Dennis Jachim **Technical Manager**	10/13/05
Laurie Fetterman **QA/QC Manager**	10/13/05
Donald Cortes **Laboratory Director**	10/13/05
Bruce Anderson **Inorganics Manager**	10-13-05

This Standard Operating Procedure has been prepared for the sole use of STAT Analysis Corporation.

Copy Number: _____

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1.0 Identification of Test Method

Total Organic Carbon by high temperature combustion method, EPA 415.1.

2.0 Applicable Matrix or Matrices

This method is applicable to potable and non-potable water. The procedure is applicable only to homogeneous samples, which can be injected into the apparatus reproducibly using a microliter type syringe. The syringe opening limits the maximum size of particles, which may be included in the sample.

3.0 Detection Limits

The lab follows the procedure found in 40CFR Part 136B to determine the MDL on an annual basis. See the STAT Analysis SOP 1210 for the MDL Procedure, frequency and acceptance criteria. The MDLs measured by the laboratory and all supporting documentation are in the laboratory QA files for review.

The laboratory determined MDL must always be less than the reporting limit (RL). The RLs will usually range from three to ten times the laboratory measured MDLs, but this relationship may vary dependent on dilution of sample aliquots, matrix interferences, or method specific requirements.

The reporting limits for this method is 1mg/L for waters. The method detection limit is 0.5 mg/L. Reporting limits are based upon the lowest calibration standard. The applicable range for aqueous samples is 1 to 100 mg/L.

4.0 Scope and Application

This method is used to determine total organic carbon in aqueous samples.

This method is restricted to use by or under the supervision of analysts experienced in the use of the Thermo Euroglas TOC 1200 Analyzer.

NOTE: Each analyst must demonstrate the ability to generate acceptable results with this method.

5.0 Summary of Test Method

The sample is introduced into a high temperature furnace, where organic carbon oxidizes to form CO_2. Liquid samples are introduced into the furnace with a syringe in a boat. After oxidation, the boat retracts, cools down, and is ready for introduction of the next

sample. Samples can also be introduced using an auto sampler. The sample is flushed with a mixture of argon and oxygen as carrier gas, led through a copper oxide scrubber and transferred to the inorganic carbon scrubber. The inorganic carbon scrubber contains 10% phosphoric acid and has an injection port for analysis of inorganic carbon. After the scrubber, the gas is dried in a Perma-pure dryer and passed through particle filter. In the final step, CO_2 is measured by a non-dispersive infrared detector.

6.0 Definitions

The STAT Analysis Corporation Quality Assurance Manual (QAM) contains the definitions of standard terms used in this SOP.

7.0 Interferences

7.1 Carbonate and bicarbonate carbon interferes with organic carbon result and must be removed or accounted for in the final calculation.

7.2 Acidification and purging with purified gas to remove inorganic carbon also results in loss of volatile organic carbon.

8.0 Safety

8.1 All samples must be assumed as hazardous and appropriate precautions taken during handling.

8.2 Safety glasses, gloves, lab coats and closed toe shoes are to be worn when handling samples or reagents.

8.3 Potential health hazards from the samples cannot be determined. Exposure should be minimized to the extent possible. Other safety precautions must be conducted in accordance with the Chemical Hygiene Plan.

8.4 The toxicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable.

8.5 A reference file of material safety data sheets (MSDS) is available in each room for personnel involved in an analysis using chemicals.

9.0 Equipment and Supplies

The following apparatus is recommended for performing this procedure. Equivalent items can be used, if with their use, the analytical and QA/QC requirements in this SOP can be met.

9.1 Instrument: Thermo Euroglas TOC 1200.

9.2 Data is processed using a Microsoft Windows based software Controller V5.44A.

9.3 Analytical balance, capable of measuring 0.001 g.

9.4 Carrier gas: Argon (50%) and oxygen (50%). Ultra high purity (UHP).

9.5 Purging gas: Helium, UHP.

9.6 Miicro syringes - 10 µL, 25 µL, 100 µL.

9.7 Thermometer capable of measuring 90-110 °C with suitable precision and accuracy.

9.8 Autopipettor: 0.010 to 0.10 mL, 0.10 to 1.0 mL, 1.0 to 5.0 mL

9.9 Volumetric flasks, Class A with ground glass stoppers; 50 mL, 100 mL, 250 mL, and 500 mL.

9.10 10 mL glass tubes

10.0 Reagents and Standards

The following reagents and standards are required to perform this procedure. When instructions are given on how to prepare a specific volume of a reagent or standard, larger or smaller volumes can be prepared as needed so long as the final concentrations remain the same. Any other deviations from the reagents or standards listed in this SOP could be detrimental to the quality of the data produced. Such deviations would have to be approved and documented.

10.1 At least one of the standards must be traceable to a NIST traceable source when available. The manufacturer should include a certificate of analysis for each standard. If one is not provided, contact the manufacturer. Retain all certificates in the designated binder (see SOP 1010 Analytical Standards and Reagents Receipt and Preparation).

10.2 Instructions for labeling and record keeping of reagents and standards are contained in SOP 1010 Analytical Standards and Reagents Receipt and Preparation.

10.3 Reagents – In methods where the purity of reagents is not specified, analytical reagent grade shall be used. Reagents of lesser purity than those specified by the test method shall not be used.

10.4 Standards

10.4.1 Standards must be prepared volumetrically using class volumetric glassware, calibrated micropipettes, or gas tight syringes. Do not use disposable pipettes to prepare standards.

10.4.2 The use of alternative standards will be allowed as long as the analytical and quality objectives of the SOP can be met.

10.5 Reagent Water: Reagent water will be interference free. Demineralized, carbon dioxide free water should be used. All references to water in this method will refer to reagent water unless otherwise specified.

10.6 Phosphoric acid solution, 10%: Trace Metal grade. Put 440 mL of reagent water in a flask and add 60 mL of concentrated phosphoric acid (85%). Total volume will be 500 mL.

10.7 Prepare Calibration Standards:

10.7.1 Oven dry potassium hydrogen phthalate (KHP) for one hour at 105 degrees centigrade. Dissolve 2.1254 gm of dried KHP in reagent water. Dilute to 1,000 mL to make stock solution of 1,000 mg/L, where 1.00 mL equals 1.00 mg carbon. Preserve the stock by acidifying with phosphoric acid to pH less than or equal to 2. Stock solutions are stable for up to a year.

10.7.2 An alternate stock solution for use in initial calibration verification (ICV), continuing calibration verification (CCV), laboratory control sample (LCS), and matrix spike and matrix spike duplicate (MS/MSD) is made from a second source of KHP. Stock solutions are stable for up to a year.

10.7.3 Dilute with reagent water to make a minimum of five calibration standards ranging from 1 mg/l to 100 mg/L. Table 1 provides the details regarding standard preparation.

Table 1 Calibration Standards

Calibration Standard Concentration, mg/L	Amount of stock solution to add to 50 mL volumetric flask, mL
1	0.05
10	0.5
25	1.25
50	2.5
100	5

11.0 Sample Collection, Preservation, Shipment and Storage

11.1 All samples are stored away from all standards, reagents, food, and other potentially contaminating sources in order to prevent cross contamination.

11.2 All sample containers should be pre-washed with detergents, acids, and reagent water. Plastic and glass containers are both suitable.

11.3 Aqueous samples must be acidified to a pH < 2 with phosphoric acid.

11.4 The maximum holding time is 28 days.

12.0 Quality Control

The following details the QC requirements that apply to this analysis. Each Quality Control Indicator (QCI) provides information pertaining to either method or individual sample performance. Our goal is to produce defensible data of known and documented quality. The results of these QCI samples are used to assess the acceptability of data.

12.1 Blanks

Method Blank analysis is performed to determine if any contamination is present in the analytical process and is used to evaluate acceptance of the batch of samples. A method blank shall be prepared once per preparation batch of 20 or less samples per matrix type. If more than 20 samples are prepared, a second blank shall be prepared after the twentieth sample. The method blank shall be processed through all preparatory steps used for the samples, including cleanup procedures. The blank shall be analyzed using the same instrument and conditions as the samples.

12.2 Laboratory Control Sample (LCS)

The LCS is used to evaluate the performance of the total analytical system, including all preparation and analysis steps. The LCS shall be prepared once per preparation batch of 20 or less samples per matrix type. If more than 20 samples are prepared, a second LCS shall be prepared after the twentieth sample. The LCS shall be processed through all preparatory steps used for the samples, including cleanup procedures. The LCS must be analyzed using the same instrument and conditions as the samples. The LCS is prepared by diluting 0.5 mL of second source stock solution (1.00 mL = 1.00 mg, see Section 10.7.2)) to 10 mL.

12.3 Duplicates

Duplicates of field samples or of the LCS must be prepared in compliance with the method requirements and client directives. Note: the analysis of the Matrix Spike Duplicate (MSD) is used as a substitute for the laboratory duplicate.

12.4 Matrix Spike and Matrix Spike Duplicate (MS/MSD)

MS/MSDs indicate the effect of the sample matrix on the precision and accuracy of the results generated using the selected method. This information does not determine the validity of the entire batch. MS/MSDs must be analyzed at a minimum of 1 per 20 samples per matrix per preparation procedure, or as specified by the required test method. For cases where the sample cannot be divided (e.g., wipes, air samples, not enough sample provided by customer) and thus a MS/MSD pair cannot be prepared for the preparation batch, an LCS/LCSD pair is analyzed. Spiking solution for MS/MSD is prepared by diluting 0.5 mL of second source stock solution (1.00 mL = 1.00 mg, see Section 10.7.2) to 10 mL.

Samples chosen for matrix spiking are rotated among different clients and/or different client projects. This is accomplished through communication between the Department Manager and the analyst. In addition, designated samples, as indicated by client request or contract requirement, are matrix spiked.

The MS/MSD pair shall be processed through all preparatory steps used for the samples. They shall be analyzed using the same instrument and conditions as the samples. Some clients may require different spiking levels, these specific needs are documented on the request for analysis forms.

13.0 Calibration and Standardization

13.1 Initial Calibration (ICAL)

In addition to achieving the reference method requirements for the minimum number of calibration standards and the acceptance criteria (statistics) for calibration curve fit, the following ICAL criteria also apply:

The ICAL must be a minimum of 5 standards, not including a blank.

The ICAL must be verified with a second source standard (ICV) prior to the analysis of samples.

Results of samples not bracketed by the ICAL range must be qualified on the final report. If possible, dilute the sample or extract and reanalyze in order to achieve a result within the calibrated range of the instrument.

The lowest calibration standard may establish the reporting limit. The reporting limit may also be based upon another point in the calibration curve. It must be greater than the detection limit.

13.2 Initial Calibration Verification (ICV)

In addition to the method requirements, the following ICV criteria also apply:

Must be a second source standard from the ICAL standards or from a different manufacturer lot number.

Must be traceable to NIST, when available.

Must be analyzed every day a preparation batch is performed.

13.3 Continuing Calibration Verification (CCV)

In addition to the method requirements, the following CCV criteria also apply:

Must be a second source standard from the ICAL standards or from a different manufacturer lot number.

Must be analyzed each day samples are analyzed.

Must be analyzed after every 10 samples and at the end of each analytical batch.

If the CCV results obtained are outside the acceptance criteria (+or –10%), corrective actions must be performed. If routine corrective actions fail to produce an acceptable *second consecutive (immediate)* CCV, then either the lab has to demonstrate performance after corrective action with two consecutive successful CCVs, or a new ICAL must be performed. If the instrument has not demonstrated acceptable performance, sample analyses cannot continue until a new ICAL is established and verified with an ICV. However, sample data associated with an unacceptable CCV may be reported as qualified data under the following special conditions.

When the acceptance criteria for CCV are exceeded high, i.e., high bias, and there are associated samples that are non-detects, then those non-detects may be reported. Otherwise the samples affected by the unacceptable calibration verification must be reanalyzed after a new ICAL has been established, evaluated and accepted.

When the acceptance criteria for the CCV are exceeded low, i.e., low bias, those sample results may be reported if they exceed a maximum regulatory limit/decision level. Otherwise the samples affected by the unacceptable verification must be reanalyzed after a new ICAL is established and verified with an ICV.

When the acceptance criteria for the CCV are exceeded and it is not possible to reanalyze the sample due to limited sample quantity AND the laboratory cannot obtain a new sample, the data may be reported with the appropriate data qualifiers if the client has been contacted and agrees, in writing, to accept the qualified data.

13.4 Records:

Initial and Continuing Calibration Records will contain, at a minimum, the following:

Calibration date
Instrument
Analysis date
Analyst's initials or signature
Standard Concentration (appropriate units) and number of standards
Response (appropriate units)
Calibration curve
Evaluation of and Statistics for ICAL curve fit in order to judge calibration curve acceptance

13.5 Initial/Continuing Calibration Blank (ICB/CCB – Reagent Blank)

In addition to the method requirements, the following ICB/CCB criteria also apply:

Must be prepared and analyzed with each preparation batch.

Note: The Method Blank may act as the ICB/CCB.

Must be analyzed after Initial Calibration Verification (ICV).

Must be analyzed after every Continuing Calibration Verification (CCV).

Calibration Acceptance Summary (see Table 2):

Table 2 Quick reference of instrument Calibration Requirements

QCI	Frequency	Standards	Control Limits	Corrective Action
ICAL	As needed	Minimum 5 standards (1, 10, 25, 50, and 100 mg/L).	$r \geq 0.995$	Correct problem, then repeat initial calibration
ICV	Analyzed daily	25 mg/L	90-110 % of true value	Correct problem, then repeat ICV or repeat initial calibration
CCV	Analyzed daily, after every 10th sample, and at end of analytical batch	50 mg/L	90-110 % of true value	Correct problem then repeat CCV or repeat initial calibration
ICB/CCB	Analyzed after each ICV and CCV	Reagent water	Absolute value <RL	Correct problem, then repeat ICB/CCB or repeat initial calibration

Note: All standards and blanks are preserved by adding one drop (per 50 mL) of phosphoric acid.

Support Equipment

Autopipettes - Check autopipette to ensure standardization is within control limits (see SOP 1040 General Laboratory Practices for Pipette Calibration).

Balances - Be sure the balance is checked prior to use and performance criteria are met (see SOP 1040 General Laboratory Practices for Calibration of Balances).

Thermometers - Check the thermometer to ensure the calibration is not expired (see SOP1040 General Laboratory Practices for Thermometer Calibration).

14.0 Procedure

14.1 Sample Preparation:
Inorganic carbon is removed by transferring a representative portion (5 mL) to a 10-mL glass tube, and purging with helium for two minutes.

14.2 Instrument Set-up
Fill scrubber with 10% phosphoric acid. Connect all tubing and fittings. Set argon and oxygen at 50-60 mm. Turn furnace setting 1 and 2 to 1000 degree centigrade. Open the TOC software program on the computer.

14.3 Sample Analysis:
100 µL of sample is withdrawn using a syringe with a blunt-tipped needle. Inject standards or samples and click "analyze." Response will be displayed on the screen. Record the response. Repeat injection until two measurements are obtained that are reproducible to within ± 20%. For samples with low concentrations (5 mg/L or less), it may be necessary to perform a manual integration of the peak area.

15.0 Data Reduction, Calculations and Loading

15.1 A calibration curve is prepared by plotting response versus standard concentration. Using linear regression, slope and intercept is calculated. The correlation coefficient of the calibration curve must be greater than or equal to 0.995. The intercept should be minimal. Sample concentration is calculated from the regression equation.

15.2 Report only those values that fall between the lowest and highest calibration standards. Samples exceeding the highest standard must be diluted and reanalyzed.

15.3 The procedure for uploading data into the LIMS system is detailed in SOP 1400 LIMS.

16.0 Method Performance

Demonstration of Capability (DOC)

All parameters of interest must meet the method acceptance criteria before actual sample analysis begins. See SOP 1230 Training for the procedure to perform and document the DOC. The DOCs for the analysts performing this method are located in the analysts' training form folders located in the QA office files.

A quality control (QC) reference concentrate is required containing each analyte at a concentration of 25 mg/L using the ICVsolution. The QC reference sample is made using stock standards prepared independently from those used for calibration.

Calculate the mean recovery (X) and standard deviation (s) and the average % Recovery (%R). Compare X and s and %R with the corresponding acceptance criteria for accuracy and precision, respectively.

Note: X must be within 25 ± 5 mg/L and s must be less than 5 mg/L and %R must be within 100 ± 20%. If X and s and %R for all analytes meet the acceptance criteria, the system performance is acceptable and analysis of actual samples can begin. If any individual X or %R falls outside the range for accuracy, or any individual s exceeds the precision limit, then the system performance is unacceptable for that analyte and corrective action must be taken.

Locate and correct the source of the problem and repeat the test only for those analytes that failed to meet criteria. Repeated failure, however, will confirm a general problem with the measurement system. If this occurs, locate and correct the source of the problem and repeat the test for all compounds of interest.

Comparison to Reference Method Data

EPA Method 415.1 reports accuracy ranging up to 15.27% as bias.

In-House Control Limits

Method performance data is on file in the laboratory QC department. Comparison of method performance data for the laboratory to the reference method criteria occurs when laboratory in-house acceptance limits are generated. In-house generated data is compared to the specifications of the reference method. If the in-house limits are within the specifications of the reference method, the control limits are updated in LIMS. If the in-house limits are not within specifications, an investigation is performed to determine the cause(s) of the problem and a corrective action is completed. The analysis may continue until enough data points are collected to regenerate new control limits. Any QC data generated outside of reference method limits during that time frame, is flagged.

The laboratory maintains performance records to document the quality of data that is generated. Method accuracy for samples is assessed and records maintained. After the analysis of 20

laboratory control samples, calculate the average percent recovery (R) and the standard deviation of the percent recovery (S).

Control limits for the method parameters are generated by the QC staff and distributed to the analysts via updates to the LIMS control charts. The control limits are calculated based on in-house performance data. At a minimum, these limits are updated annually.

17.0 Pollution Prevention

17.1 The preparation of excessive volumes of laboratory reagents and standards shall be avoided so that waste and potential for pollution are minimized. Samples, reagents and standards shall be disposed in compliance with the laboratory waste disposal program, SOP 1130. With the consent of the client, the samples may be returned to their origin for treatment.

17.2 Uncontaminated paper waste, glass and cans should be separated for recycling. Laboratory staff are required to protect the laboratory's and our clients' business information when disposing of recycling or waste from the facility.

18.0 Data Assessment and Criteria for Quality Control Measures

The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When results of QC samples indicate atypical method performance, a calibration verification standard is used to confirm the measurements were performed in an in-control mode of operation. The data review is conducted according to SOP 1250 Data Review.

Method Blank (MB)

If the blank exceeds the RL (usually the lowest calibration standard), the source of contamination must be investigated and corrective actions taken.

Affected samples must be reprocessed and reanalyzed or Data must be appropriately qualified if:

1) The concentration of a targeted analyte in the blank is at or above the reporting limit as established by the SOP or by regulation, AND is greater than 1/10 of the amount measured in any sample.

2) The blank contamination otherwise affects the sample results as per the test method requirements or the individual project data quality objectives.

Laboratory Control Sample (LCS)

The results of the individual batch LCS are calculated in percent recovery (%R) and compared to established acceptance criteria (in-house limits). LCS %R limit is 100 ± 20%. If the LCS is outside the acceptance criteria, the analytical system is "out of control". Any affected samples associated with an out of control LCS must be reprocessed and reanalyzed or the results reported with appropriate data qualifiers.

Matrix Spikes

The results from MS/MSD are primarily designed to assess the precision and accuracy of analytical results in a given matrix and are expressed as percent recovery (%R) and relative percent difference (RPD). See the STAT QAM, Section 5.4 for the calculation for RPD. Results are compared to established acceptance criteria (in-house limits). MS/MSD %R limits are 100 ± 25% and RPD limits are 20%. For matrix spike results outside established criteria, corrective action must be documented, or the data for the spiked sample is reported with appropriate data qualifying codes.

> Note: If the original sample result is sufficiently high (greater than four times the MS/MSD spike level), then % R limits may not apply. The sample should be diluted and reanalyzed.

Duplicates

The results from laboratory Duplicates are designed to assess the precision of analytical results in a given matrix and are expressed as relative percent difference (RPD). See the STAT QAM, Section 5.4 for the calculation for RPD. Results are compared to established acceptance criteria (in-house limits). RPD limits are 20 %. For duplicates results outside established criteria, corrective action must be documented, or the data for the duplicate sample is reported with appropriate data qualifying codes.

19.0 Corrective Actions for Out-of-Control Data

The process for handling unacceptable and out of control data is found in SOP 230 Corrective Action.

If the ICV, ICB, CCB, CCV, MB, LCS/LCSD, MS/MSD, lab duplicate, or some other QC sample recovery falls outside the designated acceptance range, the laboratory performance is judged to be out of control, and the problem must be immediately identified and corrected. The analytical result for that parameter in the samples is suspect and is only reported for regulatory compliance purposes with the appropriate corrective action form. Immediate corrective action includes reanalyzing all affected samples by using any retained sample before the expiration of

the holding time. Final data results must be qualified in the client report for reported results not meeting the laboratory-defined criteria.

1) Review standards preparation logbooks. Check all calculations and ensure dilution factors are properly recorded.
2) Re-prepare the suspected standard or QC sample to identify possible preparation errors of the standard or QC sample.
3) Re-Analyze the samples when the CCV or LCS is not within acceptable limits.
4) Perform routine preventative maintenance following manufacturer's specification. Record all maintenance in the instrument logbook.

20.0 Contingencies for Handling Out-of-Control or Unacceptable Data

Every effort is made to prevent problems from occurring. When out of control or unacceptable data occurs, the first option is to identify the problem and reanalyze the samples within the holding times. When this is not possible, the QA Manager and/or the Laboratory Director reviews data and discusses options with the client. Reanalysis or reporting the data with qualification are alternatives. Out of control or unacceptable data reported to the client must include the data qualifier, flag and discussion on the rationale for reporting.

Holding time exceedence, or improper preservation are noted on the corrective action form and included on the final report.

20.1 The process for handling unacceptable and out of control data is found in the Laboratory QAM Section 10. The reporting of data that is out of control must be approved and documented by Quality Assurance Manager and either the Technical Manager or the Laboratory Director.

20.2 Client Requested Modifications:

20.2.1 Clients must request modifications from the laboratory SOP in writing to the lab.

20.2.2 The Laboratory Director, Technical Manager and Quality Assurance Manager will evaluate the requested client deviations, determine the feasibly of the deviation and the potential effects on the data.

20.2.3 If it is determined that the laboratory will perform the requested deviations, the Laboratory Director, Technical Manager and Quality Assurance Manager will decide if a method validation study is required.

20.2.4 The designated project manager will retain all documentation concerning the requested deviation, including all correspondence with the client, in the client folder.

20.2.5 The final analytical report must include the statement "*This report has analyses* Data Review forms *performed using client requested modifications* ".

21.0 Waste Management

The STAT Analysis Corporation SOP 1130 Waste Disposal identifies proper waste management practices for the chemicals and biological materials used in this procedure. Samples are stored and discarded in accordance with SOP 1130 Waste Disposal.

22.0 References

22.1 Methods for Chemical Analysis of Water and wastes, Method 415.1. U. S. EPA Office of Research and Development, EPA-600/4-79-020. March 1983.
22.2 Standard methods for the Examination of Water and Wastewater, 20th Edition. APHA, AWWA, AEF. 1998.
22.3 Thermo Euroglas TOC 1200: Manufacturers' Equipment Instruction Manuals
22.4 STAT Analysis Corporation Quality Assurance Manual
22.5 STAT SOP 003 Chemical Hygiene Plan
22.6 STAT SOP 230 Corrective Action
22.7 STAT SOP 1000 Control and Use of Laboratory Notebooks
22.8 STAT SOP 1010 Analytical Standards and Reagents Receipt and Preparation
22.9 STAT SOP 1040 General Laboratory Practices
22.10 STAT SOP 1130 Waste Disposal
22.11 STAT SOP 1210 Method Detection Limits
22.12 STAT SOP 1250 Data Review
22.13 STAT SOP 1230 Training
22.14 STAT SOP 1400 LIMS

23.0 Forms, Figures, Tables, Diagrams, Flowcharts, Attachments or Validation Data.

Not applicable.

STAT Analysis Corporation

STANDARD OPERATING PROCEDURE 4710

Automated Cyanide Analysis By EPA 9012A

Revision 00
Effective Date: December 19, 2002

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1.0 Identification of Test Method

SOP Title: Automated Cyanide Analysis by EPA 9012A is also known as HCN or CN in the laboratory records.

2.0 Applicable Matrix or Matrices

This method is used to determine the concentration of inorganic cyanide in aqueous samples, wastes, leachate, and soils. The method detects inorganic cyanides that are present as either soluble salts or complexes. It is used to determine values for both total cyanide and cyanide amenable to chlorination. This method is used to quantify the concentration of cyanide from the distillation procedure detailed in STAT SOP 4610 Cyanide Distillation (EPA Method 9010B). This method may also be used to quantify the concentration of cyanide from the reactivity test (see STAT SOP 4615 Reactive Cyanide and Sulfide Distillation using EPA Chapter 7).

3.0 Detection Limits

The lab follows the procedure found in 40CFR Part 136B to determine the MDL for each matrix type on an annual basis. See the STAT Analysis SOP 1210 for the MDL procedure, frequency and acceptance criteria. The MDLs measured by the lab and all supporting documentation are in the laboratory QA files for review.

The laboratory determined MDL must always be less than the reporting limit (RL). The RL will usually range from three to ten times the laboratory measured MDL but this relationship may vary dependent on dilution of sample aliquots, matrix interferences, moisture adjustments (in solid samples), or method-specified requirements.

The applicable range for aqueous samples is 0.005 to 0.5 mg/L. The applicable range for soil samples is 0.25 to 12.5 mg/Kg (as received basis). Sample distillates with concentrations greater than the highest calibration standard are diluted and then reanalyzed. Samples with high concentrations of cyanide may also be redistilled using a smaller sample size and then analyzed.

4.0 Scope and Application

The method is designed for the analysis of aqueous distillates for cyanide. Samples and QC samples are distilled prior to analysis.

The distillation procedure described in SOP 4610 Cyanide Distillation is designed for the determination of cyanides in aqueous solutions, wastes, leachates, and soils. This distillation method is not applicable to oil or multiphasic samples or samples not amenable to the distillation procedure.

Note: It is not possible to use this method to differentiate between different kinds of Cyanides. Cyanide is defined as cyanide ion and complex cyanides converted to hydrocyanic acid (HCN) by reaction in a reflux system of a mineral acid in the presence of magnesium ion.

This method is restricted to use by or under the supervision of analysts experienced in the use of the LaCHAT AutoAnalyzer.

Note: Each analyst must demonstrate the ability to generate acceptable results with this method.

5.0 Summary of Method

The cyanide, as hydrocyanic acid (HCN), is released from samples containing cyanide by means of a reflux-distillation operation under acidic conditions and absorbed in a scrubber containing sodium hydroxide solution. The cyanide ion in the absorbing solution is then determined by automated UV colorimetry. This Solution is analyzed on the LaCHAT AutoAnalyzer. In the automated colorimetric measurement, the cyanide is converted to cyanogen chloride (CNCl) by reaction with Chloramine-T at a pH less than 8 without hydrolyzing to the cyanate. After the reaction is complete, a red-blue color is formed on the addition of pyridine-barbituric acid reagent. The color produced is proportional to the concentration of cyanide and is absorbed at 570 nm. The concentration of NaOH must be the same in the standards, the scrubber solutions, and any dilution of the original scrubber solution to obtain colors of comparable intensity.

6.0 Definitions

The STAT Analysis Corporation Quality Assurance Manual (QAM) contains the definitions of standard terms used in this SOP.

Preparation batch - composed of one to 20 environmental samples of the same NELAC-defined matrix, meeting the above mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be 24 hours (NELAC).

Analytical batch - composed of prepared environmental samples (extracts, digestates or concentrates) which are analyzed together as a group. An analytical batch can include prepared samples originating from various environmental matrices and can exceed 20 samples (NELAC).

7.0 Interferences

7.1 Interferences are eliminated or reduced by using the distillation procedure described in SOP 4610 Cyanide Distillation.

7.2 Sulfides adversely affect the colorimetric and titration procedures. Sulfides are eliminated prior to distillation.

7.3 Oxidizing agents such as chlorine are removed immediately after sampling by the addition of ascorbic acid. If chlorine is not removed, most cyanide compounds may decompose and the results may be low.

7.4 High results may be obtained for samples that contain nitrate and/or nitrite. During the distillation nitrate and nitrite will form nitrous acid that will react with some organic compounds to form oximes. These compounds formed will decompose under test conditions to generate HCN. The interference of nitrate and nitrite is eliminated by pretreatment with sulfamic acid.

8.0 Safety

8.1 All samples must be assumed as hazardous and appropriate precautions taken during handling.

8.2 Safety glasses, gloves, lab coats and closed toe shoes are to be worn.

8.3 Other safety precautions must be conducted in accordance with the Chemical Hygiene Plan. Other actions can also be applied if deemed necessary. A reference file of material safety data sheets (MSDS) is available in each room for personnel involved in an analysis using chemicals.

8.4 The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable. Cautions are included for known extremely hazardous materials.

8.5 The following chemicals have the potential to be highly toxic or hazardous, for detailed explanation consult the MSDS.

8.5.1 Potassium Cyanide is poisonous. Use extreme caution when handling this material. Currently the pure compound is not used in the laboratory.
8.5.2 Pyridine has an extremely obnoxious odor. Handle this reagent in the fume hood.

9.0 Equipment and Supplies

9.1 LaCHAT AutoAnalyzer consisting of the following components:
9.1.1 Autosampler Cetac
9.1.2 Reagent Pump
9.1.3 System Unit LaCHAT 8000
9.1.4 Computer
9.1.5 Printer

9.2 Centrifuge Tubes, 50 mL graduated

9.3 Volumetric Flasks, Class A: 1000mL, 250mL, 100mL, 25mL with stoppers

9.4 Autopipetter: 0.010 to 0.10 mL, 0.10 to 1.0 mL, 1.0 to 5.0 mL

9.5 Test Tubes, 15 mL and Tube Racks

9.6 Plastic and glass bottles for solution storage

10.0 Reagents and Standards

The following reagents and standards are required to perform this procedure. When instructions are given on how to prepare a specific volume of a reagent or standard, larger or smaller volumes can be prepares as needed so long as the final concentrations remain the same. Any other deviations from the reagents or standards listed in this SOP could be detrimental to the quality of the data produced. Such deviations would have to be approved and documented (see 230 Corrective Action SOP).

10.1 Instructions for labeling and record keeping of reagents and standards are contained in SOP 1010 Standard and Reagent Preparation.

10.2 Reagents - In methods where the purity of reagents is not specified, analytical reagent grade shall be used. Reagents of lesser purity than those specified by the test method shall not be used.

10.3 Use reagent water (10 megohm) for all solutions. Degassing with helium: To prevent bubble formation, degas all solutions except the standards with helium. Use He at 140kPa (20 lb/in^2) through a helium degassing tube (LaCHAT Part No. 50100.) Bubble He through the solution for one minute.

10.4 Reagent 1. Carrier, Nondigested Standard Diluent, Absorber Solution (0.25N NaOH). In a 1 L volumetric flask dissolve 10 g sodium hydroxide pellets in 1.0 L reagent water. Prepare up to 5 L of this solution. Store in a carboy container. Prepare fresh every six months or as needed.

10.5 Reagent 2. Phosphate Buffer: In a 1 L volumetric flask, dissolve 97 g anhydrous potassium dihydrogen phosphate [potassium phosphate, monobasic, anhydrous, (KH_2PO_4)] in approximately 800 mL reagent water. Dilute to the mark with reagent water and invert three times. Stir with a magnetic stirrer for 30 minutes. Prepare fresh monthly.

10.6 Reagent 3. Chloramine T solution: Dissolve 2.0 g of Chloramine-T hydrate in 500 mL of reagent water and refrigerate until ready to use. Prepare fresh daily. Solid stock should be replaced within one year.

10.7 Reagent 4. Pyridine-Barbituric Acid Reagent: In the fume hood, place 15.0 g barbituric acid in a 1 L beaker and add 100 mL reagent water, rinsing down the sides of the beaker to wet the barbituric acid. Add 75 mL pyridine (C_5H_5N), stirring until the barbituric acid dissolves. Add 15 mL concentrated hydrochloric acid (12M HCl), then add an additional 825 mL reagent water and mix. Prepare fresh weekly. Store in a glass bottle away from light.

10.8 Standards

10.8.1 At least one of the standards must be traceable to a NIST traceable source when available. The manufacturer should include a certificate of analysis for each standard. If one is not provided, contact the manufacturer. Retain all certificates in the designated binder (see SOP 1010 Reagent Receiving).

10.8.2 Standards must be prepared volumetrically using class A volumetric glassware, calibrated micro-pipettes, or gas tight syringes. Do not use disposable pipettes to prepare standards.

10.8.3 Cyanide Stock Calibration Standard: 1000 mg CN/L Commercially Purchased. Store per manufacturer's recommendations and shelf life. If shelf life not stated, then this solution may be used for twelve months if stored in the original container at 4°C and shows no sign of deterioration.

10.8.4 Intermediate Cyanide Calibration Solution: (10 mg CN/L or 10 µg CN/mL): Dilute 0.5 mL of Cyanide Stock Standard to 50 mL with 0.25N NaOH. Prepare this solution fresh monthly and store in a 50 mL centrifuge tube at 4°C.

10.8.5 Cyanide Working Calibration Standards. Dilute the Intermediate Cyanide Calibration Solution to 250 mL with 0.25N NaOH to make the following Calibration Standards: see Table 1. Prepare these solutions fresh daily and store in 50 mL centrifuge tubes.

10.8.6 Calibration standards for distillation: see SOP 4610 Section 10.13.4 for LCS preparation and concentrations.

10.8.7 Stock ICV/CCV Cyanide Standard (2nd Source) 1000 mgCN/L: Commercially purchased. Store per manufacturer's recommendations and shelf life. If shelf life not stated, then this solution may be used for twelve months if stored in the original container at 4°C and shows no sign of deterioration.

10.8.8 Intermediate ICV/CCV Cyanide Solution: (10 mg CN/L or 10 µg CN/mL): Dilute 0.5 mL of ICV/CCV Stock Standard to 50 mL with 0.25N NaOH. Prepare this solution fresh monthly and store in a 50 mL centrifuge tube at 4°C.

10.8.9 Working ICV Standard: 100 µg CN/L (0.1 mg CN/L)- Dilute 0.50 mL of Intermediate ICV/CCV Cyanide Solution to 50 mL with 0.25N NaOH. Prepare this solution fresh daily and store in a 50 mL centrifuge tube.

10.8.10 Working CCV Standard: 250 µg CN/L (0.25 mg CN/L) - Dilute 1.25 mL of Intermediate ICV/CCV Cyanide Solution to 50 mL with 0.25N NaOH. Prepare this solution fresh daily and store in a 50 mL centrifuge tube.

The daily calibration standards are prepared as follows (use autopipetters and flasks as listed in Section 9). Add the listed volume of the Intermediate Cyanide Calibration Solution to each flask, dilute to mark with 0.25N NaOH, cap and mix well.

Table 1 Cyanide Calibration Standards

Calibration Standard Concentration, µg/L	Amount of solution to add to volumetric, mL	Concentration of solution added to volumetric, µg/mL	Final Volume, mL	µg CN per 50 mL
500	2.5	10	50	25
250	1.25	10	50	12.5
100	0.50	10	50	5.0
50	0.25	10	50	2.5
10	0.050	10	50	0.50
5.0	0.025	10	50	0.25

11.0 Sample Collection, Shipment, Preservation and Storage

See SOP 4610 for details. Samples shall be placed on ice immediately after collection. The holding time is 14 days for a refrigerated sample (4°C) with proper chemical preservation (pH > 12). Distillation and analysis must occur within the 14 day period to be compliant.

12.0 Quality Control

The following details the QC requirements that apply to this analysis. Each Quality Control Indicator (QCI) provides information pertaining to either method or individual sample performance. Our goal is to produce defensible data of known and documented quality.

The results of these QCI samples are used to assess the acceptability of data.

12.1 Blanks

Method Blank analysis is performed to determine if any contamination is present in the analytical process and is used to evaluate acceptance of the batch of samples. A method blank shall be prepared once per preparation batch of 20 or less samples per matrix type (see Section 6 for definition of a prep batch). If more than 20 samples are prepared a second blank shall be prepared after the twentieth sample. The method blank shall be processed through all preparatory steps used for the samples, including cleanup procedures. The blank shall be analyzed using the same instrument and conditions as the samples.

12.2 Laboratory Control Sample (LCS)

The LCS is used to evaluate the performance of the total analytical system, including all preparation and analysis steps. The LCS shall be prepared once per preparation batch of 20 or less samples per matrix type. If more than 20 samples are prepared a second LCS shall be prepared after the twentieth sample. The LCS shall be processed through all preparatory steps used for the samples, including cleanup procedures. The LCS shall be analyzed using the same instrument and conditions as the samples. Refer to SOP 4610 for preparation and concentration instructions. OPTION: Two LCSs (a high and a low concentration) may be distilled with each batch to ensure that the distillation process is effective and in control.

12.3 Duplicates

Duplicates of field samples or of the LCS must be prepared in compliance with the method requirements and client directives. Note: the analysis of the Matrix Spike Duplicate (MSD) is used as a substitute for the laboratory duplicate. In those cases when there is insufficient sample to perform either a duplicate analysis or MSD analysis, the duplicate analysis of the LCS (LCS/LCSD) is used to judge the precision of the analytical results.

12.4 Matrix Spike and Matrix Spike Duplicate (MS/MSD)

MS/MSDs indicate the effect of the sample matrix on the precision and accuracy of the results generated using the selected method. This information does not determine the validity of the entire batch. MS/MSDs must be analyzed at a minimum of 1 per 20 samples per matrix per preparation procedure, or as specified by the required test method. If an MS/MSD pair is not analyzed in the preparation batch, an LCS/LCSD pair is analyzed.

Samples chosen for matrix spiking are rotated among different clients and/or different client projects. This is accomplished through communication between the Department Manager and the analyst. In addition, designated samples, as indicated by client request or contract requirement, are matrix spiked.

The MS/MSD pair shall be processed through all preparatory steps used for the samples. They shall be analyzed using the same instrument and conditions as the samples. Refer to SOP 4610 for preparation and concentration instructions. Some clients may require different spiking levels, these specific needs are documented on the request for analysis forms.

13.0 Calibration and Standardization

Initial Calibration (ICAL)

In addition to achieving the reference method requirements for the minimum number of calibration standards and the acceptance criteria (statistics) for calibration curve fit, the following ICAL criteria also apply:

13.1 The ICAL must be a minimum of 5 standards, not including a blank.

13.2 The ICAL must be verified with a second source standard (ICV) prior to the analysis of samples.

13.3 Results of samples not bracketed by the ICAL range must be qualified on the final report. If possible, dilute the sample or extract and reanalyze in order to achieve a result within the calibrated range of the instrument.

13.4 The lowest calibration standard establishes the reporting limit: RL = 0.005 mg/L for waters and 0.25 mg/Kg for soils (as received basis). The RL must be greater than the detection limit.

13.5 Samples must be quantitated from the initial calibration curve and may not be quantitated from any instrument CCV.

Initial Calibration Verification (ICV)

In addition to the method requirements, the following ICV criteria also apply:

13.6 Must be a second source standard from the ICAL standards or from a different manufacturer lot number.

13.7 Must be traceable to NIST when available.

13.8 Must be analyzed when an ICAL is not performed on the day of analysis, prior to sample analysis.

Continuing Calibration Verification (CCV)

In addition to the method requirements, the following CCV criteria also apply:

13.9 May be analyzed at the beginning of the batch to check the CCV recovery.

13.10 Must be analyzed after every 10 samples and at the end of each analytical batch.

13.11 If the CCV results obtained are outside the acceptance criteria, corrective actions must be performed. If routine corrective actions fail to produce an acceptable *second consecutive (immediate)* CCV, then either the lab has to demonstrate performance after corrective action with two consecutive successful CCVs, or a new ICAL must be performed. If the instrument has not demonstrated acceptable performance, sample analyses cannot continue until a new ICAL is established and verified with an ICV. However, sample data associated with an unacceptable CCV may be reported as qualified data under the following special conditions:

13.11.1 When the acceptance criteria for CCV are exceeded high, i.e., high bias, and there are associated samples that are non-detects, then those non-detects may be reported. Otherwise the samples affected by the unacceptable calibration verification must be reanalyzed after a new ICAL has been established, evaluated and accepted.

13.11.2 When the acceptance criteria for the CCV are exceeded low, i.e., low bias, those sample results may be reported if they exceed a maximum regulatory limit/decision level. Otherwise the samples affected by the unacceptable verification must be reanalyzed after a new ICAL is established and verified with an ICV.

13.11.3 When the acceptance criteria for the CCV are exceeded and it is not possible to reanalyze the sample due to limited sample quantity AND a new sample cannot be obtained by the laboratory, the data may be reported with the appropriate data qualifiers if the client has been contacted and agrees, in writing, to accept the qualified data.

13.12 Records: Initial and Continuing Calibration Records will contain, at a minimum, the following:

Calibration date
Test method
Instrument
Analysis date
Each analyte name
Analyst's initials or signature
Standard Concentration (appropriate units) and number of standards
Response (appropriate units)
Calibration curve or response factor
Evaluation of and Statistics for ICAL curve fit in order to judge calibration curve acceptance
Evaluation of and Acceptance Limits for ICV analysis in order to judge calibration curve acceptance
Evaluation of and Acceptance Limits for CCV analysis in order to judge continuing calibration acceptance
Calibration Standards and Reagent Solutions IDs

Calibration Acceptance Summary (see Table 2):

Table 2 Calibration Requirements

QCI	Frequency	Standards	Control Limits	Corrective Action
ICAL	Daily or as needed, minimum monthly	Minimum 5 standards, see Table 1 for concentrations	$r^2 = 0.99$	Correct problem then repeat initial calibration
ICV	After each new ICAL, and at the beginning of each batch	100 µg/L	± 10% of true value	Correct problem then repeat initial calibration
CCV	Beginning (optional), every 10 samples, and end of the batch	250 µg/L	± 10% of true value	Correct problem then repeat CCV or repeat initial calibration

Support Equipment

Autopipettes - Check autopipette to ensure standardization is within control limits (see SOP 1040 for Pipette Calibration).

Balances - Be sure the balance is checked prior to use and performance criteria are met (see SOP 1040 for Calibration of Balances).

14.0 Procedure

14.1 Instrument Start Up

14.1.1 Turn on the power to all modules by turning on the power strip and allow the autosampler to perform its startup routine. Wait until the autosampler stops with the probe above the wash bath.
14.1.2 If necessary, install the manifold on the channel you want to run. (See Appendix E.)
14.1.3 Make all the injection fluidic connections.
14.1.4 Make all the cell fluidic connections.
14.1.5 Set all pump tubes on the pump. (Varies method to method.)
14.1.6 Run reagent water through all the lines to make sure there are no leaks.
14.1.7 If there are no leaks, put actual reagents in line.
14.1.8 ALWAYS start pumping Buffer Solution FIRST.
14.1.9 Pour the calibration Standards into Standard vials, and place into the autosampler Standards Rack.
14.1.10 Pour the Samples into 15 mL test tubes and place into the Sample Rack.
14.1.11 If necessary, insert the interference filter into the upper slot in the detector.
14.1.12 Turn on the Heater by increasing the Set Point to 60°C.
14.1.12.1 Locate the heater control on the right hand side of the channel
14.1.12.2 Press the Set Point Key (Left of the arrow keys) until the display shows the letters SP for Set Point.
14.1.12.3 Press the big arrow keys for setting the temperature.
14.1.12.4 Once the temperature has been set, press the ENTER key to save the information.
14.1.12.5 Press the Set Point key once. The display will show the current temperature in Celsius. The red light will be lit when the heater is ON.

14.2 Software Set up

14.2.1 Double click on the **Omnion FIA** icon. Then click **OK**. The autosampler probe should go into the wash bath and the dilutor activity may be heard, the injection valves may turn to the inject state if they were not already there.
14.2.2 Log In with your user name and password. [User name: demo with no password will also get you in]. The Main Menu should appear.
14.2.3 From the Main Menu click on the Instrument button labeled **FIA Instrument 1.** Each valve allocated to this instrument will be cycled in turn from Load to Inject and back to Inject again. Omnion will automatically open the last Method and Tray that was used. (The names will appear at the top in the title bar.)

14.3 Open the Cyanide Method (To Create a Method see Appendix B)

14.3.1 Click on the **Method** button, or from the Main Menu click on **File**, then **Open Method**. This will open the Open Method Dialog window.
14.3.2 Double click on the method file you want to open: **Cyanide.met**. Or click once then click on **OK**.
14.3.3 From the Main Menu click on the Instrument button labeled **FIA Instrument 1.** Each valve allocated to this instrument will be cycled in turn from Load to Inject and back to Inject again. Omnion will automatically open the last Method and Tray that was used. (The names will appear at the top in the title bar.)

14.4 Opening and Editing the TRAY

14.4.1 Click on the **Tray** button or from the Main Menu, click on **File,** then **Open Tray**.
14.4.2 Click twice on the name of the tray you wish to open. (**Cyanide.tra**) The First rows of the tray spreadsheet are blue. This denotes that these samples are actually Calibration Standards. This is from the method and will not change. The Sample **Type** is **Cal Std**. And the **Level** is NEVER 0, it will be a number form 1 to 14 (This will match the level in the Analyte Table in the method.) The Cup Number (**Cup #**) refers to the cup number in the Standard Rack and will be a number between 1 and 14.
14.4.3 Edit the **Sample ID**. Using the mouse, move the pointer to the cell and click once; type in the new ID. In the Sample Rack Loading Aid (Top Left) the sample cup you are editing will be in green.)
14.4.4 The Cup Numbers (**Cup #**) for sample will be anything between 1 to 90.
14.4.5 The **Level** column is **0** for all samples of **Sample Type** of **unknown**
14.4.6 The **Reps** for samples and standards is **1**.
14.4.7 To Schedule manual QC See Appendix C (DQM Plan)

14.5 Click on the **Run Tray** button. (Or from the Main Menu, click on **Tray** then **Run Tray**.)

14.5.1 Leave the Method and Tray boxes empty to use the one that are active (open).
14.5.2 In the Data File box enter the name for your run. i.e. 981006Ca. YYMMDD C (for Calibration) and a (for number of the run... a b c ...) The extension *.fdt (FIA Data) is used by default.
14.5.3 The Autosampler Position refers to the autosampler sample rack position; 1, 2 or 3.
14.5.4 **Skip Recalibration Block** Box can be checked when you want to run a tray that contains Cal standards and samples but you want only want to run samples
14.5.5 While the tray is processing, you can view the peaks and runtime report.

14.5.6 If the baseline does not appear on the screen change Display options.
14.5.7 Click **Method**, then **Display Options**
14.5.8 Specify the channel: 1.
14.5.9 Specify the voltage scale on the Y axis (i.e. -1 to 3).
14.5.10 Click **OK**.

14.6 Analyze samples for Cyanide. Click on the **RUN** button. The tray will start running. After the pump is allowed to pump at a normal speed for the period specified it the method, pump timing, the autosampler will move to the first calibration standard. The Standards and samples are done in Row order no matter where they are located on the sampler.

14.7 While running you will see a **STOP** sign on the tool bar, to suspend the tray click on the STOP sign. The Tray will pause and the computer gives you the choices of aborting or resuming the tray. At the end of the tray, after the last sample ID entered is reported, the sample probe should return to the wash bath and the **STOP** button will turn back into the **RUN** button.

14.8 System Shutdown Procedure

14.8.1 Remove the regent transmission lines and place into the rinse solution and pump for 5 minutes at standard speed.
14.8.2 Place the lines into reagent water and allow the system to rinse 5 to 10 minutes at standard speed.
14.8.3 Remove the lines from the reagent water and allow all liquid to be pumped out of the manifold.
14.8.4 Turn off the pump and release the pump tube cartridges tension. Press the tube cartridges holders on the sides of the Ismatec pump.
14.8.5 Turn off the Header by Reducing the Set Point to a temperature lower than room temperature. (e.g. 15°C).
14.8.6 Close all files
14.8.7 Switch off the master power strip

14.9 Documentation requirements. Record the following information in the appropriate logbook or data file. Include any deviations from this procedure.

Analyst initials, date [and time if required by the specific project or QAPP] of analysis, sample number or ID, initial sample volume or weight processed, final digestate volume, calibration standard sample or solution identifier, QC sample or solution identifier, reagent solutions identifiers, any dilution information, [beginning and ending times of analytical steps if required by the specific project or QAPP], data file name or batch ID, instrument method name, visual observations, and any other information as deemed necessary.

14.10 Routine Maintenance – Record all maintenance in the logbook. See Appendix F

15.0 Data Reduction, Calculations and Loading

15.1 The data system will then prepare a calibration curve by plotting response versus standard concentration. Sample concentration is calculated from the regression equation.

NOTE: The LIMS program will convert µg/L or µg/Kg (part per billion) concentrations from the instrument readout to mg/L or mg/Kg (part per million).

15.2 Report only those values that fall between the lowest and highest calibration standards. Samples exceeding the highest standard must be diluted and reanalyzed.

15.3 Aqueous Samples: The concentration readout for aqueous sample distillates is µg CN/L. It does not need further data reduction unless the initial sample volume was less than 50 mL. If less than 50 mL sample was distilled, calculate the concentration as follows:

Concentration in mg CN/L = readout * 0.001 (50 mL/ initial sample volume analyzed in mL)

15.4 For sample results greater than the highest calibration standard, dilute the sample in a 15 mL tube using 0.25N NaOH. Pipet in the appropriate volume of sample into the tube, dilute to total volume 10 mL with 0.25N NaOH, cap and mix well. Record the volume of distillate used for analysis. Dilution Factor = (10 mL/ distillate volume analyzed in mL). Use the dilution factor and calculate the concentration in aqueous samples as follows:

Concentration in mg CN/L = readout * 0.001 (10 mL/ distillate volume analyzed in mL)

15.5 Reactive Cyanide Distillation Samples: The concentration readout for soil and waste samples that underwent the reactive cyanide distillation procedure must be multiplied by the following factor: Factor = (50/ sample weight in g). Calculate the concentration of Releasable Cyanide in soil and waste samples as follows:

Concentration (Releasable CN) in mg CN/Kg = readout * 0.001 (50/ sample weight in g)

15.6 For sample results greater than the highest calibration standard, dilute the sample distillate in a 15 mL centrifuge tube using 0.25N NaOH. Pipet in the appropriate volume of distillate into the tube, dilute to total 10 mL with 0.25N NaOH, cap and mix well. Record the volume of distillate used for analysis. Dilution Factor = (10 mL/ distillate volume analyzed in mL). Calculate the concentration of Releasable Cyanide in soil and waste samples as follows:

Concentration (Releasable CN) in mg CN/Kg = readout * 0.001 (50/ wt g) * (10 mL/ distillate mL)

15.7 Soil Samples: The concentration readout for soil samples must be multiplied by the following factor: Factor = (50 / sample weight in g). Calculate the concentration in soil samples as follows:

Concentration in mg CN/Kg = readout * 0.001 (50/ sample weight in g)

For soil sample results greater than the highest calibration standard, follow the dilution procedure in section 15.6

15.8 Soil samples reported on a dry weight basis: The concentration is divided by the decimal equivalent of the percent residue of the soil at 105^0C.

15.9 Report results in mg CN/L, or mg CN/Kg, or Releasable Cyanide in mg CN/Kg.

15.10 The procedure for uploading data into the LIMS system is detailed in SOP 1400 LIMS.

16.0 Method Performance

Demonstration of Capability (DOC)

All parameters of interest must meet the method acceptance criteria before actual sample analysis begins. See SOP 1230 Training for the procedure to perform and document the DOC. The DOCs for the analysts performing this method are located in the analysts' training form folders located in the QA office files.

A quality control (QC) reference concentrate is required containing cyanide at a concentration of 0.05 mg/L for aqueous samples and 2.5 mg/Kg for soil samples using the ICV/LCS solution. The QC reference sample is made using stock standards prepared independently from those used for calibration. Other lower concentrations may be used.

For each analyte calculate the mean recovery (X) and standard deviation (s) and the average % Recovery (%R). Compare X and s and %R with the corresponding acceptance criteria for accuracy and precision, respectively. Note: For aqueous samples, X must be within 0.05 ± 0.005 mg/L and s must be less than 0.005 mg/L and %R must be within 100 ± 10%. Note: For soil samples, X must be within 2.5 ± 0.5 mg/Kg and s must be less than 0.5 mg/Kg and %R must be within 100 ± 20%. These limits are taken from established in-house criteria If X and s and %R for all analytes meet the acceptance criteria, the system performance is acceptable and analysis of actual samples can begin. If X or %R falls outside the range for accuracy, or s exceeds the precision limit, then the system performance is unacceptable for that analyte and corrective action must be taken.

The Analyst performing the analysis on the LaCHAT AutoAnalyzer need only perform one DOC (either the aqueous or the soil DOC) to demonstrate capability in the analysis.

Comparison to Reference Method Data

There is no stated reference method criteria for LCS, Duplicate Sample or MS/MSD recoveries in EPA Method 9012A. The method does require the recovery of an independent calibration check standard (ICV) to be within ± 15% of the true value. The method also recommends that high and low calibration standards be distilled to monitor the distillation procedure. Recovery of the distilled standards is to be within ± 10% of the true value. The laboratory distills one LCS solution with each batch instead of two calibration standards. The in-house recovery acceptance limits for the ICV and the LCS samples is 100 ± 10% of true value. This satisfies the method requirement for the ICV and the method recommendation for the distillation check.

In-House Control Limits

Method performance data is on file in the laboratory QC department. Comparison of method performance data for the laboratory to the reference method criteria occurs when laboratory in-house acceptance limits are generated. In-house generated data is compared to the specifications of the reference method. If the in-house limits are within the specifications of the reference method, the control limits are updated in LIMS. If the in-house limits are not within specifications, an investigation is performed to determine the cause(s) of the problem and a corrective action is completed. The analysis may continue until enough data points are collected to regenerate new control limits. Any QC data generated outside of reference method limits during that time frame is flagged.

The laboratory maintains performance records to document the quality of data that is generated. Method accuracy for samples is assessed and records maintained.

Control limits for the method parameters are generated by the QC staff and distributed to the analyses via updates to the LIMS control charts. The control limits are calculated based on in-house performance data. At a minimum, these limits are updated annually.

17.0 Pollution Prevention

The preparation of excessive volumes of laboratory reagents and standards shall be avoided so that waste and potential for pollution are minimized. Samples, reagents and standards shall be disposed in compliance with the laboratory waste disposal program and applicable waste disposal regulations. With the consent of the client, the samples may be returned to their origin for treatment.

Uncontaminated paper waste, glass and cans should be separated for recycling. Laboratory staff are required to protect the laboratory's and our clients' business information when disposing of recycling or waste from the facility.

18.0 Data Assessment and Criteria for Quality Control Measures

The laboratory must maintain records to document the quality of data that is generated. Ongoing quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. The data review is conducted according to SOP 1250 Data Review.

Method Blank (MB)

If the blank exceeds the RL (the lowest calibration standard), the source of contamination must be investigated and corrective actions taken.

Affected samples must be reprocessed and reanalyzed **or** Data must be appropriately qualified if:

1) The concentration of a targeted analyte in the blank is at or above the reporting limit as established by the SOP or by regulation, AND is greater than 1/10 of the amount measured in any sample.

2) The blank contamination otherwise affects the sample results as per the test method requirements or the individual project data quality objectives.

Laboratory Control Sample (LCS)

The results of the individual batch LCS are calculated in percent recovery (%R) and compared to established acceptance criteria (in-house limits). LCS %R limits are 100 ± 10% for both aqueous and soil samples. If the LCS is outside the acceptance criteria, the analytical system is "out of control". Any affected samples associated with an out of control LCS must be reprocessed and reanalyzed or the results reported with appropriate data qualifiers.

Matrix Spikes

The results from MS/MSD are primarily designed to assess the precision and accuracy of analytical results in a given matrix and are expressed as percent recovery (%R) and relative percent difference (RPD). See the STAT QAM, Section 5.4 for the calculation for RPD. Results are compared to established acceptance criteria (in-house limits). For aqueous samples, MS/MSD %R limits are 100 ± 25% and RPD limits are 20%. For soil samples, MS/MSD %R limits are 100 ± 25% and RPD limits are 20%. For matrix spike results outside established criteria corrective action must be documented, or the data for the spiked sample is reported with appropriate data qualifying codes.

Duplicates

The results from laboratory Duplicates are designed to assess the precision of analytical results in a given matrix and are expressed as relative percent difference (RPD). See the STAT QAM, Section 5.4 for the calculation for RPD. Results are compared to established acceptance criteria (in-house limits). RPD limits are 20%. For duplicates results outside established criteria corrective action must be documented, or the data for the duplicate sample is reported with appropriate data qualifying codes.

19.0 Corrective Actions for Out-of-Control Data

The process for handling corrective actions is found in SOP 230 Corrective Action.

If the CCV, MB, LCS/LCSD, MS/MSD, or lab duplicate recovery of any parameter falls outside the designated acceptance range, the laboratory performance for that parameter is judged to be out of control, and the problem must be immediately identified and corrected. The analytical result for that parameter in the samples is suspect and is only reported for regulatory compliance purposes with the appropriate corrective action form. Immediate corrective action includes reanalyzing all affected samples by using any retained sample before the expiration of the holding time. Final data results must be qualified in the client report for reported results not meeting the laboratory defined criteria.

1) Review standards preparation logbooks. Check all calculations and ensure dilution factors are properly recorded.

2) Re-prepare the suspected standard or QC sample to identify possible preparation errors of the standard or QC sample.

3) Re-Analyze the samples when the CCV or LCS are not within acceptable limits.

4) Perform routine preventative maintenance following manufacturer's specification. Record all maintenance in the instrument logbook.

20.0 Contingencies for Handling Out-of-Control Or Unacceptable Data

Every effort is made to prevent problems from occurring. When out of control or unacceptable data occurs the first option is to identify the problem and reanalyze the samples within the holding times. When this is not possible, the QA Manager and/or the Laboratory Director reviews data and discusses options with the client. Reanalysis or reporting the data with qualification are alternatives. Out of control or unacceptable data reported to the client must include the data qualifier, flag and discussion on the rationale for reporting.

The process for handling unacceptable and out of control data is found in the Laboratory QAM Section 11. The reporting of data that is out of control must be approved and documented by Quality Assurance Manager and either the Technical Manager or the Laboratory Director.

21.0 Waste Management

The STAT Analysis Corporation SOP 1130 Waste Disposal identifies proper waste management practices for the chemicals and biological materials used in this procedure. Samples are stored and discarded accordance with SOP 1130 Waste Disposal.

22.0 References

22.1 Method 9012A, U.S. EPA SW-846 "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods" Update III, December 1996
22.2 Determination of Cyanide by Flow Injection Analysis, QuikChem Method 10-204-00-1-V
22.3 STAT SOP 4610 Total and Amenable Cyanide: Distillation by EPA 9010B
22.4 STAT SOP 4615 Reactive Cyanide and Sulfide Distillation
22.1 STAT SOP 1040 General Laboratory Procedures
22.2 STAT SOP 1020 Glassware Cleaning
22.3 STAT SOP 1010 Standard and Reagent Preparation
22.5 STAT SOP 1000 Control and Use of Laboratory Notebooks
22.6 STAT SOP 230 Corrective Actions
22.7 STAT SOP 1400 LIMS
22.8 STAT SOP 1130 Waste Disposal
22.9 STAT SOP 003 Chemical Hygiene Plan
22.10 STAT SOP 1250 Data Review
22.11 STAT SOP 1230 Training
22.12 STAT SOP 1210 Method Detection Limits (MDLs)
22.13 STAT Analysis Corporation Quality Assurance Manual
22.14 QuikChem 8000 Automated Ion Analyzer Omnion FIA Software.
22.15 QuikChem 8000 Automated Ion Analyzer Continuum Series "Flow Injection Analyzer" Hardware Installation and System Operation.

23.0 Forms, Figures, Tables, Diagrams, Flowcharts, Attachments or Validation Data

23.1	Appendix A	Troubleshooting
23.2	Appendix B	Creating a Method
23.3	Appendix C	DQM Plan
23.4	Appendix D	Manifold Diagram
23.5	Appendix E	Manifold Installation/ Removal
23.6	Appendix F	Maintenance Schedule

Appendix A – Trouble Shooting

Keep all modules clean and dry at all times.

Keep in Stock:	Pump tubes	green
		red
		red
	Teflon tubing:	0.8 mm id Manifold
		0.5 mm id Low Flow Manifold
		0.6 mm id Restriction Coil
		o-rings
		Transmission Tubing

Routine Maintenance (See Appendix F for the Maintenance Schedule)

Pump

- After each day rinse the cartridges in DI Water to wash any spills. Clean pump surfaces, except rollers, with a wet cloth. Dry all surfaces
- If rusty clean rollers with steel wool. A light coat of silicon spray can be applied by spraying on a lint free cloth and holding it to the moving rollers
- Check for wear, cracks or acid damage on the cartridges ad holders
- Replace pump tubes that start to show signs of wear
- If the pump tubes burst, clean all cartridges and holders, as well as, the pump, Immediately.
- All surfaces should be kept clean. Use a damp cloth to clean the module surfaces. Dry surfaces thoroughly.

Valve Modules

- Keep the instrument clean and dry at all times.
- Replace o-rings once per month
- When changing the o-rings, clean the valve ports with a cotton swab and reagent water. This will help remove any dirt or precipitate that may prevent a good seal. If a leak persists, replace the new o-rings and make sure the connector itself does not have precipitate on the thread.
- All surfaces should be kept clean. Use a damp cloth to clean the module surfaces. Dry all surfaces thoroughly.
- The internal sample loop valve will give thousands of injections without trouble. The rotor seal wears with use and is the only part that needs routine replacement.

Detector Modules and Flow Cell

- If a flow cell appears to leak remove it immediately to keep all liquid form the electronics inside the detector head.

Instrument Troubleshooting

For problems with the instrument see the QuikChem 8000 Automated Ion Analyzer Continuum Series “Flow Injection Analyzer” Hardware Installation and System Operation Manual under the Troubleshooting Section.

Appendix B – Creating A Method

1.1 Click on the **Method** button, or from the Main Menu click on **File**, then **New Method**.
1.2 Then Method will open and you will see the Analyte Table
1.3 Click on Analyte Name of channel and press backspace to delete. Enter the new analyte name. If an analyte name is not present the system will ignore that channel.
1.4 Fill out the analyte Table.

Channel	1
Analyte Name	Cyanide
Concentration	µg CN/L
Level 1	**500**
Level 2	**250**
Level 3	**100**
Level 4	**50**
Level 5	**10**
Level 6	**5**
Level 7	**0.00**

Calibration Rep Handling	Average
Calibration Fit Type	2nd Order Polynomial
Force Through Zero	No
Weighting Method	None
Concentration Scaling	None
Chemistry	Direct
Injection to Start Peak	6.0 s
Peak Base Width	25s
% Width Tolerance	70%
Threshold	5000

1.3 From the Main Menu, click on **Method**, then **Valve Timing**
1.4 Enter the **Method Cycle Period**. 40s
1.5 Sample Reaches the first valve 18s (For Standard Pump Sample Assembly) (travel time from sample probe to port 6 usually 24 s if dilutor enter 28s)
1.6 **Load Period** 20s
Load Time 0s
Inject Period 20s
Notice that Load Period + Injection Period = Cycle Period
1.7 Click **OK**

1.8 From the Main Menu, click on **Method**, then **Sampler Timing**.
1.9 The Sample Prep Sequence box is optional
1.10 Enter the **Minimum Probe in Wash Period** 5.0 s
1.11 Enter the **Probe in Sample Period** 34s
1.12 Click **OK**.

1.13 From the Main Menu, click on Method, then Pump Timing
1.14 Check the **Go to Standby on Idle** box X
1.15 Enter **Idle Before Standby** 180.0s
1.16 Enter **At Speed Before Analysis** 45.0s
1.17 Click **OK**.

1.16 From the Main Menu, click on **File**, then **Save Method As**
1.17 The FIA Method File Header will appear. Write a method description (analyte and sample loop size) and click **OK**. (i.e. **Cyanide Sample Loop XXX cm**)
1.18 The Method Save As dialog box will appear.
1.19 C:\ Omnion\Methods\
Change the name to **Cyanide.met**

II To Fine Tune the Method
1.0 After you have run a data.
1.1 Open a file from the main menu click on File, Open Data. and click twice on the Data file name. i.e. 981006Ca.fdt.
1.2 Load the original method form this data by clicking on the Data menu the Load Method.
1.3 You should see the peaks on the screen.
1.4 Click on Data then Reanalyze Data. (Or click on the Reanalyze button.)

2.0 Fine Tuning the Threshold
2.1 Look before and after the tray to see some baseline.
2.2 From the menu click on **Method**, then **Graphical Events Programming...**
2.3 Click on **Threshold**.
2.4 The Status bar will prompt you to "Select Start of Baseline Section".
2.5 Set the cursor at the beginning of the baseline region and click once.
2.6 You will be prompted to "Select End of Baseline Section".
2.7 Move the mouse pointer to the end of the baseline region and click again.
2.8 Omnion calculates a Threshold value.
2.9 Click on **OK** to enter the value in the Analyte Table of your method

3.0 Fine Tuning the Peak Base Width
3.1 From the menu click on **Method**, then **Graphical Events Programming...**
3.2 Click on **Peak Base Width**.
3.3 You will be prompted to "Select Start of Peak"
3.4 Set the cursor at the beginning of the high standard and click once.
3.5 You will be prompted to "Select End of Peak"
3.6 Move the cursor to the end of the peak and click again.
3.7 Omnion calculates a Peak Base Width.
3.8 Click on **OK** to enter the value in the Analyte Table of your method

4.0 Save these new method parameters by clicking on **File**, then **Save Method As**.

5.0 Viewing a Method's Calibration
5.1 Up to 4 replicates of each Standard can be applied to a method's calibration.
5.2 If not already open, load the method form the data file by clicking on Data, Load Method.
5.3 Click on the button. (or from the main menu click on **Method**, then **Review Analyte Calibration Curve**. The Review Analyte Calibration window will appear.
5.4 Click **Fit**, then **Clear**. to 'Clear' the Calibration Replicate Table.
5.5 Click **Exit**.
5.6 Click the **Analyze** button. The re-analysis occurs exactly as it did in the actual tray run.
5.7 Click on the **Review Calibration** button again to see the curve.

6.0 Editing the Calibration
6.1 Clicking twice on any of the results in the calibration replicate Table will turn it red and make it unused in the calibration.
6.2 To Use the point again, click twice on it again, and it will turn form red back to blue.

Appendix C – DQM Plan

DQM Plan

Consists of one or several DQM Sets. Each Sets has one or more samples. The DQM has 3 sections; the DQM Set box, the DQM Sample Box, and the Channel Data box.

1.0 Adding DQM Sets
1.1 Click Tray, then Load DQM.
1.2 In the DQM Set Box click on the drop-down button showing the **DQM Set ID**, type in a new name. (Check Standards, Duplicates, Matrix Spikes)
1.3 For the Check Standards Set check the **Automatic** box **X**.
1.4 Click **ADD** to add the set.

NOTE: Automatic Sets never have their sample info in the tray table and the samples are loaded in the standards rack. Manual sets have their sample info in the tray table and the samples are loaded in the sample rack.

2.0 Adding DQM Samples
2.1 In the DQM Sample Box, click on the drop-down button showing the **DQM Sample ID** and type in a new name (ICB, ICV, CCV, CCB, Method Blank, Dup 1, Spike, Spike Dup)
2.2 Click on the **Append** button.
2.3 **Replicates** should be **2**
2.4 Click on the drop-down button showing the **Type** and select the type of sample. (Blank, Unspiked, Spiked, AbsChkStd, RelChkStd, Dup 1, Dup 2)
2.5 For the Automatic Check Samples enter the **Standard Rack Cup**.

3.0 Editing Channel Data information.
3.1 In the Channel Data Box, select the appropriate channel.
3.2 If you can't see the Test 1 row, click on the **Add Test** button.
3.3 The Test Explanation spells out the test that will be done for this DQM Sample and depends on what Type the DQM Sample is.
3.4 If the standard has a known concentration it needs to be entered in the **Known Conc** box along with the **Conc Units**.
3.5 Enter the **Test Limit**. 10.000% difference.
3.6 Select a Fail Action from the drop-down menu. **Recalibrate & Repeat**, **Alarm & message**.
3.7 Enter the Pass/ Fail Message.

NOTE: A Test Passes if test value < = Test Limit
A Test Fails if Test value > Test Limit

3.8 You can perform more then 1 test on each check sample.

4.0 Scheduling Automatic DQM Sets
4.1 From the Main Menu, click on **Tray**, then **Auto DQM Schedule**
4.2 Select the **Auto DQM Set** from the drop-down menu.
4.3 Check the box(es) for the frequency of the sample
4.4 Click **OK**.

5.0 Inserting Manual DQM Sets
5.1 Click on the **Tray Table** button.
5.2 Click on the row number Before which you want to insert the check sample.
5.3 From the Main Menu, click on **Tray**, then **Manual DQM Insertion**.
5.4 Click on the **Manual DQM Set** you wish to insert.
5.5 Enter the **Sample ID**'s of the DQM samples to reflect the actual identity of the samples. (Note: The manual DQM sample rows are green.)
5.6 Renumber the Cup Numbers (**Cup #**) below the inserted Manual DQM Set by clicking and dragging all the rows and cup numbers you wish to renumber.
5.7 Click on **Tray**, then **Renumber Cups** (or **Ctrl-R**)
5.8 Enter the **Starting Number**
5.9 Enter an **Increment** of **1.**
5.10 Then click **OK**.

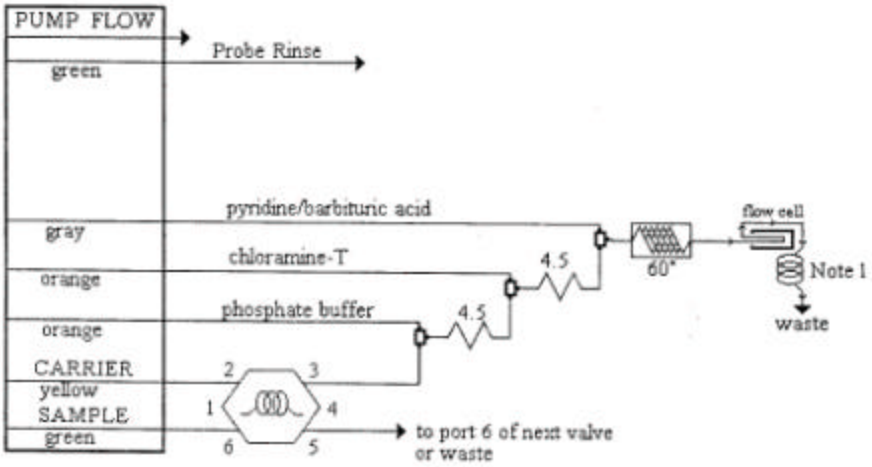
6.0 Calibration Pass/Fail Criteria
6.1 From the Main Menu, click on Method, then Calibration Failure Criteria
6.2 Select the appropriate channel.
6.3 Check the Minimum Correlation Coefficient (R2) Box and enter 0.995
6.4 Check the Maximum % Residual All Levels Box, and enter 10.0.
6.5 If the calibration passes, a message will be reported and the tray will continue to the nest row.
6.6 If the calibration fails, a fail message will be reported and you will be given a choice to Abort or Continue the tray.

7.0 Save the DQM Plan
7.1 From the Main Menu, click File, then Save DQM Plan, or Save DQM Plan As... and enter the File name CN.dqm. The default extension is *.dqm.

Appendix D – Manifold Diagram

17. TABLE, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

17.1. CYANIDE MANIFOLD DIAGRAM



Sample loop = 150 cm x 0.8 mm i.d.
QC8000 Sample loop = 150 cm x 0.8 mm i.d.

Interference Filter = 570 nm

CARRIER is 0.25 M sodium hydroxide solution (Reagent 1).

All manifold tubing is **0.8 mm (0.030 in) i.d.** This is **5.2 uL/cm**.

4.5 is **70** cm of tubing on a **4.5** cm coil support

APPARATUS: An injection valve, a 10 mm path length flow cell, and a colorimetric detector module are required. The shows **650 cm of tubing** wrapped around the heater block at the specified temperature.

Note 1: 2 meter back pressure loop, 0.52 mm i.d.

j:\users\tsd\ws\methods\1020401V.DOC 16 29-Sep-95dp

Appendix E – Manifold Installation/Removal

1.0 Unwrap the transmission lines from around the manifold and place the manifold over the sample processing module.
1.1 Remove the transmission lines from the union on the 650 cm side of the heating unit, insert both ends through the hole in the manifold and reseat the manifold onto the sample processing module.
1.2 Make the Injection Valve Connections as follows:
1.3 Port 1 & 4 - The Sample Loop 0.8 mm i.d. length 40 cm.
1.4 Port 2 - Carrier line is connected to Port 2 -> from valve, disconnect from fitting and connect to port 2 0.8 mm id and 30 cm long.
1.4 Port 3 - 20 cm 0.8 mm id between port 3 and the fitting on the manifold next to the label -> from valve where the carrier line was connected.
1.5 Port 5 - 15 cm 0.8 mm id. between port 5 and the waste line.
1.6 Port 6 - Sample Line. 130 cm (Varies method to method) connected to the probe on the autosampler, pump tube adapter, and 20 cm tubing connected to port 6 of valve.
2.0 Flow Cell Top tubing connected to waste line. Bottom line connected to the fitting in the manifold next to the label to flow cell ->.
Attach one of the lines from the heater to the union going to the flow cell.
Attach the other heater line to the pyridine-Barb. Acid Tee fitting.
3.0 Pump
3.1 Sample Line - Autosampler to injection valve 6
3.2 Wash Line - Reagent water to wash reservoir on the autosampler
3.3 Reagents Lines- Varies from method to method.
3.4 On the Ismatec Pump Cartridges the arrows point towards the System Unit with the tension lever on the left.
3.5 Place all of the reagents lines into corresponding containers or Reagent water.
3.6 Move tension levers to the maximum tension (Top Far Right Position)
3.7 Clamp down all pump tube cartridges. (Press down one side at a time.)
3.8 Move tension lever back from the top far right until it makes a clicking sound.
3.9 Set the reagent pump speed to 35.
3.10 Turn on the pump.
3.11 Depress the green button to turn the pump ON. The System Unit will take control over the pump speed. (The yellow button is the override standby button.)
3.12 Check to confirm that the probe wash reservoir is filing with rinse water.
3.13 Check for Leaks on the manifold, valve, flow cell or any of the connections.
3.14 Do NOT leave any pump tubes clamped down when the pump is shut off for more then a few minutes.
3.15 To Remove cartridges, Press the sides of the pump holder on which the cartridge is engaged.
4.0 Insert the interface filter into the detector module.

II Manifold Removal Procedure

1.0 Rinse the manifold

1.1 Detach the manifold tubing from the manifold fitting that is connected to Port 3 at the injection valve. Leave the piece of tubing attached to the injection valve.

1.2 Disconnect the carrier pump tube from Port 2 of the injection valve. Take this tubing and connect it to the manifold fitting that was connected to Port 3.

1.3 Detach output of the manifold from union on the flow cell tubing leave the union connected to the flow cell

1.4 Remove the back pressure loop, if necessary

1.5 Detach heating unit tubing from the manifold, and reconnect to the union underneath the manifold (650 cm side.)

1.6 Remove all manifold pump tubes from cartridges.

1.7 Remove the interface filter from the detector module

1.8 Remove the sample loop from Port 1 & 4 valve

1.9 Remove manifold from the Sample Processing Module (Channel)

1.10 Carefully wrap the transmission lines around the manifold and store it in the plastic bubble bag.

Appendix F – Maintenance Schedule

Daily	
AutoSampler	Clean Surfaces
AutoDilutor	Clean Surfaces
	Prime dilutor with DI water after using any other diluent
Pump	Clean Surfaces
	Rinse cartridges
Detector	Dry and Clean all Surfaces
System Unit	Keep Dry and Clean
Weekly	
Injection Valves	Clean Ports and valve connections
Monthly	
Autosampler	Clean rods/ moving parts
Pump	Spray silicon on cloth and rub on rollers
	Replace pump tubes
	Clean pump tube adapters
Manifold	Clean union and tee
6 Months	
Injection valves	Replace o-rings
Manifold	Replace o-rings
Yearly	
Manifold	Replace all tubing
Flow Cells	Replace flares and o-rings
Computer	Clean hard drive

Attachment 2

Pace Analytical Services, Inc.
Quality Assurance Manual and Standard Operating Procedures

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103	150	S-GB-ALL-O-002-Rev.01	Determination of Volatile Organics by GC/MS Reference Method: SW-846 Method 8260B with 5030B and 5035 and EPA 625
151	164	S-ALL-GB-O-003-Rev.00	Separatory Funnel Extraction Reference Method: EPA Method 3510C
165	193	S-ALL-GB-O-008-Rev.00	Determination of Semi-Volatile Organics by GC/MS)Selective Ion Monitoring) Reference Method: SW-846 Method 8270C-SIM
194	218	S-GB-I-043-Rev.01	Total Cyanide Using Micro-Distillation and Lachat 8000 Flow Injection Reference Method: SW-846 Method 9012A and EPA 335.4
219	239	S-GB-M-004-Rev.00	The Determination of Mercury by Cold Vapor Atomic Absorption Spectroscopy Reference Method: SW-846 Methods 7470A and 7471B
240	280	S-GB-M-006-Rev.00	Determination of Trace Metals in Waters and Wastes by inductively Coupled Plasma Mass Spectroscopy Reference Method: SW-846 Methods 6020A, 3010A and 3050B
281	290	S-GB-O-005-Rev.01	Soil/Semi Solid Sample Preparation for the Analysis of Gasoline Range Organics and Petroleum Range Organics By Wisconsin Modified GRO Reference Method: Wisconsin Modified Method for Determination of Gasoline Range Organics, SW-846 Method 5030B and 5035
291	333	S-GB-O-009-Rev.1	Aromatic Volatiles by Gas Chromatography using Photoionization Detectors Reference Method: SW-846 8021B and EPA 602

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343	361	S-GB-O-045-Rev.01	Microwave Extraction for the Determination of Polynuclear Aromatic Hydrocarbons Base\Neutral\Acids in Solid Matrices Reference Method: SW-846 Method 3546
362	382	S-MN-O-561-Rev.00	Determination of Parent and Alkylated PAH Compounds in Solid and Liquid Matrices by Gas Chromatography/Mass Spectrometry (GC/MS): Capillary Column Technique with Selective Ion Monitoring

QUALITY MANUAL

Quality Assurance/Quality Control Policies and Procedures

Prepared by Pace Analytical Services, Inc.
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Any printed documents in use within a Pace Analytical Services, Inc. laboratory have been reviewed and approved by the persons listed on the cover page. They can only be deemed official if proper signatures are present.

This is COPY# 173 distributed on 10-24-08 by BLH and is ____ CONTROLLED or X UNCONTROLLED.

Signature Page

This document, with the necessary addenda, has been accepted as the Quality Manual.

Laboratory General Manager	7/10/06 Date	Green Bay Laboratory Laboratory
Quality Manager	7/6/06 Date	
Technical Director	7/6/06 Date	
Technical Director	7/6/06 Date	
Technical Director	7/6/06 Date	
Technical Director	7/6/2006 Date	
Technical Director	7-10-06 Date	

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1.0 INTRODUCTION & ORGANIZATIONAL STRUCTURE

"To meet the business needs of our customers for high-quality, cost-effective analytical measurements and services"

Pace Analytical Statement of Purpose

1.1 Introduction to Pace

Pace Analytical Services, Inc. is a privately held, full-service analytical testing firm operating a nationwide system of laboratories. Pace offers extensive services beyond standard analytical testing, including: bioassay for aquatic toxicity, air toxics, industrial hygiene testing, explosives, high resolution mass spectroscopy (including dioxins, furans and coplanar PCB's), radiochemical analyses, product testing, pharmaceutical testing, field services and mobile laboratory capabilities. Pace has implemented a consistent Quality System in each of its laboratories and service centers. In addition, the company utilizes an advanced data management system that is highly efficient and allows for flexible data reporting. Together, these systems ensure data reliability and superior on-time performance. This document defines the Quality System and QA/QC protocols.

Pace Analytical's goal is to continue to combine its expertise in laboratory operations with customized solutions to meet the specific needs of its clients.

1.2 Statement of Purpose

To meet the business needs of our customers for high quality, cost-effective analytical measurements and services.

1.3 Quality Policy Statement and Goals of the Quality System

Pace Analytical is committed to providing the highest quality product to our clients, while maintaining good professional practices.

The management of Pace Analytical is responsible for maintaining the highest possible standard of service for our clients by following a documented quality system. The overall objective of this quality system is to provide reliable data by adhering to rigorous quality assurance policies and quality control procedures as documented in this Quality Manual.

All personnel within the Pace network are required to be familiar with all facets of the quality system and implement these policies and procedures in their daily work. This daily focus on quality is applied with the initial project planning, and is continued through all field and laboratory activities and ultimately, to the final report generation.

The management of Pace demonstrates its commitment to quality by providing the resources, including facilities, equipment and personnel to ensure the adherence to these documented policies and procedures. All Pace personnel comply with all current applicable state, federal, and industry standards (such as the NELAC and ISO 17025 standards).

1.4 Pace Analytical Core Values

- **INTEGRITY**
- **VALUE EMPLOYEES**
- **KNOW OUR CUSTOMERS**
- **HONOR COMMITMENTS**
- **FLEXIBLE RESPONSE TO DEMAND**
- **PURSUE OPPORTUNITIES**
- **CONTINUOUSLY IMPROVE**

1.5 Code of Ethics

Pace Analytical's fundamental ethical principles are as follows:

- Each Pace Analytical employee is responsible for the propriety and consequences of his or her actions.
- Each Pace Analytical employee must conduct all aspects of Company business in an ethical and strictly legal manner, and must obey the laws of the United States and of all localities, states and nations where Pace Analytical does business or seeks to do business.
- Each Pace Analytical employee must reflect the highest standards of honesty, integrity and fairness on behalf of the Company with clients, suppliers, the public, and one another.

Strict adherence by each Pace Analytical employee to this Code of Ethics and to the Standards of Conduct is essential to the continued vitality of Pace Analytical.

Failure to comply with the Code of Ethics and Standards of Conduct will result in disciplinary action up to and including termination and referral for civil or criminal prosecution where appropriate. An employee will be notified of an infraction and given an opportunity to explain, as prescribed under current disciplinary procedures.

1.6 Standards of Conduct

1.6.1 Data Integrity

The accuracy and integrity of the analytical results produced at Pace Analytical are the cornerstones of the company. Lack of data integrity is an assault on our most basic values and puts Pace Analytical and its employees at grave financial and legal risk. Therefore, employees are to accurately prepare and maintain all technical records, scientific notebooks, calculations and databases. Employees are prohibited from making false entries or misrepresentations of data (e.g., dates, calculations, results or conclusions).

Managerial staff must make every effort to ensure that personnel are free from any undue pressures that may affect the quality or integrity of their work; including commercial, financial, over-scheduling and working condition pressures.

1.6.2 Confidentiality

Pace Analytical employees must not (directly or indirectly) use or disclose confidential or proprietary information except when in connection with their duties at Pace Analytical. This is effective over the course of employment and for a period of two years thereafter.

Confidential or proprietary information, belonging to either Pace Analytical and/or its clients, includes but is not limited to test results, trade secrets, research and development matters, procedures,

methods, processes and standards, company-specific techniques and equipment, marketing and client information, inventions, materials composition, etc.

1.6.3 Financial Responsibility

Pace Analytical employees must accurately keep all books, records and accounts for which they are responsible. Employees are responsible for maintaining and safeguarding all company funds and/or assets in their possession or control. Additionally, all employees are responsible for submission of accurate reporting documents pertaining to payroll (timesheets, etc.) and reimbursement requests (expense reports, tuition reimbursement, etc.).

1.6.4 Drug-free Workplace

Pace Analytical recognizes that alcoholism and other drug dependencies are a significant social problem with a potential for causing severe detriment to the workforce. Employees have the right to work in an alcohol and drug-free environment. Employees are not to report to work under the influence of alcohol or controlled substances as prescribed in the Drug-free Workplace Program. The possession, use and sale of alcohol and controlled substances as well as detailed information regarding drug testing is described in the Drug-Free Workplace Program Policy handout provided to all new employees. Additional copies are available from Human Resources. Employees are obligated to conform to the strict Drug-Free Workplace Program Policy.

1.6.5 Conflict of Interest

Pace Analytical employees must avoid situations that might involve a conflict of interest or appear questionable to others. The employee must be careful in two general areas:

- Participation in activities that conflict or appear to conflict with Pace Analytical responsibilities.
- Offering or accepting anything that might influence the recipient or cause another person to believe that the recipient may be influenced. This includes bribes, kickbacks or illegal payments.

Employees are not to engage in outside business or economic activity relating to a sale or purchase by the Company. Other questionable activities include service on the Board of Directors of a competing or supplier company, significant ownership in a competing or supplier company, employment for a competing or supplier company or participation in any outside business during the employee's work hours.

1.6.6 Non-Harassment

Pace Analytical endeavors to provide a workplace free of both harassment and discrimination. Harassment of an employee or job applicant on the basis of race, color, creed, religion, national origin, sex, disability, age, marital status, sexual orientation, or any characteristic protected by applicable municipal, state, and federal laws is both illegal and a violation of company policy. Pace Analytical maintains a Sexual Harassment Prevention policy that clearly defines the company's stance against sexual harassment and provides a mechanism for reporting infractions. The Sexual Harassment Prevention Policy is addressed in employee orientation, and employees are provided the Policy handbook. Additional copies are available from Human Resources.

1.6.7 Proper and Professional Conduct

Employees are bound to use fairness, honesty and regard for the law in their business relationships with Pace Analytical investors, clients, suppliers, employees, and applicants as well as all local, national and international communities and governments.

1.6.8 Protection of Property

Pace Analytical employees have an obligation to protect all company and client property against loss, theft and misuse. Employees are responsible for maintaining an orderly, clean workplace. Employees are also liable for using company and client property for intended purposes only. Employees are prohibited from using company property for their personal use without the expressed permission of their supervisor or General Manager. No such use of property may be made after termination of employment with Pace Analytical. Employees must also make every effort to prevent the misuse of company and client property by other persons. Misuse includes selling, loaning or giving away company or client property.

1.6.9 Communication

Each employee is responsible for obtaining the information necessary to follow directives in the Code of Ethics and the Standards of Conduct, and for reporting to their management or Human Resources representative any observed deviations from these policies. The identity of the employee reporting the infraction will not be disclosed without his/her permission unless disclosure is unavoidable during an investigation. No adverse action will be taken against a Pace Analytical employee because he/she has reported a suspected impropriety. These reports will be treated in confidence to the maximum extent consistent with the fair and rigorous enforcement of the Code of Ethics and Standards of Conduct.

1.6.10 Compliance

All employees are required to read, understand and comply with the various components of the standards listed in this document. As confirmation that they understand this responsibility, each employee is required to sign an acknowledgment form annually that becomes part of the employee's permanent record.

1.7 Laboratory Organization

The Pace Corporate Office centralizes company-wide accounting, business development, financial management, human resources development, information systems, marketing, quality, safety and training activities. Pace Analytical's Director of Quality, Safety & Training is responsible for assisting the development, implementation and monitoring of quality programs for the company. See Figure 1.1 for the Corporate Organizational structure.

Each laboratory within the system operates with local management, but all share common systems and receives support from the Corporate Office.

A General Manager supervises each regional laboratory. Quality Managers at each lab report directly to their General Manager but receive guidance and direction from the Director of Quality, Safety & Training.

Under the direction of the General Manager, the technical staff of the laboratory is generally organized into the following functional groups:

- Organic Sample Preparation
- Wet Chemistry Analysis

- Metals Analysis
- Volatiles Analysis
- Semi-volatiles Analysis
- Radiochemical Analysis
- Product Testing
- Equipment Maintenance
- Microbiology

Appropriate support groups are present in each laboratory. Figure 1.2 represents a typical organizational structure for a laboratory operation. The organizational structure for a specific laboratory is part of each laboratory's addendum to this Quality Manual.

1.8 Laboratory Job Descriptions

1.8.1 General Manager

1. Oversees all functions of the operations.
2. Authorizes personnel development including staffing, recruiting, training, workload scheduling, employee retention and motivation.
3. Prepares budgets and staffing plans.
4. Monitors the Quality Systems of the laboratory and advises the Quality Manager accordingly.
5. Ensures compliance with all applicable state, federal and industry standards.

1.8.2 Quality Manager

1. Oversees the laboratory Quality Systems while functioning independently from laboratory operations. Reports directly to the General Manager.
2. Monitors Quality Assurance policies and Quality Control procedures to ensure that the laboratory achieves established standards of quality.
3. Maintains records of quality control data and evaluates data quality.
4. Conducts periodic internal audits and coordinates external audits performed by regulatory agencies or client representatives.
5. Reviews and maintains records of proficiency testing results.
6. Maintains the document control system
7. Assists in development and implementation of appropriate training programs.
8. Provides technical support to laboratory operations regarding methodology and project QA/QC requirements.
9. Maintains certifications from federal and state programs.
10. Ensures compliance with all applicable state, federal and industry standards.

1.8.3 Project Manager

1. Coordinates all aspects of specific projects.
2. Focal point for client contact pertaining to project requirements and project status.
3. Arranges bottle orders and shipment of sample kits to clients.
4. Verifies login information relative to project requirements and field sample Chains-of-Custody.
5. Communicates with operations staff to update and set project priorities.
6. Provides results to clients in the requested format (verbal, hardcopy, electronic, etc.).
7. Works with clients, laboratory staff, and other appropriate Pace Analytical staff to develop project statements of work or resolve problems of data quality.

1.8.4 Operations Manager or Department Manager/Supervisor

1. Oversees the day-to-day production and quality activities of the laboratory.
2. Ensures that quality assurance and quality control criteria of analytical methods and projects are satisfied.
3. Assesses data quality and takes corrective action when necessary.
4. Approves and releases technical and data management reports.
5. Ensures compliance with all applicable state, federal and industry standards.

1.8.5 Group Supervisor/Leader

1. Trains analysts in laboratory operations and analytical procedures.
2. Organizes and schedules analyses with consideration for sample holding times.
3. Implements data verification procedures by assigning data verification duties to appropriate personnel.
4. Evaluates instrument performance and supervises instrument calibration and preventive maintenance programs.
5. Reports non-compliance situations to laboratory management including the Quality Manager.

1.8.6 Analyst

1. Analyzes samples according to published methods and laboratory procedures.
2. Monitors quality control data. This includes examination of raw data such as chromatograms as well as an inspection of reduced data, calibration curves, and laboratory notebooks.

1.8.7 Sample Management Personnel

1. Signs for incoming samples and verifies the data entered on the Chain-of-Custody forms.
2. Enters the sample information into the Laboratory Information Management System (LIMS) for tracking and reporting.
3. Stages samples according to EPA requirements.
4. Assists Project Managers in filling bottle orders and sample shipments.

1.8.8. Systems Administrator or Systems Manager

1. Assists with the creation and maintenance of electronic data deliverables (EDDs)
2. Coordinates the installation and use of all hardware, software and operating systems
3. Performs troubleshooting on all aforementioned systems
4. Trains new and existing users on systems and system upgrades
5. Maintains all system security passwords
6. Maintains the electronic backups of all computer systems

1.8.9. Safety/Chemical Hygiene Officer

1. Maintains the laboratory Chemical Hygiene Plan
2. Plans and implements safety policies and procedures
3. Maintains safety records
4. Organizes and/or performs safety training
5. Performs safety inspections and provides corrective/preventative actions
6. Assists personnel with safety issues (e.g. personal protective equipment)

1.9 Training and Orientation

Additional information can be found in SOP ALL-Q-020 ***Training Procedures***.

Each new employee receives a five part orientation: human resources, data integrity ethics, safety, Quality Systems, and departmental.

The human resources orientation includes benefits, salary, and company policies. All records are stored with Human Resources.

The data integrity system of each lab contains four elements:

- Data integrity training
- Signed data integrity documentation for all employees
- In-depth, periodic monitoring of data integrity –including but not limited to:
  - logbook checks
  - raw data review
  - final report review
  - manual integration checks
- Documentation of review and investigations regarding data integrity issues.

The safety orientation includes an in-depth review of the Pace Analytical Chemical Hygiene Plan/Safety Plan, which are consistent with the requirements of OSHA's Hazard Communication Program (29 CFR 1910.1200) and other pertinent regulations.

The Quality Systems orientation provides the new employee with information through an introduction to the Quality Manual and SOPs, acceptable record keeping practices, and the individual's responsibility to data quality.

The new employee's Department Supervisor provides the employee with a basic understanding of the role of the laboratory within the structure of Pace Analytical and the basic elements of that individual's position.

Supervised training uses the following techniques:

- Hands-on training
- Lectures and training sessions
- Method-specific training
- Conferences and seminars
- Short courses
- Specialized training by instrument manufacturers
- Proficiency testing programs.

Group Supervisors/Leaders are responsible for providing documentation of training and proficiency for each employee under their supervision. The employee's training file indicates what procedures an analyst or a technician is capable of performing, either independently or with supervision. The files also include documentation of continuing capability (see Section 3.4 for details on Demonstration of Capability requirements). Training documentation files for each person are kept in a central location in each laboratory. The Quality Manager is responsible for maintaining the training files.

All procedures and training records are maintained and available for review during laboratory audits. These procedures are reviewed/updated annually by lab management.

1.10 Laboratory Safety

It is the policy of Pace Analytical to make safety and health an integral part of daily operations and to ensure that all employees are provided with safe working conditions, personal protective equipment, and requisite training to do their work without injury. Each employee is responsible for his/her own safety by complying with established company rules and procedures.

Sample receiving areas and laboratories are equipped with suitable hoods, protective clothing and eye wear, gloves, barrier creams and any other appropriate measures to prevent or minimize staff contact with hazardous substances. Other appropriate safety equipment such as eyewash stations, drench showers, spill absorbents and neutralizers, fire extinguishers, and first aid materials are available.

Each laboratory has a designated Safety/Chemical Hygiene Officer and Safety Committee that meets regularly and discusses agenda topics and addresses action items. The Safety/Chemical Hygiene Officer facilitates the preparation and maintains the Chemical Hygiene Plan/Safety Manual, provides safety and occupational health orientation to new employees, conducts safety training and review sessions as required, and maintains up-to-date familiarity with safety and occupational health issues pertinent to the laboratory.

1.11 Security and Confidentiality

Security is maintained by controlled access to laboratory buildings. Exterior doors to laboratory buildings remain either locked or continuously monitored by Pace Analytical staff. Keyless door-lock combinations (and computer access codes/logins) are changed on a regular basis. Posted signs direct visitors to the reception office and mark all other areas as off limits to unauthorized personnel. All visitors to the facilities must sign the Visitor's Logbook maintained by the receptionist and/or a staff member will accompany them during the duration of their stay on the premises. In this instance, the staff member will escort the visitor back to the reception area at the end of his/her visit where he/she signs out. Prior to departure of the last staff member at the close of each day, the facility is checked for security.

Additional security is provided where necessary, e.g., specific secure areas for sample, data and client report storage, as requested by clients or in cases of national security. These areas are lockable within the facilities, or are in secure offsite storage. Access is limited to specific individuals or their designees. Security of sample storage areas is the responsibility of the Sample Custodian. Security of samples and data during analysis and data reduction is the responsibility of Group Supervisors. Security of client report archives is the responsibility of the Client Services Manager. These secure areas are locked whenever these individuals or their designees are not present in the facility.

Access to designated laboratory sample storage locations is limited to authorized personnel only. Provisions for lock and key access are provided. No samples are to be removed without proper authorization. If requested by client or contract, samples are not to be removed from secure storage areas without filling out the associated internal Chain-of-Custody records.

Standard business practices of confidentiality are applied to all documents and information regarding client analyses. Specific protocols for handling confidential documents are described in Pace Analytical SOPs. Additional protocols for internal identification of samples and data by number only are implemented as required under contract-specific Quality Assurance Project Plans (QAPPs).

All information pertaining to a particular client, including national security concerns will remain confidential. Data will not be released to outside agencies without written authorization from the client.

Figure 1.1

Corporate/Management Structure

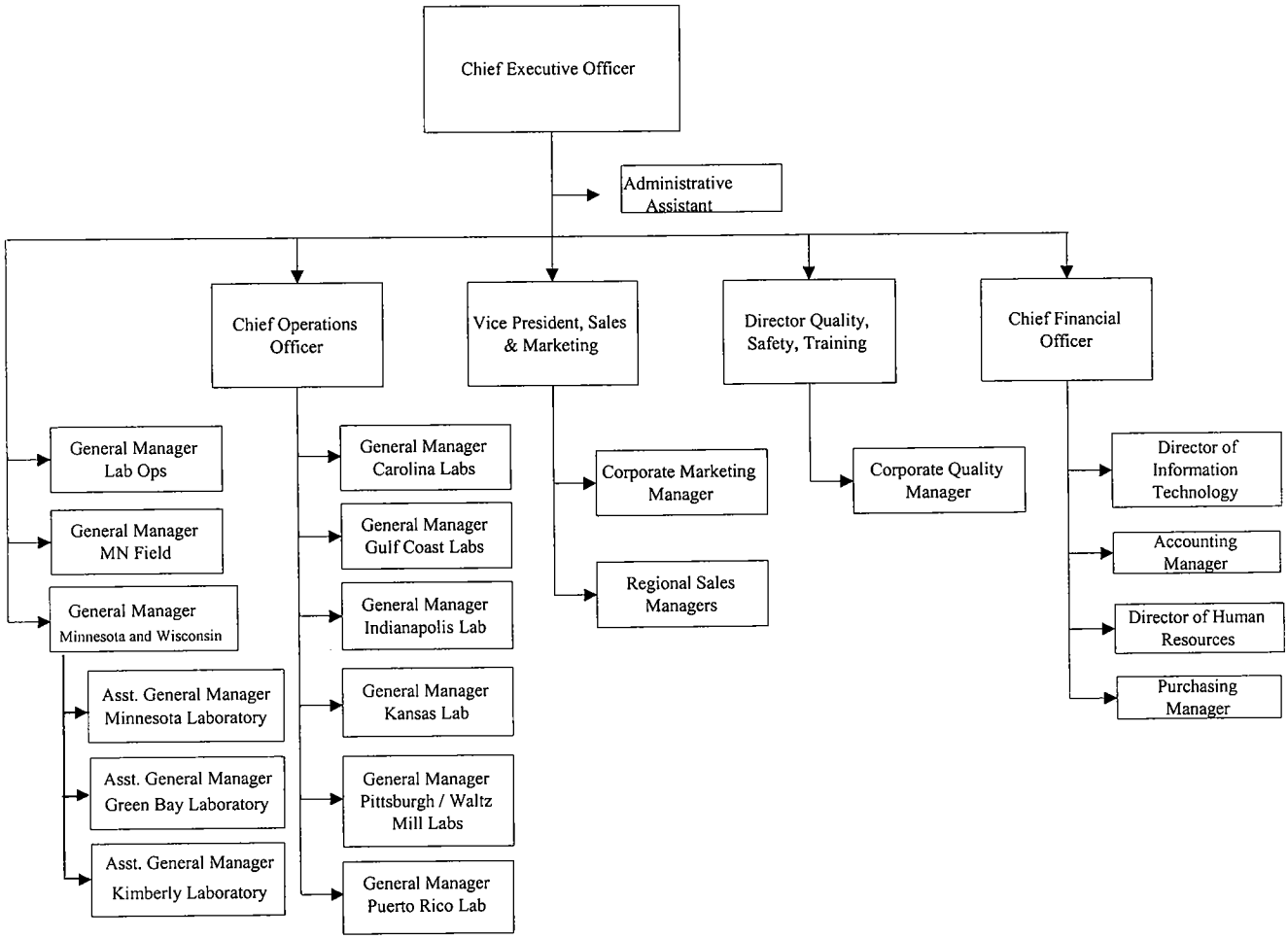
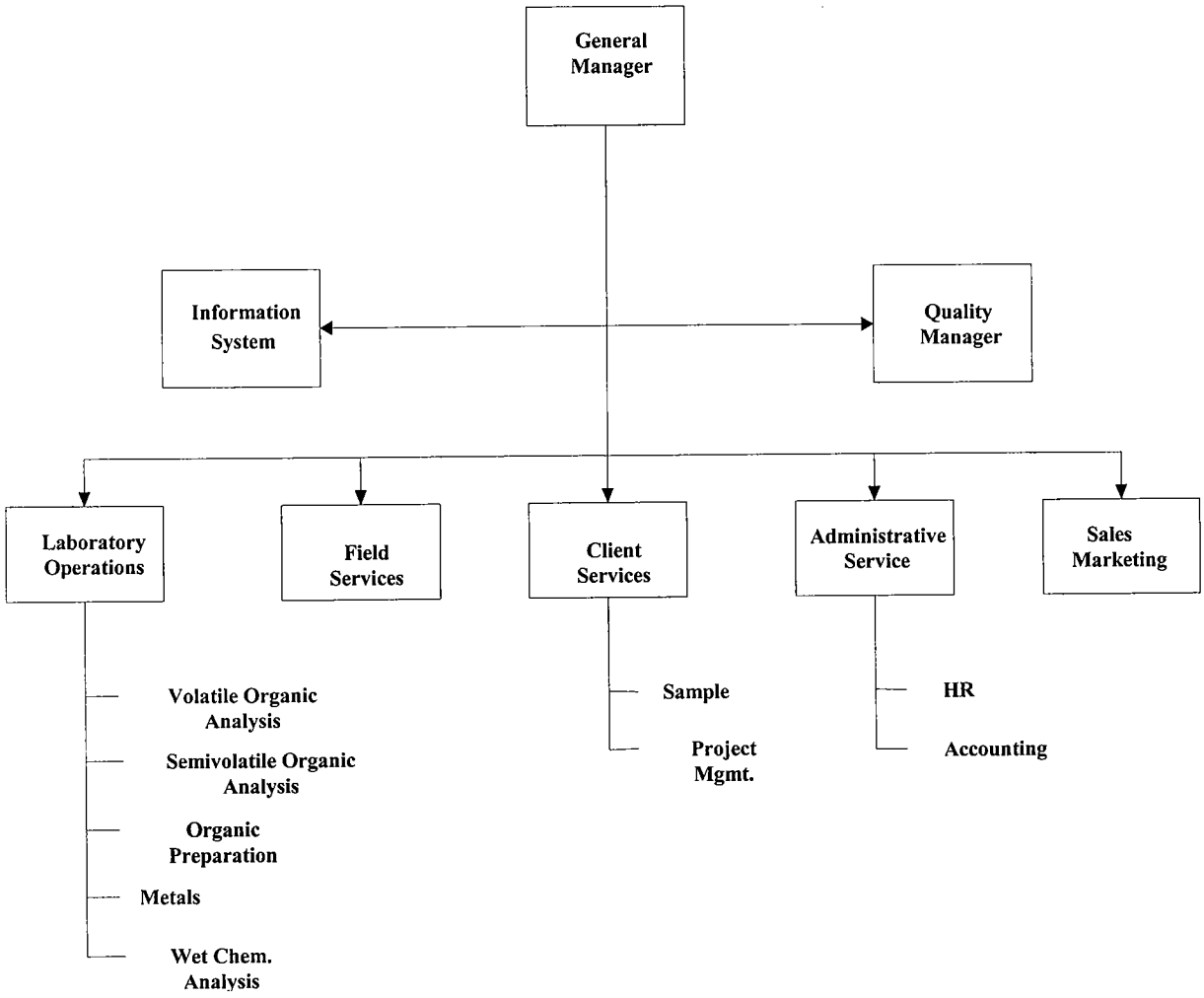


Figure 1.2

Typical Laboratory Organizational Chart



2.0 SAMPLE CUSTODY

Additional information can be found in SOP ALL-C-001 ***Sample Management.***

2.1 Sampling Support

Each individual Pace Analytical laboratory provides shipping containers, sample containers (including applicable chemical preservatives), custody documents, and field quality control samples (e.g., trip blanks) to support field-sampling events. Tables 2.1, 2.2, 2.3 and 2.4 list general guidelines for sample container types, preservatives and holding times for a variety of methods. Note that all analyses listed are not necessarily performed at all Pace Analytical locations and there may be additional laboratory analyses performed that are not included in these tables. Pace laboratories may provide pick-up and delivery services to their clients when needed.

2.2 Project Initiation

Prior to accepting new work, the lab reviews its capability to perform this work. The purpose of this review is to establish that the lab has sufficient resources (personnel, equipment capacity, analytical method capability, etc.) to complete the required work. Once client needs and data quality objectives are defined, client services personnel or sales representatives contact the laboratory management. Members of the management staff review current instrument capacity, personnel availability and training, analytical procedures capability, laboratory certifications and projected sample load. Management will then inform the sales and client services personnel whether the lab can accept the new projects. This communication is preferably via written correspondence or email, although it may occur during daily operations meetings.

The laboratory maintains records of all such reviews, including discussions with clients. The lab also maintains records of sub-contracted work and keeps a file of all sub-contractor information including current certifications.

2.3 Sample Acceptance Policy

In accordance with regulatory guidelines, Pace Analytical Services has compiled the following sample acceptance policy for all samples received at our laboratories.

If the samples do not meet the sample receipt acceptance criteria outlined below, the laboratory shall document all non-compliances and contact the client and either reject the samples or fully document any decision to proceed with the analyses of samples which do not meet these criteria. Any results reported from samples not meeting these criteria will be appropriately qualified on the final report.

All samples must:

- Have unique client identification that are clearly marked with durable waterproof labels on the sample containers and that match the chain of custody.
- Have clear documentation on the chain of custody related to the location of the sampling site with the time and date of sample collection.
- Have the sampler's name and signature
- Have the requested analyses clearly marked
- Have clear documentation of any special analysis requirements (data deliverables, etc.);
- Be in appropriate sample containers with clear documentation of the preservatives used.
- Be correctly preserved unless method allows for laboratory preservation.

- Be received within holding time. Any samples with hold times that are exceeded will not be processed without prior client permission.
- Have sufficient sample volume to proceed with the analytical testing. If insufficient sample volume is received, analysis will not proceed without client approval.
- Be received within appropriate temperature ranges, (for samples requiring cooling to 4 °C, the acceptable range is just above freezing to 6°C, as defined by NELAC). The cooler temperature is recorded directly on the COC. Samples that are delivered to the lab immediately after collection are considered acceptable if there is evidence that the chilling process has been started, for example by the arrival of the samples on ice. If samples arrive that are not compliant with these temperature requirements, the client will be notified. The analysis will NOT proceed unless otherwise directed by the client. If less than 72 hours remain in the hold time for the analysis, the analysis may be started while the client is contacted to avoid missing the hold time. Data will be appropriately qualified on the final report.

Samples for drinking water analysis will be rejected at the time of receipt if improperly preserved, or if received past holding time, with the exception of VOA samples that are tested at the time of analysis.

2.4 Chain-Of-Custody

A chain-of-custody (COC) (see figure 2.1) document provides the legal documentation of samples from time of collection to completion of analysis. It is important that these documents be as complete as possible. Pace Analytical has implemented standard operating procedures to ensure that sample custody objectives of traceability and responsibility are achieved for every project.

Field personnel or client representatives complete a chain-of-custody form for all samples. Samples are received by the laboratory accompanied by these forms.

If sample shipments are not accompanied by the correct documentation, the Sample Receiving department will notify the Project Manager. The Project Manager is then responsible for obtaining the correct documentation/information from the client so that analysis of samples can proceed.

The sampler is responsible for providing the following information on the chain-of-custody:

- Client project name
- Project location or number
- Field sample number/identification
- Date and time sampled
- Sample type (matrix)
- Preservative
- Requested analyses
- Sampler signature
- Relinquishing signature
- Date and time relinquished
- Sampler remarks (if applicable)
- Custody Seal Number (if applicable)
- Regulatory Program Designation
- The state where the samples were collected to ensure all applicable state requirements are met
- Turnaround time requested
- Purchase order number

The record is filled out completely and legibly with indelible ink. Errors are corrected by drawing a single line through the initial entry and initialing and dating the change. All transfers of samples must be recorded on the chain-of-custody in the "relinquished" and "received by" sections. All information except signatures should be printed.

2.5 Sample Receipt

Sample receiving personnel inspect each sample shipment upon arrival. The following items are checked:

- Presence of custody seals or tapes on the shipping containers
- Presence of Chain-of-Custody or similar documentation
- Presence of sample tags or labels
- Agreement between the sample tags or labels, Chain-of-Custody, and any client documentation.
- Condition of the samples when received, including:
  - Sample temperature: samples are acceptable if the arrival temperature is within 2°C of the required temperature, except as specified in the applicable test method or other state or federal regulation. Samples that are hand-delivered directly from the field on the same day that they are collected are acceptable if there is evidence that the chilling process has begun (arrival on ice).
  - Sample condition: Intact, broken/leaking
  - Headspace in VOA vials
  - Sample holding time
  - Sample pH when required
  - Adequate sample volume
  - Appropriate containers/preservatives

If discrepancies are found, the Pace Analytical Project Manager is contacted immediately. If the Project Manager is not available, the Quality Manager is contacted for further directions. Discrepancies are documented and reported with analytical results.

2.6 Sample Log-in

After the sample inspection, all sample information on the chain-of-custody is entered into the Laboratory Information Management System (LIMS).

Sample data must include, at a minimum:

- Client name and contact
- Client number
- Pace Analytical project number
- Pace Analytical Project Manager
- Sample descriptions
- Due dates
- List of analyses requested

All samples received are logged into the LIMS system within one working day of receipt. Sample login may be delayed due to client clarification of analysis needed, corrective actions for sample receipt non-conformance, or other unusual circumstances.

All sample containers are assigned a unique laboratory identification code that is unequivocally linked to the field identification code. This code is placed on the sample container as a durable label.

Sample labels are printed from the LIMS system and affixed to each sample container.

Samples with hold times that are near their expiration date/time may be sent directly to the laboratory for analysis at the discretion of the Project Manager and/or General Manager.

2.7 Sample Storage

2.7.1 Storage Conditions

Samples are stored away from all standards, reagents, food or other potential sources of contamination. Samples are stored in a manner that prevents cross-contamination (e.g. volatile samples are stored separate from other samples). All sample fractions, extracts, leachates and other sample preparation products are stored in the same manner as actual samples or as specified by the analytical method

2.7.2 Temperature Monitoring

Samples are taken to the appropriate storage location (ambient, refrigerator, freezer) immediately after the sample receipt and check-in procedures are completed . All sample storage areas are located in limited access areas and are monitored to ensure sample integrity.

The temperature of each refrigerated storage area is maintained at $4^{\circ}C \pm 2^{\circ}C$ unless state or program requirements differ. The temperature of each freezer storage area is maintained at $<0^{\circ}C$ unless state or program requirements differ. The temperature of each storage area is monitored and recorded each workday. If the temperature falls outside the acceptable limits, the following corrective actions are taken and appropriately documented:

- The temperature is rechecked after two hours to verify temperature exceedance. Initiate corrective action if necessary.
- The Quality Manager and/or laboratory management are notified if the problem persists.
- The samples are relocated to a proper environment if the temperature cannot be maintained after corrective actions are implemented.
- The affected clients are notified.
- Documentation is provided on analytical report.

2.7.3 Hazardous Materials

Pure product or potentially heavily contaminated samples are tagged as "hazardous" or "lab pack" and are stored separately from other samples.

2.7.4 Foreign Soils

Depending on the soil disposal practices of the laboratory, foreign soils and soils from USDA regulated areas are segregated. The USDA requires these samples to be incinerated or sterilized by an approved treatment procedure.

2.8 Sample Protection

Pace laboratory facilities are operated under controlled access to ensure sample and data integrity. Visitors must register at the front desk and be properly escorted.

Samples are removed from their storage areas by designated personnel and returned to the storage areas, if necessary, immediately after the required sample quantity has been taken.

Upon client request, additional and more rigorous chain-of-custody protocols for samples and data can be implemented. For example, some projects may require complete documentation of sample custody within the secure laboratory.

2.9 Subcontracting Analytical Services

Additional information can be found in SOP ALL-Q-017 ***Subcontracting Samples***.

Every effort is made to perform chemical analyses for Pace Analytical clients within the laboratory that receives the samples. When subcontracting to a laboratory other than the receiving laboratory (inside or outside the Pace network) becomes necessary, a preliminary verbal communication with an appropriate laboratory is undertaken. Clients are notified in writing of the lab's intention to subcontract any portion of the testing to another laboratory. Work performed under specific protocols may involve special considerations.

Prior to subcontracting samples to a laboratory outside Pace Analytical, the potential sub-contract laboratory will be pre-qualified by verifying that the subcontractor meets the following criteria:

- All certifications required for the proposed subcontract are in effect,
- Sufficient professional liability and other required insurance coverage is in effect, and
- Is not under investigation by any federal, state, or local government agency for data integrity issues and has not been under such investigation at any time during the past 5 years.

The contact and preliminary arrangements are made between the Pace Analytical Project Manager and the appropriate subcontract laboratory personnel. The specific terms of the subcontract laboratory agreement include :

- Method of analysis
- Number and type of samples expected
- Project specific QA/QC requirements
- Deliverables required
- Laboratory certification requirement
- Price per analysis
- Turn around time requirements

Chain-of-custody forms are generated for samples requiring subcontracting to other laboratories. The sample receiving personnel re-package the samples for shipment, create a transfer chain-of-custody form and record the following information:

- Pace Analytical Laboratory Number
- Matrix
- Requested analysis
- Special instructions (quick turn-around, required detection or reporting limits, unusual information known about the samples or analytical procedure).
- Signature in "Relinquished By"

All subcontracted sample data reports are sent to the Pace Analytical Project Manager.

Any Pace Analytical work sent to other labs within the Pace network is handled as subcontracted work (also known as inter-regional) and all final reports are labeled clearly with the name of the laboratory performing the work.

2.10 Sample Retention and Disposal

Additional information can be found in SOP ALL-S-002 ***Waste Handling***.

Samples (and sample by-products) must be retained by the laboratory for a period of time necessary to protect the integrity of the sample or sample by-product (e.g. method holding time) and to protect the interests of the laboratory and the client.

Unused portions of samples are retained by each laboratory based on program or client requirements for sample retention and storage. The typical sample retention time is a minimum of 30 days past the submission of the report. Any Pace laboratory not following this retention/disposal time must have a specific policy for retention and disposal of samples in their Quality Manual addendum.

After this period expires, non-hazardous samples are properly disposed of as non-hazardous waste.

The preferred method for disposition of hazardous samples is to return the excess sample to the client. It may not be feasible to return samples, or the client may require Pace Analytical to dispose of excess samples. In that case, Pace Analytical will arrange for proper disposal by an approved contractor.

Table 2.1 Inorganic Parameters in Aqueous Samples

Parameter	Method			Container	Volume Needed (mL)	Preservative	Max Hold Time
	EPA Water	Standard Methods	EPA Waste SW-846				
Acidity	305.1	2310B		P, G	100	4°C	14 Days
Alkalinity	310.1/310.2	2320B		P, G	250	4°C	14 Days
Anions by IC, including Br, Cl, F, NO_2, NO_3, PO_4, SO_4, SO_3	300.0		9056	P, G	100	4°C	By anion
Bacteria, Total Plate Count		9221D		WK/P	100	4°C, $Na_2S_2O_3$	24 Hours
BOD/cBOD	405.1	5210B		P, G	500	4°C	48 hours
COD	410.1/410.2/ 410.4	5220C		P, G	250	pH<2 H_2SO_4, 4°C	28 Days
Chloride	325.2/325.3	4500-Cl	9250/9251/9252	P, G	100	none required	28 Days
Chorine, Residual	330.1/330.5/ 330.2	4500-Cl		P, G	500	none required	Immediate
Color	110.3/110.2	2120B,C,E		P, G	250	4°C	48 Hours
Cyanide, Reactive			Chapter 7	P, G	100	none required	28 Days
Cyanide, Total and Amenable	335.2/335.3/ 335.4	4500-CN	9010/9012	P, G	500	4°C; pH>12 NaOH, ascorbic acid if chlorine present	14 Days (24 hrs if sulfide present)
Flashpoint/Ignitability			1010/1030	P, G	50	none required	28 Days
Fluoride	340.1/340.2	4500-Fl C,D		P	500	none required	28 Days
Hardness, Total ($CaCO_3$)	130.2/130.1	2340B or C		P, G	250	pH<2 HNO_3, 4°C	6 Months
Nitrogen, Ammonia	350.1/350.2/ 350.3	4500-NH_3		P, G	500	pH<2 H_2SO_4, 4°C	28 Days
Nitrogen, Kjeldahl	351.2/351.3	4500-N_{org}		P, G	1000	pH<2 H_2SO_4, 4°C	28 Days
Nitrogen, Nitrate	352.1/353.2/ 353.3	4500-NO_3		P, G	100	4°C	48 Hours
Nitrogen, Nitrite	354.1	4500-NO_2		P, G	100	4°C	48 Hours
Nitrogen, Nitrate & Nitrite	353.2	4500-NO_3		P, G	100	pH<2 H_2SO_4, 4°C	28 Days
Nitrogen, Organic	351.3	4500-N_{org}		P, G	100	pH<2 H_2SO_4, 4°C	28 Days
Odor	140.1	2150B		G	1000	4°C	24 Hours
Oil and Grease/HEM	1664A	5520B,D	9070	G	1000	pH<2 H_2SO_4, 4°C	28 Days
Oxygen, Dissolved	360.1	4500-D		G	500	none required	Immediate
pH	150.1/150.2	4500-H	9040/9041	P, G	100	none required	Immediate
Phenol, Total	420.1/420.2		9065/9066	G	1000	pH<2 H_2SO_4, 4°C	28 Days
Phosphorus, Orthophosphate	365.1/365.2/ 365.3	4500-P		P	100	Filter, 4°C	48 Hours
Phosphorus, Total	365.1/365.2/ 365.4	4500-P		P, G	100	pH<2 H_2SO_4, 4°C	28 Days
Silica, Dissolved	370.1	4500-Si D		P	100	4°C	28 Days
Solids, Total	160.3	2540B		P, G	100	4°C	7 Days
Solids, Total Volatile	160.4	2540E		P, G	100	4°C	7 Days
Solids, Total Dissolved	160.1	2540C		P, G	100	4°C	7 Days
Solids, Total Suspended	160.2	2540D		P, G	100	4°C	7 Days
Solids, Settleable	160.5	2540F		G	1000	4°C	48 Hours
Specific Conductance	120.1	2510B	9050	P, G	100	4°C	28 Days
Sulfate	375.4/375.2	4500-SO_4	9036/9038	P, G	100	4°C	28 Days
Sulfide, Reactive			Chapter 7	P, G	100	none required	28 Days
Sulfide, Total	376.1, 376.2	4500-S	9030	P, G	500	pH>9 NaOH and ZnOAc	7 Days
Sulfite	377.1	4500-SO_3		P, G	500	none required	Immediate
Surfactants	425.1	5540C		P, G	250	4°C	48 Hours
Total Organic Carbon (TOC)	415.1/415.2	5310B,C,D	9060	G	100	pH<2 H_2SO_4 or HCl,4°C	28 Days
Total Organic Halogen (TOX)	450.1	5320	9020/9021	G, no headspace	500	4°C	14 Days
Turbidity	180.1	2130B		P, G	100	4°C	48 Hours
Metals (and other ICP elements)	200.7/200.8		6010/6020	P, G	500	pH<2 HNO_3	6 Months
Mercury	245.1		7470	P, G	250	pH<2 HNO_3	28 Days
Low Level Mercury	1631			G		BrCl, 4°C	90 days (if preserved and oxidized)
Hexavalent Chromium	218.4	3500-Cr	7196	P, G	500	4°C	24 Hours
Paint Filter Liquid Test.			9095	P, G	100	none required	N/A
Ferrous Iron		3500-Fe-D		G	100	none required	Immediate

Table 2.2 Organic Parameters in Aqueous Samples

Parameter	Method			Container	Volume Needed (mL)	Preservative	Max Hold Time
	EPA Drinking Water	EPA Water	EPA Waste SW-846				
Aromatic and Halogenated Volatiles		601/602	8021	40-mL vial	3 vials	pH<2 HCl, 4°C, $Na_2S_2O_3$ if Cl_2 present	14 Days
Volatiles	524.1/524.2			40-mL vial	3 vials	pH<2 HCl, 4°C, $Na_2S_2O_3$ if Cl_2 present	14 Days
Volatiles		624		40-mL vial	3 vials	pH<2 HCl, 4°C, $Na_2S_2O_3$ if Cl_2 present	14 Days (7 unpreserved)
Volatiles			8260	40-mL vial	3 vials	pH<2 HCl, 4°C, $Na_2S_2O_3$ if Cl_2 present	14 Days
Gas Range Organics			8015M	40-mL vial	3 vials	pH<2 HCl	14 Days
EDB & DBCP	504.1		8011	40-mL vial	3 vials	4°C, $Na_2S_2O_3$ if Cl_2 present	14 Days
Base/Neutrals and Acids		625	8270	G	1000	4°C, $Na_2S_2O_3$ if Cl_2 present	7/40 Days
Base/Neutrals, Acids & Pesticides	525.1/525.2			G	1000	4°C, $Na_2S_2O_3$ if Cl_2 present	7/30 Days
Organochlorine Pesticides and PCB's		608	8081/8082	G	1000	4°C, $Na_2S_2O_3$ if Cl_2 present	7/40 Days
Organophosphorous Pesticides			8141	G, amber	1000	4°C, $Na_2S_2O_3$ if Cl_2 present	7/40 Days
Polynuclear Aromatic Hydrocarbons		610	8310	G	1000	4°C, $Na_2S_2O_3$ if Cl_2 present	7/40 Days
Chlorinated Herbicides	515.1		8151	G, amber	1000	4°C, $Na_2S_2O_3$ if Cl_2 present	14/28 Days**
Haloacetic Acids	552.1/552.2			40-mL vial, amber	3 vials	NH_4Cl, 4°C	14/7 Days
Diesel Range Organics			8015M	G	1000	4°C	7/40 Days
Explosives			8330	G	1000	4°C	7/40 Days
2, 3, 7, 8-TCDD	1613B			G	1000	none required	90/40 Days
Methane, Ethane, & Ethene			3810M	20-mL vial	3 vials	pH<2 HCl, 4°C	14 Days

Table 2.3 Inorganic and Organic Parameters in Solid Samples

Parameter	EPA Method	Container	Weight Needed (g)	Preservative	Max Hold Time
Metals	6010 or 6020	G	100	4°C	6 months
Mercury	7471	G	100	4°C	28 days
Aromatic and Halogenated Volatiles	5035/8021	5035 vial kit	1 kit	See Note	14 days
Volatiles	5035/8260	5035 vial kit	1 kit	See Note	14 days
Gasoline Range Organics	5035/8015M	5035 vial kit	1 kit	See Note	14 days
Base/Neutrals and Acids	8270	G	100	4°C	14/40 Days
Organochlorine Pesticides and PCBs	8081/8082	G	100	4°C	14/40 Days
Organophosphorous Pesticides	8141	G	100	4°C	14/40 Days
Polynuclear Aromatic Hydrocarbons	8310	G	100	4°C	14/40 Days
Chlorinated Herbicides	8151	G, amber	100	4°C	14/40 Days
Diesel Range Organics	8015M	G	100	4°C	14/40 Days
Explosives	8330	G	100	4°C	14/40 Days
2, 3, 7, 8-TCDD	1613B	G	100	none required	90/40 Days

Note: 5035 vial kit contains

2 vials water, preserved by freezing **or**
2 vials aqueous $NaHSO_4$, preserved at 4°C **and**
1 vial methanol preserved at 4°C **and**
1 vial unpreserved stored at 4°C

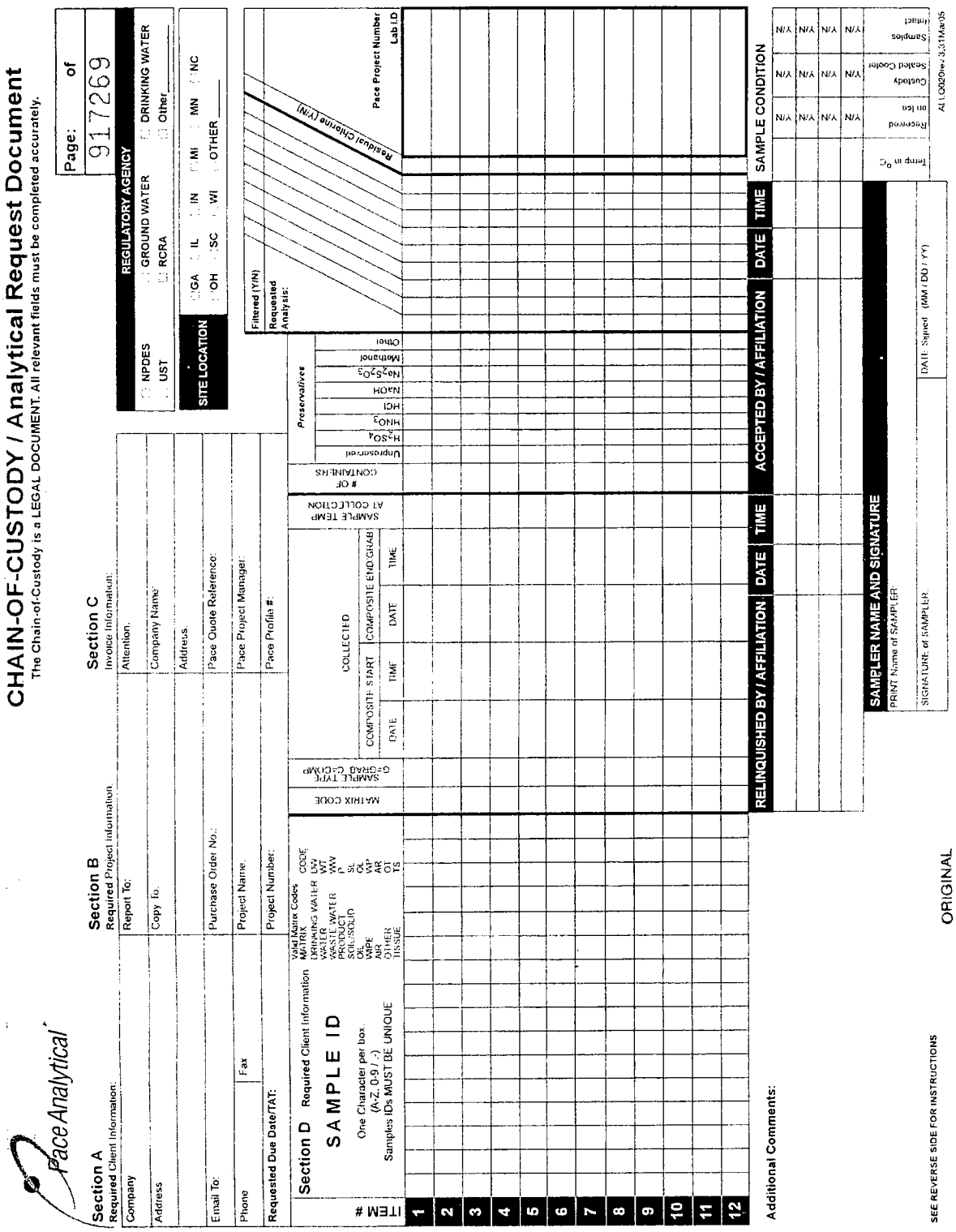
Table 2.3 Inorganic and Organic Parameters in Air Samples

Parameter	EPA Method	Container	Recommended Max Hold Time
Permanent Gases	3C	Summa Canister	14 Days
Permanent Gases	3C	Tedlar Bag	48 Hours
Methane, Ethane, Ethene	3C-M	Summa Canister	14 Days
Methane, Ethane, Ethene	3C-M	Tedlar Bag	48 Hours
Non-Methane Organics	25C	Summa Canister	14 Days
Non-Methane Organics	25C	Tedlar Bag	48 Hours
BTEX/Total Hydrocarbons	TO-3	Summa Canister	14 Days
BTEX/Total Hydrocarbons	TO-3	Tedlar Bag	48 Hours
Organochlorine Pesticides & PCBs	TO-4	PUF	7/40 Days
Dioxins & Furans	TO-9	PUF	30/45 Days
Polynuclear Aromatic Hydrocarbons	TO-13	PUF	7/40 Days
Volatiles	TO-14	Summa Canister	14 Days
Volatiles	TO-14	Tedlar Bag	48 Hours
Volatiles	TO-15	Summa Canister	14 Days
Ozone Precursors	TO-15	Summa Canister	14 Days
Particulates	PM10	Filters	6 Months
Metals	IO-3.5	Filters	6 Months
Stationary SourceParticulates	5	Filter/Solutions	6 Months
Lead Emissions	12	Filter/Solutions	6 Months
Stationary Source Dioxins & Furans	23	XAD Trap	30/45 Days
Stationary Source Metals	29	Filters	6 Months, 28 Days for Hg
Stationary Source Mercury	101	Filters	6 Months, 28 Days for Hg
Stationary Source PM10	201A	Filters	6 Months
Condensable Particulate Emissions	202	Solutions	6 Months
Hydrogen Halide & Halogen Emissions	26	Solutions	6 Months

Table 2.4 Rad Chem Parameters

Parameter	Method			Container	Volume Needed (mL)	Preservative	Max Hold Time
	EPA Water	Standard Methods	EPA SW-846				
Gross Alpha and Gross Beta	900.0		9310	P, G	1000	pH<2 HNO_3	180 days
Gross Alpha (NJ 48Hr Method)	NJAC 7:18-6			P, G	1000	pH<2 HNO_3	48 Hrs
Gamma Emitting Radionuclides	901.1			P, G	1000	pH<2 HNO_3	180 days
Alpha Emitting Radium Isotopes	903.0		9315	P, G	1000	pH<2 HNO_3	180 days
Radium-226 Radon Emanation Technique	903.1			P, G	1000	pH<2 HNO_3	180 days
Radium-228	904.0		9320	P, G	1000	pH<2 HNO_3	180 days
Radioactive Strontium	905.0			P, G	1000	pH<2 HNO_3	180 days
Tritium	906.0			G	1000	pH<2 HNO_3	180 days
Uranium Radiochemical Method	908.0	D5174-97		P, G	1000	pH<2 HNO_3	180 days

Figure 2.1 CHAIN-OF-CUSTODY FORM (Example)



3.0 ANALYTICAL CAPABILITIES

3.1 Analytical Method Sources

Pace Analytical laboratories are capable of analyzing a full range of environmental samples from a variety of matrices, including air, surface water, wastewater, groundwater, soil, sediment, biota, and other waste products. Methodologies are applied from regulatory and professional sources including EPA, ASTM, USGS, NIOSH and, State agencies. Section 11 is a representative listing of general analytical protocol references. In some situations, Pace Analytical develops and validates methodologies that may be more applicable to a specific problem or objective. Pace Analytical discloses in writing to its clients and regulatory agencies any instances in which modified methods are being used in the analysis of samples.

3.2 Analytical Method Documentation

The primary form of documentation of analytical methods is the Standard Operating Procedure (SOP). SOPs contain pertinent information as to what steps are required by an analyst to successfully perform a procedure. The required contents for the SOPs are specified in the company-wide SOP for Preparation of SOPs (ALL-Q-001). The SOPs are consistent company-wide documents with addenda as needed for individual laboratories.

The SOPs may be supplemented by Work Processing and Training Documents that further detail how methods are specifically performed with detailed training information.

3.3 Analytical Method Validation

When non-standard methods (e.g. methods other than EPA, NIOSH, ASTM, AOAC, etc.) are required for specific projects or analytes of interest, or when the laboratory develops a method, or modifies a standard method, the laboratory validates the method prior to applying it to client samples. Method validity is established by meeting criteria for precision and accuracy as established by the data quality objectives specified by the end user of the data. The laboratory records the validation procedure, the results obtained and a statement as to the usability of the method. The minimum requirements for method validation include determination of the limit of detection and limit of quantitation of each analyte of interest.

3.4 Demonstration of Capability (DOC)

Analysts complete an initial demonstration of capability (IDOC) study prior to starting a method or when there is a change in instrument type, personnel or test method (when a defined 'work cell' is in operation, the entire work cell must meet the criteria). The mean recovery and standard deviation of each analyte, taken from 4 replicates of a quality control standard (analyzed at 1-4 times the Limit of Quantitation), is calculated and compared to method criteria (if available) or established lab criteria for evaluation of acceptance. Each laboratory maintains copies of all demonstrations of capability, and corresponding raw data, for future reference and must document the acceptance criteria prior to the analysis of the DOC. Demonstrations of capability are renewed on an annual basis.

Additional information can be found in SOP ALL-Q-020 ***Training Procedures***.

3.5 Regulatory and Method Compliance

Pace Analytical understands that the expectations of our clients commonly include the assumption that laboratory data will satisfy specific regulatory requirements. Therefore Pace Analytical will attempt to ascertain, prior to beginning a project, what applicable regulatory jurisdiction, agency, or protocols apply to that project. This information is also required on the Chain-of-Custody submitted with samples.

Pace Analytical will make every effort to detect regulatory or project plan inconsistencies as they arise and communicate them to the clients to aid in the decision-making process.

It is Pace Analytical policy to disclose in a forthright manner any detected noncompliance that may affect the usability of data produced by our laboratories.

4.0 QUALITY CONTROL PROCEDURES

4.1 Data Integrity System

The data integrity system at Pace Analytical provides assurances to management that a highly ethical approach is being applied to all planning, training and implementation of methods. Data integrity is crucial to the success of our company and Pace is committed to providing a culture of quality throughout the organization. To accomplish this goal, Pace has implemented a data integrity system that encompasses the following four requirements:

- A data integrity training program: standardized training is given to each new employee and a yearly refresher is presented to all employees. Key topics within this training include:
  - Need for honesty in analytical reporting
  - Process for reporting data integrity issues
  - Specific examples of unethical behavior and improper practices
  - Documentation of non-conforming data that is still useful to the data user
  - Consequences and punishments for unethical behavior
  - Examples of monitoring devices used by management to review data and systems
- Signed data integrity documentation for all employees: this includes a written quiz following the Ethics training session and written agreement to abide by the Code of Ethics and Standards of Conduct explained in the employee manual
- In-depth, periodic monitoring of data integrity: including peer data review and validation, internal data audits, proficiency testing studies, etc.
- Documentation of any review or investigation into possible data integrity infractions. This documentation must be available for review for lab assessors.

Pace management makes every effort to ensure that personnel are free from any undue pressures that may affect their quality of work including commercial, financial, over-scheduling, and working condition pressures.

The management also provides a mechanism for confidential reporting of data integrity issues that includes confidentiality and a receptive environment in which all employees are comfortable discussing items of ethical concern.

4.2 Method Blank

A method blank is used to evaluate contamination in the preparation/analysis system. The method blank is processed through all preparation and analytical steps with its associated samples. Any affected sample associated with a contaminated method blank will be re-analyzed if possible or reported with an appropriate data qualifier.

A method blank is processed at a minimum frequency of 1 per preparation batch. In the case of a method that has no separate preparation step (e.g. volatiles), a method blank is processed with no more than 20 samples of a specific matrix performed by the same analyst, in the same method, using the same standards or reagents.

The method blank consists of a matrix similar to the associated samples that is known to be free of the analytes of interest.

Each method blank is evaluated for contamination. The source of any contamination is investigated and documented corrective action is taken when the concentration of any target analyte is detected above the reporting limit and is greater then 1/10 of the amount of that analyte found in any associated sample. Corrective actions may include re-analyzing the samples with a clean blank or reporting the data with the appropriate data qualifiers.

4.3 Laboratory Control Sample/Laboratory Control Sample Duplicate (LCS/LCSD)

The Laboratory Control Sample (LCS) is used to evaluate the performance of the entire analytical system including preparation and analysis. The LCS results are compared to established acceptance criteria and if the results are outside of the criteria, then the system is out-of-control. Any affected sample associated with a failing LCS will be re-analyzed if possible or reported with an appropriate data qualifier.

An LCS is processed at a minimum frequency of 1 per preparation batch. In the case of a method that has no separate preparation step (e.g. volatiles), an LCS will be processed with no more than 20 samples of a specific matrix performed by the same analyst, in the same method, using the same standards or reagents.

The LCS consists of a matrix similar to the associated samples that is known to be free of the analytes of interest that is then spiked with known concentrations of target analytes.

The LCS contains all analytes specified by a specific method or by the client or regulatory agency. In the absence of specified components, the lab will spike with the following compounds:

- For multi-peak analytes (e.g. PCBs), a representative standard will be processed.
- For methods with long lists of analytes, a representative number of target analytes may be chosen. The following criteria is used to determine the number of LCS compounds used:
  - For methods with 1-10 target compounds, the lab will spike with all compounds
  - For methods with 11-20 target compounds, the lab will spike with at least 10 compounds or 80%, whichever is greater
  - For methods with greater than 20 compounds, the lab will spike with at least 16 compounds.

The LCS is evaluated against the method or laboratory-derived acceptance criteria. Any compound that is outside of these limits is considered to be 'out of control' and must be qualified appropriately. Any associated sample containing an 'out-of-control' compound must either be re-analyzed with a successful LCS or reported with the appropriate data qualifier.

For LCSs containing a large number of analytes, it is statistically likely that a few recoveries will be outside of control limits. This does not necessarily mean that the system is out of control, and therefore no corrective action would be necessary (except for proper documentation). NELAC has allowed for a minimum number of marginal exceedances, defined as a recoveries that are beyond the LCS control limits (3X the standard deviation) but less than the marginal exceedance limits (4X the standard deviation. The number of allowable exceedances depends on the number of compounds in the LCS. If more analyte recoveries exceed the LCS control limits than is allowed (see below) of if any one analyte exceeds the marginal exceedance limits, then the LCS is considered non-compliant and corrective actions are necessary. The number of allowable exceedances is as follows:

- >90 analytes in the LCS- 5 analytes
- 71-90 analytes in the LCS- 4 analytes
- 51-70 analytes in the LCS- 3 analytes
- 31-50 analytes in the LCS- 2 analytes
- 11-30 analytes in the LCS- 1 analyte
- <11 analytes in the LCS- no analytes allowed out)

A matrix spike can be used in place of a non-compliant LCS in a batch as long as the MS passes the LCS acceptance criteria (this is a NELAC allowance). When this happens, full documentation must be made available to the data user.

4.4 Matrix Spike/Matrix Spike Duplicate (MS/MSD)

A matrix spike (MS) is used to determine the effect of the sample matrix on compound recovery for a particular method. The information from these spikes is sample or matrix specific and is not used to determine the acceptance of an entire batch (see LCS).

A **Matrix Spike/Matrix Spike Duplicate** (MS/MSD) set is processed at a frequency specified in a particular method or as determined by a specific client. In the absence of such requirements, an MS/MSD set is routinely analyzed once per every 20 client samples per matrix per method.

The MS and MSD consist of the sample matrix that is then spiked with known concentrations of target analytes. Lab personnel spike client samples that are specifically designated as MS/MSD samples or, when no designated samples are present in a batch, randomly select samples to spike that have adequate sample volume or weight. Spiked samples should be prepared and analyzed in the same manner as the original samples and should be selected from different clients if possible.

The MS and MSD contain all analytes specified by a specific method or by the client or regulatory agency. In the absence of specified components, the lab will spike with the same number of compounds as previously discussed in the LCS section.

The MS/MSD are evaluated against the method or laboratory-derived criteria. Any compound that is outside of these limits is considered to be 'out of control' and must be qualified appropriately. Batch acceptance, however, is based on method blank and LCS performance, not on MS/MSD recoveries. The spike recoveries give the data user a better understanding of the final results based on their site-specific information.

A matrix spike and sample duplicate may be performed instead of a matrix spike and matrix spike duplicate when specified by the client or method.

4.5 Surrogates

Surrogates are compounds that reflect the chemistry of target analytes and are typically added to samples for organic analyses to monitor the effect of the sample matrix on compound recovery.

Surrogates are added to each client sample (for organics), method blank, LCS and MS prior to extraction or analysis. The surrogates are evaluated against the method or laboratory-derived acceptance criteria. Any surrogate compound that is outside of these limits is considered to be 'out of control' and must be qualified appropriately. Samples with surrogate failures are typically re-extracted and/or re-analyzed to confirm that the out-of-control value was caused by the matrix of the sample and not by some other systematic error. An exception to this would be samples that have high surrogate values but no reportable hits for target compounds. These samples would be reported, with a qualifier, because the implied high bias would not affect the final results.

4.6 Sample Duplicate

A sample duplicate is a second portion of sample that is prepared and analyzed in the laboratory along with the first portion. It measures the precision associated with preparation and analysis. A sample duplicate is processed at a frequency specified by the particular method or as determined by a specific client.

The sample and duplicate are evaluated against the method or laboratory-derived criteria for relative percent difference (RPD). Any duplicate that is outside of these limits is considered to be 'out of control' and must be qualified appropriately.

4.7 Internal Standards

Internal Standards are analytes added to every standard, method blank, laboratory control sample, matrix spike, matrix spike duplicate, and sample at a known concentration, prior to analysis for the purpose of adjusting the response factor used in quantifying target analytes.

4.8 Field Blanks

Field blanks are blanks prepared at the sampling site in order to monitor for contamination that may be present in the environment where samples are collected. These field quality control samples may be referenced as field blanks, rinseate blanks, or equipment blanks. The lab analyzes these field blanks as normal samples and informs the client if there are any target compounds detected above the reporting limits.

4.9 Trip Blanks

Trip blanks are blanks that are prepared in the laboratory before the sampling event and are used to monitor for contamination of samples during transport. These blanks accompany the empty sample containers to the field and then accompany the collected samples back to the lab. These blanks are routinely analyzed for volatile sample methods.

4.10 Limit of Detection (LOD)

Additional information can be found in SOP ALL-Q-004 ***Method Detection Limit Studies***.

Pace laboratories are required to use a documented procedure to determine a limit of detection (LOD) for each analyte of concern in each matrix reported. All sample-processing steps of the preparation and analytical methods are included in this determination. For any test that does not have a valid LOD, sample results below the lowest calibration standard cannot be reported.

The LOD is initially established for the compounds of interest for each method in a clean matrix with no target analytes present and no interferences at a concentration that would impact the results. The LOD is then determined every time there is a change in the test method that affects how the test is performed or when there has been a change in the instrument that affects the sensitivity. The LOD is verified on an annual basis.

Unless otherwise noted, the method used by Pace laboratories to determine LODs is based on the Method Detection Limit (MDL) procedure outlined in 40 CFR Part 136, Appendix B. Where required by regulatory program or client, the above referenced procedure will be followed.

4.11 Limit of Quantitation (LOQ)

Additional information can be found in SOP ALL-Q-004 ***Method Detection Limit Studies***.

A limit of quantitation (LOQ) for every analyte of concern must be determined. For Pace laboratories, this LOQ is referred to as the PRL, or Pace Reporting Limit. This PRL is based on the lowest calibration standard concentration that is used in each initial calibration. Results below this level are not allowed to be reported without qualification since the results would not be substantiated by a calibration standard. For methods with a determined LOD, results can be reported out below the LOQ but above the LOD if they are properly qualified (e.g. J flag).

There must be a sufficient buffer between the LOD and the limit of quantitation (LOQ). The PRL must be higher than the LOD.

4.12 Proficiency Testing (PT) Studies

Pace Analytical laboratories participate in the NELAC-defined proficiency testing program. PT samples are obtained from NIST-approved providers and analyzed and reported at a minimum of two times per year for the relevant fields of testing per matrix.

The lab initiates an investigation whenever PT results are deemed 'unacceptable' by the PT provider. All findings and corrective actions taken are reported to the Quality Manager. A corrective action plan (including re-analysis of similar samples) is initiated and this report is sent to the appropriate state accreditation agencies for their review.

PT samples are treated as typical client samples, utilizing the same staff, methods, equipment, facilities, and frequency of analysis. PT samples are included in the laboratory's normal analytical processes and do not receive extraordinary attention due to their nature.

Comparison of analytical results with anyone participating in the same PT study is prohibited prior to the close of the study.

Additional information can be found in SOP ALL-Q-010 ***PE/PT Program***.

5.0 DOCUMENT MANAGEMENT AND CHANGE CONTROL

5.1. Document Management

Additional information can be found in SOP ALL-Q-002 ***Document Management.***

Pace Analytical Services has established a procedure for managing documents that are part of the quality system. The list of managed documents includes, but is not limited to, Standard Operating Procedures, Quality Manuals, quality policy statements, training documents, work-processing documents, charts, posters, memoranda, notices, forms, software, and any other procedures, tables, plans, etc. that have a direct bearing on the quality system.

A master list of all documents is maintained at each facility identifying the current revision status and distribution of the documents. This establishes that there are no invalid or obsolete documents in use in the lab. All documents are reviewed periodically and revised if necessary and obsolete documents are systematically discarded or archived for legal or knowledge preservation purposes.

Each document related to the quality system is uniquely identified to include the date of issue, the revision identification, page numbering, the total number of pages and the issuing authorities. For complete information on document numbering, refer to the company-wide Standard Operating Procedure Document Numbering (ALL-Q-003).

As an alternative to the hard copy system of control, secured electronic copies of controlled documents may be maintained on the local or wide-area network (LAN or WAN). These document files must be read-only for all personnel except the Quality Department and system administrator. Other requirements for this system include:

- Ready accessibility to all laboratory staff
- A complete description of the computerized aspects, including security
- A provision to explicitly indicate that all printed copies are uncontrolled and expire on the date printed.

5.1.1 Quality Manual

The Quality Manual is the company-wide document that describes all aspects of the quality system for Pace Analytical laboratories. It is document-controlled by the corporate quality office and signed copies are distributed to each of the regional Quality Managers. The regional management personnel sign the Quality Manual and the local Quality Manager is then in charge of distribution to employees and external clients or regulatory agencies and maintaining a controlled list of distributed copies. Each laboratory may attach a lab-specific addendum to the Quality Manual as needed. The Quality Manual is reviewed on an annual basis by all of the Pace Quality Managers and revised accordingly.

5.1.2 Standard Operating Procedures (SOPs)

SOPs fall into two categories: company-wide documents (starting with the prefix ALL-) or individual lab documents (starting with the individual lab abbreviation). Company-wide SOPs (ALL SOPs) are document-controlled by the corporate quality office and signed copies are distributed to each of the laboratory Quality Managers. Laboratory management personnel sign the company-wide (ALL) SOPs and the local Quality Manager distributes to employees and external clients or regulatory agencies and maintains a controlled list of distributed copies. Each laboratory may attach a lab-specific addendum to any of the company-wide (ALL) SOPs as needed. Individual lab specific SOPs are controlled by the local Quality Manager in the same manner.

SOPs are reviewed every two years at a minimum (a more frequent review may be required by state or federal agencies or clients). Documentation of this review and any applicable revisions are made in the last section of each SOP. This provides a historical record of all revisions.

All copies of superseded SOPs are removed from general use and at least one copy of each SOP is archived for audit or knowledge preservation purposes. This not only ensures that all Pace employees use the most current version of each SOP but also supplies the Quality Manager with a historical record of each SOP.

Additional information can be found in SOP ALL-Q-001 ***Preparation of SOPs***.

5.1.3 Training documents

The training documents are more detailed documents that describe lab-specific details such as computer and equipment set-up, sample preparation and analysis steps, data validation steps, documentation requirements, and data packet preparation. Documentation that an analyst has completed their training via these training documents is maintained in their training file.

5.2 Document Change Control

Changes to documents are reviewed and approved in the same manner as the original document control. Any revision to a document requires the approval of the applicable signatories. After revisions are approved, a revision number is assigned and the previous version of the document is officially retired. Copies may be kept for audit or knowledge preservation purposes.

All controlled copies of the previous document are replaced with controlled copies of the revised document and the old copies are destroyed or archived. All affected personnel are advised that there has been a revision and any necessary training can be scheduled.

6.0 EQUIPMENT AND MEASUREMENT TRACEABILITY

Additional information can be found in SOP ALL-Q-013 ***Support Equipment***.

Each Pace lab is equipped with instrumentation and support equipment to perform the required analyses. Support equipment includes chemical standards, thermometers, balances, pipettes, etc. This section will detail some of this equipment and instrumentation and the procedures necessary for its proper calibration.

6.1 Standards and Traceability

Laboratories must retain all pertinent information for all standards, reagents and chemicals to assure traceability to a national standard. This includes documentation of purchase, receipt, preparation and use.

Upon receipt, all purchased standard reference materials are recorded into a standard logbook or database. The entries include the Pace laboratory's unique identification number, the chemical name, manufacturer name, manufacturers identification numbers, receipt date and expiration date. Vendor's certificates of analysis for all standards, reagents, or chemicals are retained by the lab for future reference.

Subsequent preparations of intermediate or working solutions are also documented in a standard logbook or database. These entries include the stock standard name and lot number, the manufacturer name, the solvents used for preparation, the solvent lot number and manufacturer, the preparation steps, preparation date, expiration dates, preparer's initials, and a unique Pace Analytical lab number. This number is used in any applicable sample preparation or analysis logbook so the standard can be traced back to the standard preparation record.

All prepared standard or reagent containers include the Pace identification number, the standard or chemical name, the date of preparation, the date of expiration, the concentration and units, and the preparer's initials. This ensures traceability back to the standard preparation logbook.

If a second source standard is required to verify an existing calibration or spiking standard, this standard is purchased from a different supplier. If no second source is available, a second standard may be purchased from the same supplier but the lab is required to receive a certificate of warranty or similar documentation noting that both standards were prepared from different raw materials. Obtaining two standards from the same parent material is not acceptable for satisfying this requirement.

6.2 General Calibration Procedures

All types of support equipment and instrumentation are calibrated before use to ensure that they function properly. All calibrations are performed by, or under the supervision of, an experienced analyst at scheduled intervals against either certified standards traceable to recognized national standards, or reference standards whose values have been statistically validated. Instrumentation or support equipment that cannot be calibrated to specifications, or is otherwise defective, is taken out of service. They are clearly labeled as out-of-service until they have been repaired and tested to meet specifications. In the event that recalibration of a piece of test equipment casts doubt on the validity of test results already transmitted to the client, the client is notified in writing by the laboratory within 3 business days from the time of discovery. This allows for sufficient investigation and review of documentation to determine the impact on the analytical results. Instrumentation found to be consistently out of calibration is either repaired and positively verified or replaced.

Calibration standards for each parameter are chosen to establish the linear range of the instrument and must bracket the concentrations of those parameters measured in the samples. The lowest calibration standard is the lowest concentration for which quantitative data may be reported. Data reported below this level is considered to have less certainty and must be reported using appropriate data qualifiers (e.g. J flag) or explained in a narrative. The highest calibration standard is the highest concentration for which quantitative data may be

reported. Data reported above this level is considered to have less certainty and must be reported using appropriate data qualifiers (e.g. E flag) or explained in the narrative.

Calibration standards are prepared at a minimum of three concentration levels for inorganic analyses and a minimum of five concentrations for organic analyses. A calibration blank is also included for some inorganic analyses. Any specific method requirement for number and type of calibration standards supersedes the general requirement.

Initial calibration curves are evaluated against appropriate statistical models as required by the analytical methods. Curves that do not meet the appropriate criteria require corrective action that may include re-running the initial curve.
During the course of analysis, the calibration curve is verified by the analysis of a calibration verification standard. This verification standard must also pass acceptance criteria for sample analysis to proceed. Concentrations of calibration verification standards must be varied periodically to evaluate the entire range of the initial calibration curve.

6.3 Calibration Procedures for GC/MS (Gas Chromatograph/ Mass Spectrometer)

More detailed calibration information can be obtained from Pace Standard Operating Procedures or other similar documentation (e.g. SOP ALL-O-001 ***GC/MS Semi-volatiles***).

6.3.1 GC/MS Tuning

The first step in preparing a GC/MS instrument for sample analysis is to tune the instrument. This is accomplished through the analysis of 4-bromofluorobenzene (BFB) for volatile analysis or decafluorotriphenylphosphine (DFTPP) for semi-volatile analysis. The tune standard must pass the method acceptance criteria for mass spectral abundance for these compounds before calibration standards are evaluated.

6.3.2 Initial Calibration

The GC/MS system is initially calibrated with standards at multiple concentrations to establish the linearity of the instrument's response. The number of calibration standards used depends on the specific method criteria or client project requirements, although normally a minimum of five standards is used.

The response factor (RF) for each compound at each concentration is calculated and an average RF is obtained for each compound in the initial calibration curve. The percent relative standard deviation (%RSD) is calculated for each compound. This RSD value should be $\leq$ 15% for each reported compound and must be $\leq$ 30% for those compounds in the method identified as calibration check compounds (CCCs). For compounds with an RSD >15%, a least squares regression can be applied (the best fit value must be >0.99 to confirm linearity) or data for these compounds must be reported with the appropriate data qualifiers. A non-linear calibration curve (quadratic) may be constructed if at least 6 standards are included in the initial calibration.

The mean RF from the initial calibration curve is used to calculate the sample concentration of the compound of interest when the %RSD demonstrates linearity. Otherwise, the sample concentration is determined using the calibration curve equation generated from the initial calibration standards.

6.3.3 Calibration Verification

A calibration verification standard is analyzed with each analytical batch to verify that the initial calibration is still valid. This standard must contain all target analytes and is typically analyzed at a concentration around the midpoint of the initial calibration curve. For linear calibration using the

average response factor, the RF data from this standard is compared to the average RF from the initial calibration. Other calibration models compare the calculated concentration of the calibration verification standard to the expected concentration of the calibration verification standard. If the % Difference is greater than 20% then either the calibration verification standard must be re-analyzed with acceptable results or any data reported for those compounds that exceeded the acceptance criteria are reported with the appropriate data qualifiers.

6.4 Calibration Procedures for GC and HPLC (Gas Chromatograph and High Performance Liquid Chromatograph)

More detailed calibration information can be obtained from Pace Standard Operating Procedures or other similar documentation (e.g. SOP ALL-O-006 ***Organochlorine Pesticides*** and SOP ALL-O-007 ***Polychlorinated Biphenyls***).

6.4.1 Initial Calibration

The GC or HPLC system is initially calibrated with standards at multiple concentrations to establish the linearity of the instrument's response. The number of calibration standards used depends on the specific method criteria or client project requirements, although normally a minimum of five standards is used.

The response factor (RF) for each compound at each concentration is calculated and an average RF is obtained for each compound in the initial calibration curve. The percent relative standard deviation (%RSD) is calculated for each compound. This RSD value should be $\leq$ 20% for each reported compound. For compounds with an RSD >20%, a least squares regression can be applied (the best fit value must be >0.99 to confirm linearity) or data for these compounds must be reported with the appropriate data qualifiers.

The mean RF from the initial calibration curve is used to calculate the sample concentration of the compound of interest.

6.4.2 Calibration Verification

A calibration verification standard is analyzed within each analytical batch at method/program specific intervals to verify that the initial calibration is still valid (this standard is also run at the end of each batch). This standard must contain all target compounds except for multi-component analytes where a representative substance or mixture may be used. The calibration verification standard is typically analyzed at a concentration around the midpoint of the initial calibration curve. The RF data from this standard is compared to the average RF from the initial calibration. If the RF from any compound differs from the average RF from the initial calibration by more than ±15%, then either the calibration verification standard must be re-analyzed or any data reported for those compounds that exceeded the acceptance criteria are reported with the appropriate data qualifiers. Reported sample results must be bracketed by acceptable calibration verification standards.

6.5 Calibration Procedures for ICP, ICP/MS and AAS (Inductively Coupled Plasma, Inductively Coupled Plasma/Mass Spectrometer and Atomic Absorption Spectrometer)

More detailed calibration information can be obtained from Pace Standard Operating Procedures or other similar documentation (e.g. SOP ALL-M-002 ***ICP Metals***)

6.5.1 Initial Calibration

The ICP, ICP/MS or AAS system is initially calibrated with standards at multiple concentrations to establish the linearity of the instrument's response. The number of calibration standards used depends on the specific method criteria or client project requirements, although normally a minimum of three standards is used (ICP and ICP/MS calibration can be performed with a single standard and a calibration blank if annual linear range studies are conducted).

6.5.2 Calibration Verification

A calibration verification standard is analyzed within each analytical batch at method/program specific intervals to verify that the initial calibration is still valid (this standard is also run at the end of each batch). If the response from this standard differs from the initial calibration standard by more than 10% for ICP and ICP/MS or by more than 20% for AAS, then the instrument must be re-calibrated before proceeding with sample analysis. A calibration blank is also run with each calibration verification standard to verify the cleanliness of the system.

Interference check standards are also run per method requirements at the beginning and end of each batch and must pass method acceptance criteria.

6.6 General Equipment Calibration Procedures

6.6.1 Analytical Balances

Each analytical balance is checked and (if necessary) calibrated annually by a qualified service technician. The calibration of each balance is checked each day of use with weights traceable to NIST. Calibration weights are ASTM Class 1 (replaces Class S designation) and are re-certified annually against a NIST traceable reference. Some accrediting agencies may require more frequent checks. If balances are calibrated by an external agency, verification of their weights must be provided. All information pertaining to balance maintenance and calibration is recorded in the individual balance logbook and/or is maintained on file in the Quality department.

6.6.2 Thermometers

Certified, or reference, thermometers are maintained for checking calibration of working thermometers. Reference thermometers are provided with NIST traceability for initial calibration and are re-certified, at a minimum, yearly with equipment directly traceable to NIST.

Working thermometers are compared with the reference thermometers annually according to corporate metrology procedures. Each thermometer is individually numbered. In addition, working thermometers are visually inspected by laboratory personnel prior to use and temperatures are documented.

Laboratory thermometer inventory and calibration data are maintained in the Quality department.

6.6.3 pH/Electrometers

The meter is calibrated before use each day, and once after each four hours of continuous use using fresh buffer solutions.

6.6.4 Spectrophotometers

During use, spectrophotometer performance is checked at established frequencies in analysis sequences against initial calibration verification (ICV) with continuing calibration verification (CCV) standards.

6.6.5 Pipettes

Mechanical hand pipettes are calibrated on a quarterly basis.

6.7 Instrument/Equipment Maintenance

The objectives of the Pace Analytical maintenance program are twofold: to establish a system of instrument care that maintains instrumentation and equipment at required levels of calibration and sensitivity, and to minimize loss of productivity due to repairs.

The Laboratory Operations Manager and department manager/supervisors are responsible for providing technical leadership to evaluate new equipment, solve equipment problems and coordinate instrument repair and maintenance. The analysts have a primary responsibility to perform routine maintenance.

To minimize downtime and interruption of analytical work, preventive maintenance is routinely performed on each analytical instrument.

Department manager/supervisors are responsible for maintaining an adequate inventory of spare parts required to minimize equipment downtime. This inventory includes parts and supplies that are subject to frequent failure, have limited lifetimes, or cannot be obtained in a timely manner should a failure occur.

All major equipment and instrumentation items are uniquely identified to allow for traceability. Equipment/instrumentation are, unless otherwise stated, identified as a system and not as individual pieces. The laboratory maintains equipment records that include the following:

- The name of the equipment and its software
- The manufacturer's name, type, and serial number
- Approximate date received and date placed into service
- Current location in the laboratory
- Condition when received (new, used, etc.)
- Copy of any manufacturer's manuals or instructions
- Dates and results of calibrations and next scheduled calibration (if known)
- Details of past maintenance activities, both routine and non-routine
- Details of any damage, modification or major repairs

All instrument maintenance is documented in maintenance logbooks that are assigned to each particular instrument or system.

When maintenance is performed to repair an instrument problem, depending on the initial problem, demonstration of return to control may be satisfied by the successful analysis of a reagent blank or continuing calibration standard. The entry must include a summary of the results of that analysis and verification by the analyst that the instrument has been returned to an in-control status. In addition, each entry must include the initials of the analyst making the entry, the dates the maintenance actions were performed, and the date the entry was made in the maintenance logbook, if different from the date(s) of the maintenance.

Any equipment that has been subjected to overloading or mishandling, or that gives suspect results, or has been shown to be defective, is taken out of service and clearly identified. The equipment shall not be used to analyze client samples until it has been repaired and shown to perform satisfactorily.

6.8 Spare Parts

Department manager/supervisors are responsible for maintaining an adequate inventory of spare parts required to minimize equipment downtime. This inventory includes parts and supplies that:

- Are subject to frequent failure,
- Have limited useful lifetimes, or
- Cannot be obtained in a timely manner should failure occur.

7.0 CONTROL OF DATA

Analytical results processing, verification and reporting are the processes that result in the delivery of defensible analytical data to the data user. These processes include calculation of raw data into final concentration units, reviewing results for accuracy and assembly of the technical report for delivery to the data user.

All analytical data undergo a well-defined, well-documented multi-tier review process before being reported to the client. The following information describes procedures employed at Pace Analytical for translating raw analytical data into accurate, finished sample reports and describes data storage policies.

7.1 Analytical Results Processing

When "raw data" is manually generated by an analyst, it is recorded in either a bound notebook (run logbook), or copies of the computer printouts are appropriately labeled and filed. Logbooks and other bench records are kept in accordance with each laboratory's Standard Operating Procedure on documentation practices (this may also include the use of electronic logbooks). The primary analyst is responsible for the initial reduction and review of the data. This includes confirming compliance with required methodology; checking the calculations used; checking quality control data against known criteria; noting any discrepancies that occurred both in the necessary logbooks and as a footnote or narrative in LIMS; and entering analytical data into the LIMS system. The primary analyst then compiles the initial data package for data verification. This compilation must include sufficient documentation to review the data. It may include chromatograms or strip-chart recordings, before and after printouts of manual integrations, other computer printouts, chain-of-custody copies if available, and logbook copies. Some agencies or clients require different levels of data reporting. For these special levels, the primary analyst may also need to compile additional project information such as initial calibration data or extensive spectral data before the data package goes to the verification step.

7.2 Data Verification

Data verification is the process of examining data and accepting or rejecting it based on pre-defined criteria. This review step is designed to ensure that the reported data are free from calculation and transcription errors, that quality control parameters are evaluated, and that any discrepancies are properly documented.

Analysts performing the analysis and subsequent data reduction have the primary responsibility for the quality of the data produced. The primary analyst initiates the data verification process by reviewing and accepting the data provided QC criteria have been met for the samples being reported. Data review checklists are used to document the data review process.

The completed data package is then sent to a designated qualified reviewer (this cannot be the primary analyst). This reviewer provides an independent technical assessment of the data package and technical review for accuracy according to methods employed and laboratory protocols. All data that are manually entered into the LIMS is reviewed at a rate of 100%. This involves a quality control review for use of the proper methodology and detection limits, compliance to quality control protocol and criteria, presence and completeness of required deliverables, and accuracy of calculations and data quantitation. The reviewer also reviews analyst-generated calculations.

For results that are processed via computer, calculations are checked by the analyst (or designee) assigned to this task at a frequency designed to assure that the data reductions are valid. The results are either manually transferred to a standard reporting form or reported via computer generation of forms.

Once the data have been technically reviewed and approved, authorization for release of the data from the analytical section is indicated by initialing and dating the data review checklist or otherwise initialing and dating the data.

The Operations or Project Manager examines the report for method appropriateness, detection limits and QC acceptability. Any deviations from the referenced methods are checked for documentation and validity, and QC corrective actions are reviewed for successful resolution.

Use of checklists ensures that all data are systematically handled and no steps are omitted. Checklists are reviewed, retained, and made accessible should they need to be referenced at a later date.

7.3 Data Reporting

All data segments pertaining to a particular Pace Analytical project number are delivered to the Client Services Department (Project Manager) for assembly into the final report. All points mentioned during technical and QC reviews are included in a case narrative, if the data quality is or may be impacted.

Final reports are prepared according to the level of reporting required by the client. A standard Pace Analytical final report consists of the following components:

1. A title which designates the report as "Final Report", "Laboratory Results", "Certificate of Results", etc.
2. Name and address of laboratory (or subcontracted laboratories, if used).
3. Phone number and name of laboratory contact where questions can be referred.
4. A unique number for the report (project number). The pages of the report shall be numbered and a total number of pages shall be indicated (usually in the cover letter).
5. Name and address of client and name of project (if applicable).
6. Unique identification of samples analyzed (including client sample numbers).
7. Identification of any sample that did not meet acceptable sampling requirements (from NELAC or other governing agency), such as improper sample containers, holding times missed, sample temperature, etc.
8. Date and time of collection of samples, date of sample receipt by the laboratory, dates of sample preparation and analysis, and times of sample preparation and analysis when the holding time for either is 72 hours or less.
9. Identification of the test methods used.
10. Identification of sampling procedures if sampling was conducted by the laboratory.
11. Deviations from, additions to, or exclusions from the test methods. These can include failed quality control parameters, deviations caused by the matrix of the sample, etc., and can be shown as a case narrative or as defined footnotes to the analytical data.
12. Identification of whether calculations were performed on a dry or wet-weight basis.
13. Reporting limits used.
14. Final results or measurements, supported by appropriate chromatograms, charts, tables, spectra, etc.
15. If required, a statement of the estimated uncertainty of the test results.
16. A signature and title of person accepting responsibility for the content of the report (can be an equivalent electronic identification) and date report was issued.
17. A statement clarifying that the results of the report relate only to the samples tested or to the samples as they were received by the laboratory.
18. If necessary, a statement indicating that the report must not be reproduced except in full, without the written approval of the laboratory.
19. Identification of all test results provided by a subcontracted laboratory or other outside source.
20. Identification of results obtained outside of quantitation levels.

Any changes made to a final report shall be designated as "Revised" or equivalent wording. The laboratory must keep sufficient archived records of all lab reports and revisions. For higher levels of data deliverables, a copy of all applicable raw data is sent to the client along with a final report of results. When possible, the Pace Analytical laboratory will provide electronic data deliverables (EDD) as required by contracts or upon client request.

Client data that requires transmission by telephone, telex, facsimile or other electronic means undergoes appropriate steps to preserve confidentiality.

7.4 Data Archiving

All records compiled by Pace Analytical labs are maintained, stored and secured by the Quality Manager or by a designated Data Archivist for a minimum of five years unless superseded by federal, contractual, and/or accreditation requirements. These records can include client data reports, certificates pertaining to calibration and maintenance of equipment, raw data from instrumentation, quality control documents and logbooks. These records are retained in order to provide for possible historical reconstruction of data. Access to archived data is kept to a minimum, with the Data Archivist maintaining the archive documentation in a secure, fireproof (if possible) location. Some laboratories archive their data in an off-site facility and the Data Archivist will keep a record of this archival as well. Records that are computer-generated have either a hard copy or electronic backup copy.

In the event of a change in ownership, accountability or liability, reports of analyses performed pertaining to accreditation will be maintained by the acquiring entity for a minimum of five years. In the event of bankruptcy, laboratory reports and/or records will be transferred to the client and/or the appropriate regulatory entity.

7.5 Resolution of Client Complaints or Questions

Pace Analytical is committed to providing superior service to our customers including cooperation to clarify and resolve questions or complaints pertaining to completed analytical work. Each Pace Analytical laboratory maintains written or electronic documentation of questions and complaints received from clients or the client's authorized representative regarding work performed. The resolution or answers to the questions and complaints are also included in the documentation. In the event that an error is found when investigating the question or complaint, a revised or supplemental report is issued as necessary.

8.0 QUALITY SYSTEM AUDITS AND REVIEWS

In an effort to assess the effectiveness of the Quality Systems, all Pace Analytical laboratories are subject to internal and external audits and reviews.

8.1 Internal Audits

8.1.1 Responsibilities

The Quality Manager is responsible for designing and/or conducting internal audits. Since internal audits represent an independent assessment of laboratory functions, the auditor must be functionally independent from laboratory operations to ensure objectivity. The auditor must be familiar enough with the objectives, principles, and procedures of laboratory operations to be able to perform a thorough and effective evaluation. The Quality Manger evaluates audit observations and verifies the completion of corrective actions. In addition, an annual corporate audit is conducted by the Director of Quality, Safety & Training and/or designee.

8.1.2 Scope and Frequency of Internal Audits

Internal systems audits are conducted yearly at a minimum. The scope of these audits includes evaluation of specific analytical departments or a specific quality-related system as applied throughout the laboratory.

Examples of system-wide elements that can be audited include:

- Quality Systems documents, such as Standard Operating Procedures, training documents, Quality Manual and all applicable addenda
- Personnel and training files.
- General laboratory safety protocols.
- Chemical handling practices, such as labeling of reagents, solutions, standards, and associated documentation.
- Documentation concerning equipment and instrumentation, calibration/maintenance records, operating manuals.
- Sample receipt and management practices.
- Analytical documentation, including any discrepancies and corrective actions.
- General procedures for data security, review, documentation, reporting and archiving.
- Data integrity issues such as proper manual integrations.

When the operations of a specific department are evaluated, a number of additional functions are reviewed including:

- Detection limit studies
- Internal chain-of-custody documentation
- Documentation of standard preparations
- Quality Control limits and Control charts

Certain projects may require an internal audit to ensure laboratory conformance to site work plans, sampling and analysis plans, QAPPs, etc.

A representative number of data audits are completed annually. The report format of any discrepancy is similar to that of other internal audits.

8.1.3 Internal Audit Reports and Corrective Action Plans

Additional information can be found in SOP ALL-Q-011 ***Audits and Inspections***.

A full description of the audit, including the identification of the operation audited, the date(s) on which the audit was conducted, the specific systems examined, and the observations noted are summarized in an internal audit report. Although other personnel may assist with the performance of the audit, the Quality Manager writes and issues the internal audit report identifying which audit observations are deficiencies that require corrective action.

Once completed, the internal audit report is issued jointly to the Laboratory General Manager and the manager(s)/supervisor(s) of the audited operation at a minimum. The responsible manager(s)/supervisor(s) responds with a plan to correct all of the deficiencies cited by the due date specified in the audit report. Each response must include timetables for completion of all proposed corrective actions.

The Quality Manager reviews the audit responses. If the response is accepted, the Quality Manager uses the action plan and timetable as a guideline for verifying completion of the corrective action(s). If the Quality Manager determines that the audit response does not adequately address the correction of cited deficiencies, the response will be returned for modification.

To complete the audit process, the Quality Manager performs a re-examination of the areas where deficiencies were found to verify that all proposed corrective actions have been implemented. An audit deficiency is considered closed once implementation of the necessary corrective action has been verified. If corrective action cannot be verified, the associated deficiency remains open until that action is completed.

8.2 External Audits

Pace Analytical laboratories are audited regularly by regulatory agencies, to maintain laboratory certifications, and by clients to maintain appropriate specific protocols.

Audit teams external to the company review the laboratory to assess the existence of systems and degree of technical expertise. The Quality Manager and other QA staff host the audit team and assist in facilitation of the audit process. Generally, the auditors will prepare a formalized audit report listing deficiencies observed and follow-up requirements for the laboratory. In some cases, items of concern are discussed during a debriefing convened at the end of the on-site review process.

The laboratory staff and supervisors develop corrective action plans to address any deficiencies with the guidance of the Quality Manager. The Laboratory General Manager provides the necessary resources for staff to develop and implement the corrective action plans. The Quality Manager collates this information and provides a written report to the audit team. The report contains the corrective action plan and expected completion dates for each element of the plan. The Quality Manager follows-up with the laboratory staff to ensure corrective actions are implemented.

8.3 Quarterly Quality Reports

Additional information can be found in SOP ALL-Q-014 ***Quality System Review***.

The Quality Manager is responsible for preparing a quarterly report to management summarizing the effectiveness of the laboratory Quality Systems. This status report will include:

- Results of internal systems or performance audits
- Corrective action activities
- Discussion of QA issues raised by clients

- Results of third party or external audits
- Status of laboratory certifications
- Proficiency Testing Study Results
- Results of internal laboratory review activities
- Summary of holding time violations
- Method detection limit study status
- Training activity summary
- SOP revision summary
- 3P Implementation summary (internal program)
- Other significant Quality System items

The Corporate Director of Quality, Safety & Training utilizes the information from each laboratory to make decisions impacting the Quality Systems of the company as a whole. Each General Manager utilizes the quarterly report information to make decisions impacting Quality Systems and operational systems at a local level.

8.4 Annual Managerial Review

A managerial review of Quality Systems is performed on an annual basis at a minimum. This allows for assessing program effectiveness and introducing changes and/or improvements.

The managerial review must include the following topics of discussion:

- Policy and procedure suitability
- Manager/Supervisor reports
- Internal audit results
- Corrective and preventative actions
- External assessment results
- Proficiency testing studies
- Sample capacity and scope of work changes
- Client feedback, including complaints

This managerial review must be documented for future reference by the Quality Manager and copies of the report are distributed to laboratory staff.

9.0 CORRECTIVE ACTION

Additional information can be found in SOP ALL-Q-012 ***Corrective Action/Preventative Action Process***.

During the process of sample handling, preparation and analysis, certain occurrences may warrant the necessity of corrective actions. These occurrences may take the form of analyst errors, deficiencies in quality control, method deviations, or other unusual circumstances. The Quality System of Pace Analytical provides systematic procedures for documentation and completion of corrective actions. This can be done using a Corrective Action Tracking Log that lists the deficiency by ID, along with the deficiency source, responsible party, root cause, resolution, due date, and date resolved.

9.1 Corrective Action Documentation

The following items are examples of occurrences that warrant some form of documented corrective action:

- Quality Control data outside of acceptance criteria
- Sample Acceptance Policy deviations
- Missed holding times
- Instrument failures (including calibration failure)
- Sample preparation or analysis errors
- Sample contamination
- Errors in client reports
- Audit findings (internal and external)
- Proficiency Testing (PT) sample failures
- Client complaints or inquiries

Documentation of corrective actions may be in the form of a comment or footnote on the final report that explains the deficiency (e.g. matrix spike recoveries outside of acceptance criteria) or it may be a more formal documentation (either paper system or computerized spreadsheet). This will depend on the extent of the deficiency, the impact on the data, and the method or client requirements for documentation.

The person who discovers the deficiency or non-conformance initiates the corrective action documentation. The documentation must also include the affected projects and sample numbers, the name of the applicable Project Manager, the client name and the sample matrix involved.

The person initiating the corrective action documentation must also list suspected or known causes of the deficiency or non-conformance as well as any corrective actions that they have taken. They would then sign and date the form and pass it to their immediate supervisor or the Project Manager. The supervisors and PMs add in their observations and further corrective actions, sign and date the form and pass to any other applicable lab employee. The Quality Manager is responsible for final review and signoff of all formal corrective action forms. A copy of the form is archived with each project and a copy is kept in the quality office.

9.2 Corrective Action Completion (Specific Examples)

9.2.1. Quality Control outside of acceptance criteria: the analyst that is generating or validating Analytical data is responsible for checking the results against established acceptance criteria (quality control limits). The analyst must immediately address any deficiencies discovered. Method blank, LCS or matrix spike failures are evaluated against method, program, and client requirements and appropriate footnotes are entered into the LIMS system. Some deficiencies may be caused by matrix interferences. Where possible, matrix interferences are confirmed by re-analysis. Quality control deficiencies must be made known to the client on the final report for their review of the data for usability. If appropriate, the supervisor is alerted to the QC failure and if necessary a formal

corrective action can be initiated. This may involve the input of the Quality Manager or the General Manager. The department supervisor and/or Operations Manager are responsible for evaluating the source of the deficiency and for returning the analytical system to control. This may involve instrument maintenance, analytical standard or reagent evaluation, or an internal audit of the analytical procedure.

9.2.2. **Sample Acceptance Policy deviations:** any deviation from the Sample Acceptance Policy listed in this Manual must be documented on the Chain-of-Custody or other applicable form by the sample receiving personnel or by the Project Manager. The client must be notified of these deviations as soon as possible so they can make decisions on whether to continue with the sample analysis or re-sample. Copies of this documentation must be included in the project file. Analysts or supervisors that discover such deviations must contact the sample receiving personnel or appropriate Project Manager so they can initiate the proper documentation and client contact. If a more formalized corrective action must be documented, the Quality Manager should be made aware of the situation.

9.2.3. **Missed holding times**: in the event that a holding time requirement has been missed, the analyst or supervisor must complete a formal corrective action form. The Project Manager and the Quality Manager must be made aware of these hold time exceedances.

The Project Manager must contact the client for appropriate decisions to be made with the resolution documented and included in the client project file. The Quality Manager includes a list of all missed holding times in their Quarterly Report to the corporate office.

9.2.4. **Instrument Failures**: in the event of an instrument failure that either causes the necessity for re-analysis or questions the validity of generated results, a formal corrective action must be initiated. The analyst and supervisor must evaluate any completed data for validity and usability. They are also responsible for returning the instrument to valid operating condition and for documenting that the system is in control (e.g. acceptable calibration verification).

9.2.5. **Sample Preparation or Analysis errors**: whenever there is an error in the preparation or analysis of samples, the analyst evaluates the impact on the usability of the analytical data with the assistance of their supervisor or manager. The affected samples will be re-processed or re-analyzed under acceptable conditions. In the event that no additional sample is available for re-analysis, the client must be contacted for their decision on how to proceed. Documentation may take the form of footnotes or a formal corrective action form.

9.2.6. **Errors in client reports:** when an error on the client report is discovered, the Project Manager is responsible for initiating a formal corrective action form that describes the failure (e.g. incorrect analysis reported, reporting units are incorrect, reporting limits do not meet objectives). The Project Manager is also responsible for revising the final report if necessary and submitting it to the client.

9.2.7. **Audit findings:** the Quality Manager is responsible for documenting all audit findings and their corrective actions. This documentation must include the initial finding, the persons responsible for the corrective action, the due date for reporting back to the auditing body, the root cause of the issue, and the corrective action taken to resolve the findings. The Quality Manager is also responsible for providing any back-up documentation used to prove that a corrective action has been completed.

9.2.8. **Proficiency Testing failures**: Any PT result returned to the Quality Manager as "not acceptable" requires an investigation and applicable corrective actions. The operational staff is made aware of the PT failures and they are responsible for reviewing the applicable raw data and calibrations and list possible causes for error. The Quality Manager will review their findings and initiate another external PT sample or an internal PT sample to try and correct the previous failure. Replacement PT results must be monitored by the Quality Manager and reported to the applicable regulatory authorities.

9.2.9. **Client Complaints**: Project Managers are responsible for issuing corrective action forms for client complaints. As with other corrective actions, the possible causes of the problem are listed and the form is passed to the appropriate analyst or supervisor. After their corrective actions have been listed, the Project Manager reviews the corrective action to determine if the client needs or concerns are being addressed.

10.0 GLOSSARY

3P Program	The Pace Analytical continuous improvement program that focuses on Process, Productivity and Performance. Best Practices are identified that can be used by all Pace labs.
Accuracy	The agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components that are due to sampling and analytical operations; a data quality indicator.
Aliquot	A portion of a sample taken for analysis.
Analyte	The specific chemical species or parameter an analysis seeks to determine.
Batch	Environmental samples that are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents. A preparation batch is composed of one to 20 environmental samples of the same NELAC-defined matrix, meeting the above-mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be 24 hours. An analytical batch is composed of prepared environmental samples (extracts, digestates or concentrates) that are analyzed together as a group. An analytical batch can include prepared samples originating from various environmental matrices and can exceed 20 samples.
Blank	A sample that has not been exposed to the analyzed sample stream in order to monitor contamination during sampling, transport, storage or analysis. The blank is subjected to the usual analytical and measurement process to establish a zero baseline or background value and is sometimes used to adjust or correct routine analytical results.
Blind Sample	A sample for submitted for analysis with a composition known to the submitter. The analyst/laboratory may know the identity of the sample but not its composition. It is used to test analyst or laboratory proficiency in the execution of the measurement process.
Contract Required Detection Limit (CRDL)	Detection limit that is required for EPA Contract Laboratory Program (CLP) contracts.
Contract Required Quantitation Limit (CRQL)	Quantitation limit (reporting limit) that is required for EPA Contract Laboratory Program (CLP) contracts.
Calibration	To determine, by measurement or comparison with a standard, the correct value of each scale reading on a meter, instrument, or other device. The levels of the applied calibration standard should bracket the range of planned or expected sample measurements.
Calibration Curve	The graphic representation of known values, such as concentrations for a series of calibration standards and their instrument response.
Chain-of-Custody (COC)	A record that documents the possession of samples from the time of collection to receipt in the laboratory. This record generally includes the number and type of containers, mode of collection, collector, time of collection, preservation, and requested analyses.
Confirmation	Verification of the identity of a component through the use of an alternate scientific approach from the original method. These may include, but are not limited to: • second-column confirmation • alternate wavelength • derivatization derivative • mass spectral interpretation • additional cleanup procedures

Comparability	An assessment of the confidence with which one data set can be compared to another. Comparable data are produced through the use of standardized procedures and techniques.
Completeness	The percent of valid data obtained from a measurement system compared to the amount of valid data expected under normal conditions. The equation for completeness is: % Completeness = (Valid Data Points/Expected Data Points)*100
Calibration Verification	The process of verifying a calibration by analysis of standards and comparing the results with the known amount.
Control Chart	A graphic representation of a series of test results, together with limits within which results are expected when the system is in a state of statistical control (see definition for Control Limit)
Control Limit	A range within which specified measurement results must fall to verify that the analytical system is in control. Control limit exceedances may require corrective action or require investigation and flagging of nonconforming data.
Corrective Action	The action taken to eliminate the causes of a nonconformity, defect, or other undesirable situation in order to prevent recurrence.
Data Quality Objective (DOQ)	Systematic strategic planning tool based on the scientific method that identifies and defines the type, quality, and quantity of data needed to satisfy a specified use or end user.
Data Reduction	The process of transforming raw data by arithmetic or statistical calculations, standard curves, concentration factors, etc., and collation into a more usable form.
Demonstration of Capability	A procedure to establish the ability of the analyst to generate acceptable accuracy.
Detection Limit (DL)	General term for the lowest concentration or amount of the target analyte that can be identified, measured and reported with confidence that the analyte concentration is not a false positive value. See definitions for Method Detection Limit and Limit of Detection.
Document Control (Management)	Procedures to ensure that documents (and revisions thereto) are proposed, reviewed for accuracy, approved for release by authorized personnel, distributed properly and controlled (managed) to ensure use of the correct version at the location where the prescribed activity is performed.
Dry Weight	The weight after drying in an oven at a specified temperature.
Duplicate or Replicate Analysis	The identically performed measurement on two or more sub-samples of the same sample within a short interval of time
Environmental Sample	A representative sample of any material (aqueous, non-aqueous, or multimedia) collected from any source for which determination of composition or contamination is requested or required. Environmental samples can generally be classified as follows: • Surface Water and Ground Water • Drinking Water - Delivered (treated or untreated) water designated as potable water • Water/Wastewater - Raw source waters for public drinking water supplies, ground waters, municipal influents/effluents, and industrial influents/effluents • Sludge - Municipal sludges and industrial sludges. • Soil - Predominately inorganic matter ranging in classification from sands to clays. • Waste - Aqueous and non-aqueous liquid wastes, chemical solids, and industrial liquid and solid wastes
Equipment Blank	A sample of analyte-free media used to rinse common sampling equipment to check effectiveness of decontamination procedures.

Field Blank	A blank sample prepared in the field by filling a clean container with reagent water and appropriate preservative, if any, for the specific sampling activity being undertaken.
Field Measurement	Determination of physical, biological, or radiological properties, or chemical constituents that are measured on-site, close in time and space to the matrices being sampled/measured, following accepted test methods. This testing is performed in the field outside of a fixed-laboratory or outside of an enclosed structure that meets the requirements of a mobile laboratory.
Holding Time	The maximum time that samples may be held prior to preparation and/or analysis as defined by the method.
Homogeneity	The degree to which a property or substance is uniformly distributed throughout a sample.
Initial Calibration (ICAL)	The process of analyzing standards, prepared at specified concentrations, to define the quantitative response relationship of the instrument to the analytes of interest. Initial calibration is performed whenever the results of a calibration verification standard do not conform to the requirements of the method in use or at a frequency specified in the method.
Internal Standards	A known amount of standard added to a test portion of a sample as a reference for evaluating and controlling the precision and bias of the applied analytical method.
Laboratory Control Sample (LCS)	A blank sample matrix, free from the analytes of interest, spiked with known amounts of analytes or a material containing known amounts of analytes. It is generally used to establish intra-laboratory or analyst-specific precision and bias or to assess the performance of all or a portion of the measurement system. Sometimes referred to as Laboratory Fortified Blank, Spiked Blank or QC Check Sample.
Limit of Detection (LOD)	An estimate of the minimum amount of a substance that an analytical process can reliably detect. An LOD is analyte and matrix specific and may be laboratory-dependent.
Limit of Quantitation (LOQ) .	The minimum levels, concentrations or quantities of a target variable (e.g. target analyte) that can be reported with a specified degree of confidence
Laboratory Information Management System (LIMS)	A computer system that is used to maintain all sample information from sample receipt, through preparation and analysis and including sample report generation.
Lot	A quantity of bulk material of similar composition processed or manufactured at the same time.

Matrix	The component or substrate that contains the analyte of interest. For purposes of batch and QC requirement determinations, the following matrix distinctions are used: • **Aqueous**: any aqueous sample excluded from the definition of Drinking Water matrix or Saline/Estuarine source. Includes surface water, groundwater, effluents, and TCLP or other extracts. • **Drinking Water**: any aqueous sample that has been designated a potable or potentially potable water source. • **Saline/Estuarine**: any aqueous sample from an ocean or estuary, or other saltwater source. • **Non-aqueous liquid**: any organic liquid with <15% settleable solids. • **Biological Tissue**: any sample of a biological origin such as fish tissue, shellfish or plant material. Such sample can be grouped according to origin. • **Solids**: includes soils, sediments, sludges, and other matrices with >15% settleable solids. • **Chemical Waste**: a product or by-product or an industrial process that results in a matrix not previously defined • **Air**: whole gas or vapor samples including those contained in flexible or rigid wall containers and the extracted concentrated analytes of interest from a gas vapor that are collected with a sorbent tube, impinger solution, filter, or other device.
Matrix Spike (MS)	A sample prepared by adding a known quantity of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available. Matrix spikes are used to determine the effect of the matrix on a method's recovery efficiency. (sometimes referred to as Spiked Sample or Fortified Sample)
Matrix Spike Duplicate (MSD)	A second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of precision of the recovery of each analyte. (sometimes referred to as Spiked Sample Duplicate or Fortified Sample Duplicate)
Method Blank	A sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedures: and in which no target analytes or interferences are present at concentrations that impact the analytical results for sample analyses.
Method Detection Limit (MDL)	One way to establish a Limit of Detection (LOD); defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.
Performance Based Measurement System (PBMS)	An analytical system wherein the data quality needs, mandates or limitations of a program or project are specified and serve as criteria for selecting appropriate test methods to meet those needs in a cost-effective manner.
Precision	The degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves. Precision is usually expressed as standard deviation, variance or range, in either absolute or relative terms.
Preservation	Refrigeration and/or reagents added at the time of sample collection (or later) to maintain the chemical and/or biological integrity of the sample.
Proficiency Testing	A means of evaluating a laboratory's performance under controlled conditions relative to a given set of criteria through analysis of unknown samples provided by an external source.
Protocol	A detailed written procedure for field and/or laboratory operation that must be strictly followed.

Quality Assurance Project Plan (QAPP)	A formal document describing the detailed quality control procedures required by a specific project.
Quality Assurance (QA)	An integrated system of activities involving planning, quality control, quality assessment, reporting and quality improvement to ensure that a product or service meets defined standards of quality with a stated level of confidence.
Quality Control (QC)	The overall system of technical activities whose purpose is to measure and control the quality of a product or service so that it meets the needs of users.
Quality Manual	A document stating the management policies, objectives, principles, organizational structure and authority, responsibilities, accountability, and implementation of an agency, organization, or laboratory, to ensure the quality of its product and the utility of its product to its users.
Quality System	A structured and documented management system describing the policies, objectives, principles, organizational authority, responsibilities, accountability, and implementation plan of an organization for ensuring quality in its work processes, products (items), and services. The quality system provides the framework for planning, implementing, and assessing work performed by the organization and for carrying out required QA and QC.
Random Error	The EPA has established that there is a 5% probability that the results obtained for any one analyte will exceed the control limits established for the test due to random error. As the number of compounds measured increases in a given sample, the probability for statistical error also increases.
Raw Data	Any original factual information from a measurement activity or study recorded in a laboratory notebook, worksheets, records, memoranda, notes, or exact copies thereof that are necessary for the reconstruction and evaluation of the report of the activity or study. Raw data may include photography, microfilm or microfiche copies, computer printouts, magnetic media, including dictated observations, and recorded data from automated instruments. If exact copies of raw data have been prepared (e.g. tapes which have been transcribed verbatim, dated and verified accurate by signature), the exact copy or exact transcript may be submitted.
Reagent Grade	Analytical reagent (AR) grade, ACS reagent grade, and reagent grade are synonymous terms for reagents that conform to the current specifications of the Committee on Analytical Reagents of the American Chemical Society.
Reference Standard	A standard, generally of the highest metrological quality available at a given location, from which measurements made at that location are derived.
Reporting Limit (RL)	The level at which method, permit, regulatory and client specific objectives are met. The reporting limit may never be lower than the Limit of Detection (i.e. statistically determined MDL). Reporting limits are corrected for sample amounts, including the dry weight of solids, unless otherwise specified. There must be a sufficient buffer between the Reporting Limit and the MDL.
Representativeness	A quality element related to the ability to collect a sample reflecting the characteristics of the part of the environment to be assessed. Sample representativeness is dependent on the sampling techniques specified in the project work plan.
Sample Delivery Group (SDG)	A unit within a single project that is used to identify a group of samples for delivery. An SDG is a group of 20 or fewer field samples within a project, received over a period of up to 14 calendar days. Data from all samples in an SDG are reported concurrently.
Sample Tracking	Procedures employed to record the possession of the samples from the time of sampling until analysis, reporting and archiving. These procedures include the use of a Chain-of-Custody Form that documents the collection, transport, and receipt of compliance samples to the laboratory. In addition, access to the laboratory is limited and controlled to protect the integrity of the samples.
Sensitivity	The capability of a method or instrument to discriminate between measurement responses representing different levels (concentrations) of a variable of interest.

Standard	A substance or material with properties known with sufficient accuracy to permit its use to evaluate the same property in a sample.
Standard Blank	A calibration standard consisting of the same solvent/reagent matrix used to prepare the calibration standards without the analytes. It is used to construct the calibration curve by establishing instrument background.
Standard Operating Procedure (SOP)	A written document which details the method of an operation, analysis, or action whose techniques and procedures are thoroughly prescribed and which is accepted as the method for performing certain routine or repetitive tasks
Surrogates	A substance with properties that mimic the analyte of interest. It is unlikely to be found in environmental samples and is added to them for quality control purposes.
Systems Audit	An on-site inspection or assessment of a laboratory's quality system.
Traceability	The property of a material or measurement result defining its relationship to recognized international or national standards through an unbroken chain of comparisons.
Training Document	A training resource that provides detailed instructions to execute a specific method or job function.
Trip Blank	This blank sample is used to detect sample contamination from the container and preservative during transport and storage of the sample. A cleaned sample container is filled with laboratory pure water; any preservative used in the sample is added and then the blank is stored, shipped, and analyzed with its group of samples.
Validation	The confirmation by examination and provision of objective evidence that the particular requirements for a specific intended use are fulfilled.
Verification	Confirmation by examination and provision of evidence that specified requirements for instruments have been met. The result of verification leads to a decision either to restore in service, to perform adjustment, to repair, to downgrade, or to declare obsolete. In all cases, it is required that a written trace of the verification performed shall be kept on the measuring instrument's individual record.
Warning Limits	The limits (typically 2 standard deviations either side of the mean) shown on a control chart within which most results are expected to lie (within a 95% probability) while the system remains in a state of statistical control.
Work Cell	A defined group of analysts that together perform the method analysis. The members of the group and their specific functions within the work cell must be fully documented.
Working Range	The range of results between the Limit of Quantitation and the upper limit of measurement system calibration.

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UPPER MIDWEST REGION
QUALITY MANUAL ADDENDUM To Revision 9.1

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(Effective date of addendum is the last date signed above)

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Julie Trivedi, Quality Manager — 3/8/06 Date
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Eric Bullock, Project Manager — 3/13/06 Date
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Kang Khang, Project Coord. — 3/14/06 Date
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Jill Duranceau, — 3/13/06 Date
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Judith Leigh Anderson, — 3/8/06 Date
Quality Assurance Analyst
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Randy Naidl, Supervisor — 3/13/06 Date
921-321-9413

Jeff Buschner, Supervisor — 3/13/2006 Date
921-321-9421

Alexandria Wolf, Supervisor — 3/13/06 Date
920-321-9464 Hanson ALW 3-13-06

Phil Scott, Supervisor — 3/14/06 Date
920-321-9419

Dawn Haag, Supervisor — 3-8-06 Date
920-469-2436

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1.0 INTRODUCTION & ORGANIZATIONAL STRUCTURE

1.1 Introduction to Pace

The Upper Midwest region of Pace Analytical Services has three analytical laboratories, performing a wide variety of tests. Its capabilities include:

- Volatiles and semi-volatiles by Gas Chromatography/Mass Spectrometry (GC/MS);
- Metals analysis by Inductively Coupled Plasma spectrometry (ICP) and ICP/MS;
- Pesticide, polychlorinated biphenyls (PCB), and volatile (BTEX) analyses by gas chromatography (GC);
- Dioxin/furan analysis by high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS) and LRMS
- Volatile and semivolatile air analysis by GC and GCMS
- Polyaromatic hydrocarbon analysis by High Pressure Liquid Chromatography (HPLC);
- Gasoline, diesel and Total Petroleum Hydrocarbon analyses by Gas Chromatography (GC);
- Biota analyses for all major tests
- Mercury by cold vapor analysis
- Low level mercury analysis by Method 1631E
- And numerous inorganic wet chemical analyses

NOTE: All methods are listed in Attachment III and may be subject to change prior to addenda update. The Quality Assurance Office maintains a complete list of each method and analyte approved by NELAC and pertinent state agencies.

The Upper Midwest region is capable of analyzing a variety of environmental and non-environmental samples from different media including surface, drinking and ground waters, air, biota, soils, sediments, waste products, sludge and concretes. All analyses follow written Standard Operating Procedures that are kept on file in the Quality Assurance office. A listing of the major equipment in each facility is available through the quality assurance office in each facility.

The upper Midwest region holds certifications with approximately 40 state and federal agencies. (A complete listing may be obtained through the quality assurance office.) Pace Minneapolis, Pace Green Bay and Pace Kimberly laboratories hold accreditation by NELAC, the National Environmental Laboratory Accreditation Conference, through the accrediting authority of the Florida Department of Health. Copies of the certificates and fields of testing lists may be forwarded to you from the Quality Assurance department.

This addendum, combined with the preceding corporate quality manual, comprises the complete Laboratory Quality Manual for Upper Midwest region of Pace Analytical Services. This addendum contains information specific to the Upper Midwest region, whereas the corporate section details practices and policies that are common to all the member Pace laboratories. The Regional Quality Manager when necessary updates the addendum.

1.7 Laboratory Organization

Figure 1.1 has been expanded to show the detail of the organizational structure in the Minnesota Laboratory (see Attachment I).

1.9 Training and Orientation

Refer to the Standard Operating Procedure *Training Procedures* (ALL-Q-020) for specific information on acceptable means of documenting initial and continuing demonstrations of capability.

1.10 Laboratory Safety

The designated safety/chemical hygiene officer is Melanie Ollila for the Minneapolis laboratory and Steve Mleczko for the Pace Green Bay and Kris Burns for the Pace Kimberly laboratories. All specific information on laboratory safety is located in each facility Safety Manual/Chemical Hygiene Plan.

1.11 Security and Confidentiality

All information pertaining to a particular client and their analytical results will remain confidential including national security concerns. Data will not be released to outside agencies without the written authorization from the client.

2.0 SAMPLE CUSTODY

2.1 Sampling Support

Additions to Table 2.1 through 2.4 include but may not be limited to:

Method/Matrix	Container	Preservative	Maximum Hold Time
CARB 429 W (HRMS PAH)	1 Liter	4°C	1 Year to Extraction*
CARB 429 S (HRMS PAH)	4 or 8 oz. jar	4°C	1 Year to Extraction*
CARB 429 T (HRMS PAH)	4 or 8 oz. jar	4°C	1 Year to Extraction*
SM9221D (Fecal-col)	100mL	4°C, 10% sodium thiosulfate	6 hours
SM9223B (Total-col)	100mL	4°C, 10% sodium thiosulfate	24 hours
1614 Water	1 Liter	4°C	1 Year to Extraction*
1614 Soil	4 or 8 oz. jar	4°C	1 Year to Extraction*
1614 Tissue	4 or 8 oz. jar	4°C	1 Year to Extraction*
1653 Water	2 Liter	4°C, pH<2 H_2SO_4	30 Days to Extraction; 30 days to analysis
1668 Water	1 Liter	4°C	1 Year to Extraction*
1668 Soil	4 or 8 oz. jar	4°C	1 Year to Extraction*
8015 (MeOH, eOH)	3 40 ml vials	HCl	14 Days
8280 Water	1 Liter	4°C	30 Days to Extraction*
8280 Soil	4 or 8 ounce	4°C	30 Days to Extraction*
8290 Solid	4 or 8 ounce	4°C	30 Days to Extraction*
8290 Water	1 Liter	4°C	30 Days to Extraction*
8290 Waste	2 ounce	4°C	30 Days to Extraction*
WI GRO Water	3 40 ml vials	HCl	14 Days
WI GRO Soil	5035 vial kit	See *Note*	14 Days
WI DRO Water	1 Liter	HCl	7 Days to Extraction*

WI DRO Soil	Tared 4 oz. jar	4°C	14 Days to extraction*
Method 23/TO9	Sampling Head	4°C	30 Days to Extraction*
Method 1631E	500mL Glass	None	Oxidized in bottle within 28 days.

** 40 Days from Extraction to Analysis. (EPA 1613,WI DRO)*
45 Days from Extraction to Analysis (SW8290, 1668, 8280 and Method 23/TO9)
Note: 5035 kit contains 2 vials water, preserved by freezing or 2 vials aqueous $NaHSO_4$ preserved at 4°C and 1 vial MeOH preserved at 4°C and 1 vial unpreserved at 4°C.

2.3 Sample Acceptance Policy

For samples collected in the State of Wisconsin, Pace Green Bay will document whether the samples were received on ice (ROI) instead of documenting the temperature at the time of receipt.

2.4 Chain of Custody

Clarification: The external chain of custody (COC) is signed by the client for relinquishment of samples. The samples may be transported by the client or through the use of a ground or air carrier (e.g. Fed Ex, UPS, SpeeDee) The carrier will assign a tracking number to each cooler and this number may be traced. When the coolers are received at Pace Analytical Services, Inc., the COC is signed by sample management personnel to signify receipt.

2.5 Sample Receipt

All correspondence pertaining to samples not meeting the acceptance criteria will be fully documented and retained with the project file. All affected data will be footnoted appropriately in the final report.

2.6 Sample Log-in

The Minneapolis laboratory utilizes an "On-Hold" logbook for samples that require further clarification. The logbooks are associated with each sample refrigerator and freezer. The client ID, date, etc are entered into the book, the samples placed into the corresponding refrigerator or freezer, and the project manager associated with the affected client is contacted. The Wisconsin laboratories utilized a master log that is filled in by hand to assign a unique project number to projects. WI sample labels are printed form a program separate from LIMS using the Project Number assigned in the Master Log.

2.7 Sample Storage/Staging

2.7.2 Temperature Monitoring

The Wisconsin laboratories take the samples to the storage locations after the sample containers have been labeled and prior to entry in the LIMS.

Refrigerators are at 4°C ± 2°C unless state or program requirements differ.

2.7.2.1 Freezer Monitoring

All freezers are maintained at <0°C unless otherwise noted in analytical method SOPs. The temperature is monitored and recorded each working day. If the

temperature is greater than 0°C, corrective action is taken and appropriately documented.

2.9 Subcontracting Laboratory Services

Unless holding times will be affected and client is not available for resolution, the client will be advised in writing prior to shipment of subcontracted samples. All laboratories that perform subcontracted work shall provide documentation regarding certification status with state and federal agencies. This documentation is retained in the Quality Assurance Office.

The chain of custody forms generated will not contain any specific client information to protect client confidentiality.

2.10 Sample Disposal

Air canisters will be retained for 14 days after submission of the analytical report. At that time, the cans will be cleaned and certified per the standard operating procedures unless otherwise stated by the project contract or client request.

3.0 ANALYTICAL CAPABILITIES

3.4 Demonstration of Capability (DOC)

Alternate procedures than those outlined in NELAC Quality System Chapter 5 (current standard) are referenced in the corporate standard operating procedure, ALL-Q-020 (*Training Procedures*).

4.0 QUALITY CONTROL PROCEDURES

4.2 Method Blank

The State of Wisconsin requires the concentration of any target analyte detected in the method blank to be less than 1/20 (5%) of the amount found in any associated sample.

4.3 Laboratory Control Sample / Laboratory Control Sample Duplicate (LCS/LCSD)

Marginal exceedances must be random. If the same analyte exceeds the LCS control limit repeatedly, it is an indication of a systemic problem. The source of the error must be located and corrective action taken.

4.9 Trip Blanks

The collection date of a trip blank is generally the collection date of the associated samples. The closer the collection date of a trip blank is to its preparation date, the more reliable and valuable is the data obtained by analyzing it. In order to ensure the relevancy of trip blank data, Pace confirms that trip blanks are contaminant free prior to shipment to the client and recommends that trip blanks always accompany original bottle orders back to Pace for analysis. Identifications in such trip blanks can probably be ascribed to contamination during collection or transport.

4.10 Limit of Detection (LOD)

Further information on detection limit studies are outlined in the corporate SOP ALL-P-104 (*Method Detection Limit Studies*) and the relationship to the Limit of Quantitation.

4.11 Limit of Quantitation (LOQ)

The state of Wisconsin requires a 10/3 relationship between the Limit of Detection (LOD) and the Limit of Quantitation (LOQ).

5.0 DOCUMENT CHANGE CONTROL

5.1 Document Management

The Upper Midwest has no further changes to this section of the corporate quality manual. More detailed information on document change control may be found in MN-Q-229 (*Document Change Control*).

5.1.1 Quality Manual

The Upper Midwest Region has developed a single regional addendum instead of each laboratory attaching a lab-specific addendum.

6.0 EQUIPMENT AND CALIBRATION

6.2 General Calibration Procedure

The State of Wisconsin requires laboratories to report to the MDL (LOD) for many compounds. Results between the LOD and LOQ (see 4.11 above) are qualified as having less certainty.

6.3 Calibration Procedures for GC/MS (Gas Chromatograph/ Mass Spectrometer)

6.3.3 Calibration Verification

Clarification: If the RF from any CCC compound differs from the average RF from the initial calibration by more than 20%, then either the calibration verification standard must be reanalyzed or recalibrate. All non-CCC compounds should be within 40% from the average RF from the initial calibration unless alternate criteria are specified in the laboratory SOP.

6.4 Calibration Procedures for GC and HPLC (Gas Chromatograph and High Performance Liquid Chromatograph)

6.4.2 Calibration Verification

Method criteria supersede the information in the corporate quality manual.

Table 6.1 Summary of Calibration Requirements

Instrument	Calibration Standard	Acceptance Limit	Corrective Action
Glass Syringes, except autosampler syringes which inject a constant amount.	Prior to use an initial demonstration must be performed, at a minimum	Acceptable based on application	Replace
Automatic Dispensing Devices	Quarterly	Varies	Remove from service and fix, replace
Dial Thermometers	Quarterly	Dependent on Method	Remove from service and fix, replace
Oven	Daily with NIST traceable reference	Acceptable based on application	Remove from service and fix, replace
Refrigerator	Daily with NIST traceable reference	Acceptable based on application	Remove from service and fix, replace
Freezer	Daily with NIST traceable reference	Acceptable based on application	Remove from service and fix, replace
Instrument	Calibration Standard	Acceptance Limit	Corrective Action
Incubator	Daily with NIST traceable reference	Acceptable based on application	Remove from service and fix, replace
Waterbath	Daily with NIST traceable reference	Acceptable based on application	Remove from service and fix, replace
Bottle Top Dispensers	Biannually when the dispenser is used at variable amounts	Varies, See appropriate SOP	Remove from service and fix, replace

6.5.2 Calibration Verification for ICP, ICP-MS

The Kimberly laboratory analyzes the Interference Check Standards at the beginning of the run and every 12 hours thereafter if the run is sufficiently long to require analysis of subsequent Interference Check Standards. This practice follows the requirements of Method 6020. Pace Green Bay analyzes the Interference Check Standard at the beginning of the run and every 12 hours thereafter for Method 6020. It is analyzed at the beginning of the run only for Method 6010B.

6.6 General Calibration Procedures

6.6.1 Analytical Balances

The Manual for the Certification of Laboratories Analyzing Drinking water specifies that Class 1 or 2 weights may be used in the laboratory.

6.6.3 pH/Electrometers

Pace Green Bay calibrates the pH meter before use each day. Recalibration is only performed if CCV becomes out of control.

7.0 CONTROL OF DATA

7.5 Response to Inquiries

The project manager initiates the resolution of customer complaints. A Client Data Review Request Form is used to document complaints, project requests, or comments. The form is forwarded to the laboratory and the actions taken are recorded. When a complaint raises doubt concerning the laboratory policies, procedures, or data quality, the area in question will be internally audited. All records are maintained within the project file or Quality Assurance Office depending on the course of action taken. More detailed information on this process may be found in MN-Q-245 (*Documentation of Client Requests and Complaints*).

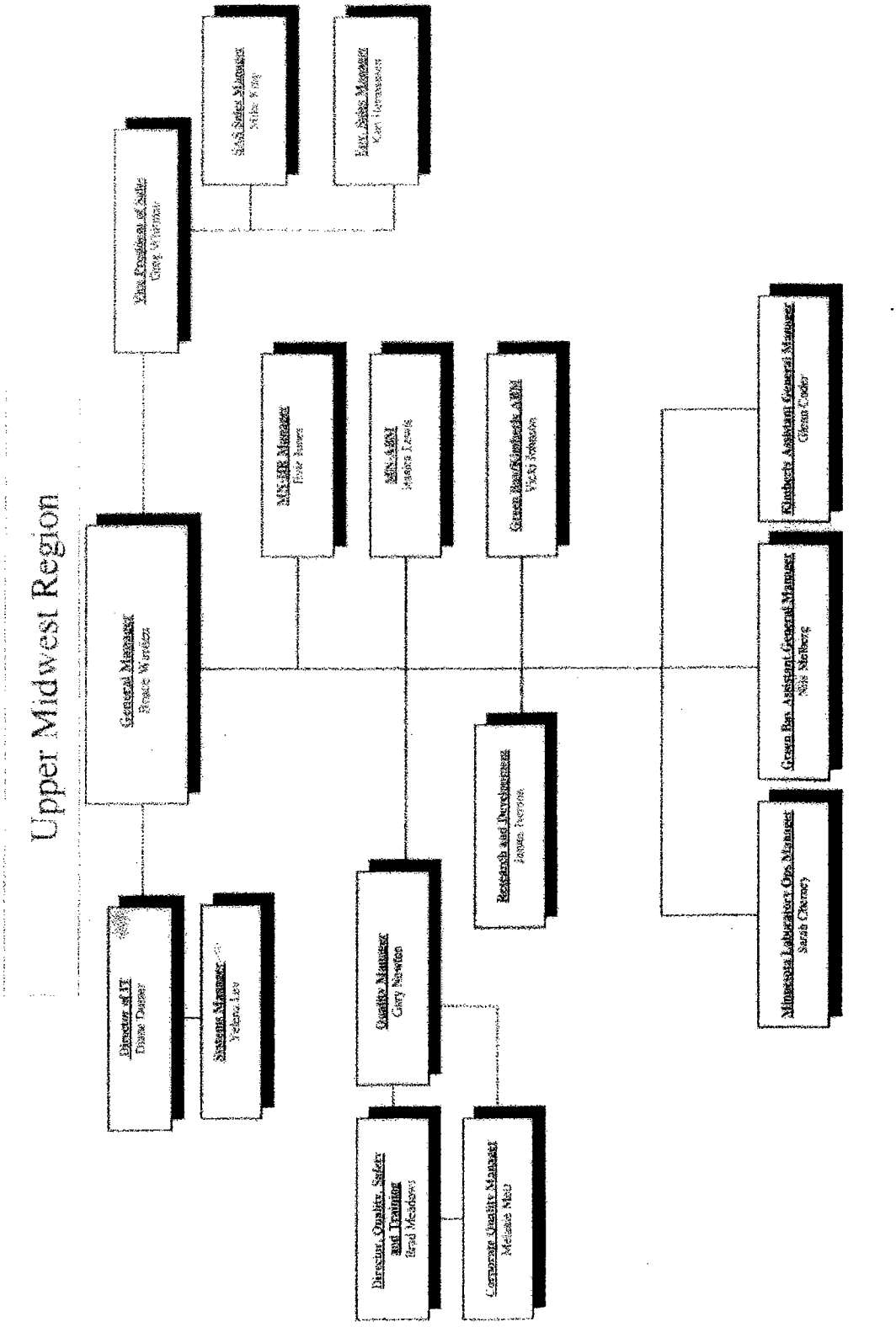
8.0 QUALITY SYSTEM AUDITS AND REVIEWS

The Upper Midwest region has no further changes to this section of the corporate quality manual.

9.0 CORRECTIVE ACTION

The Upper Midwest region has no further changes to this section of the corporate quality manual. More detailed information on the corrective action and investigation process may be found in MN-L-133 (*Out of Specification Investigation*) and ALL-Q-012 (*Corrective Action/ Preventative Action Process*).

Attachment 1



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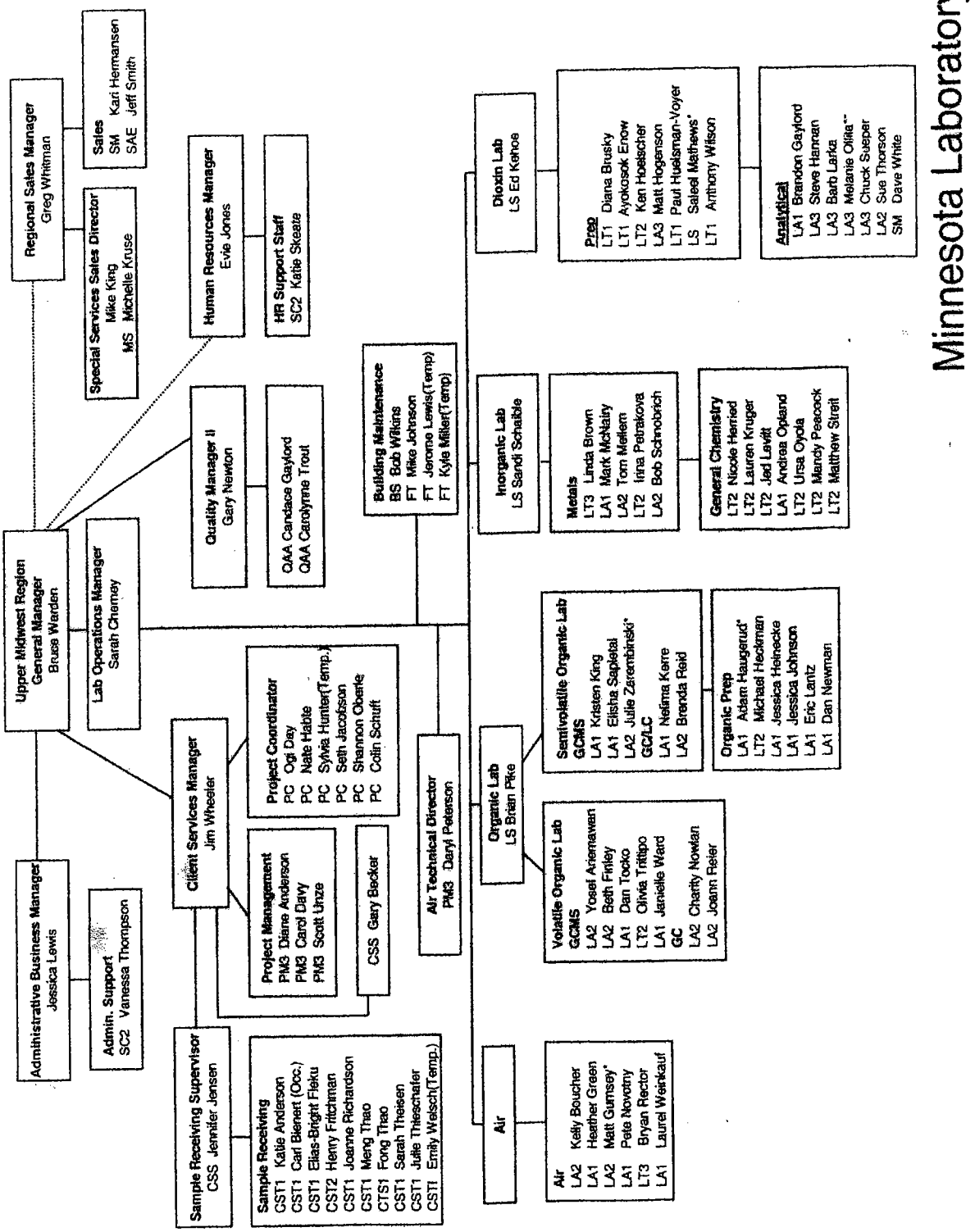

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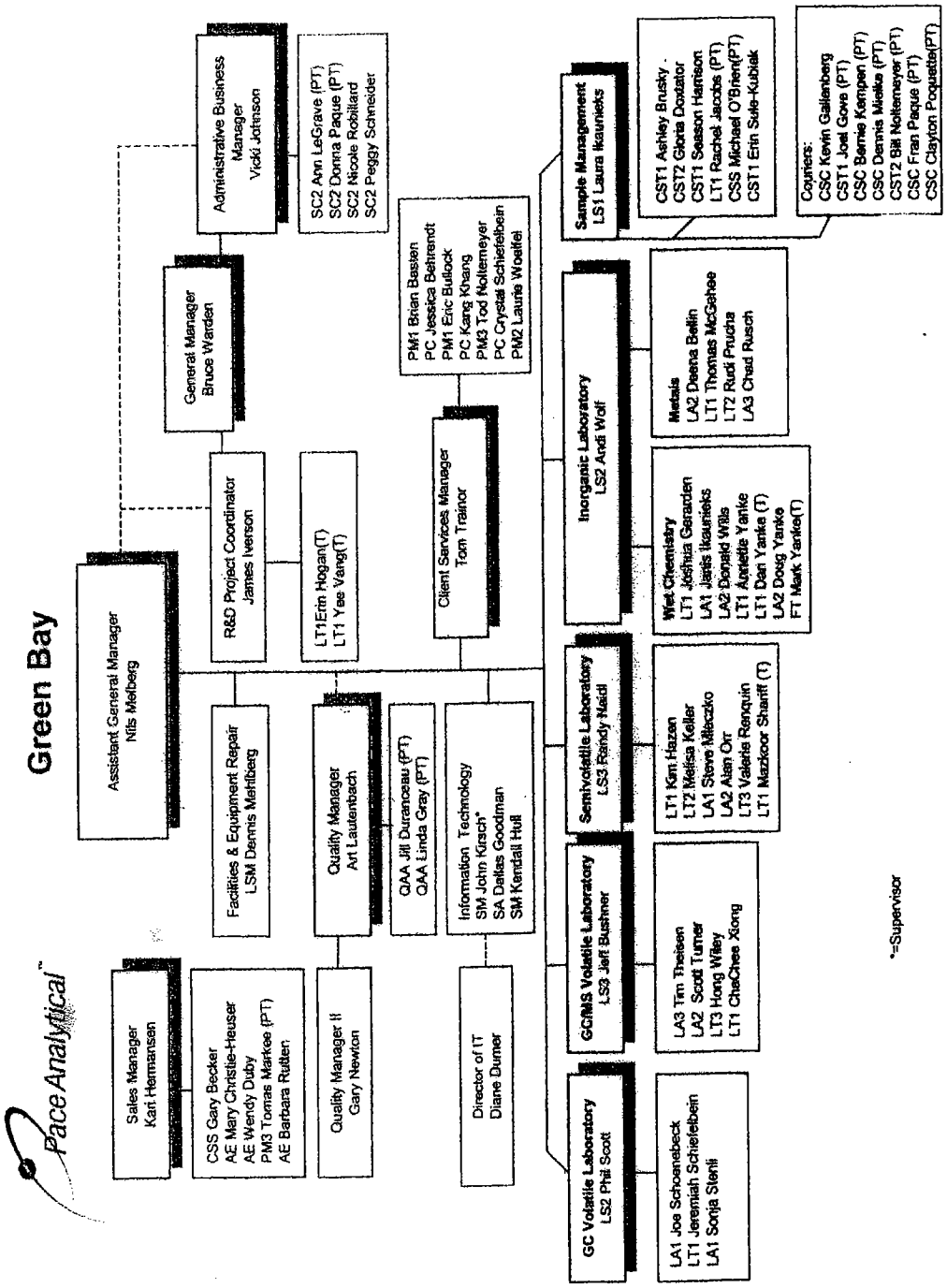

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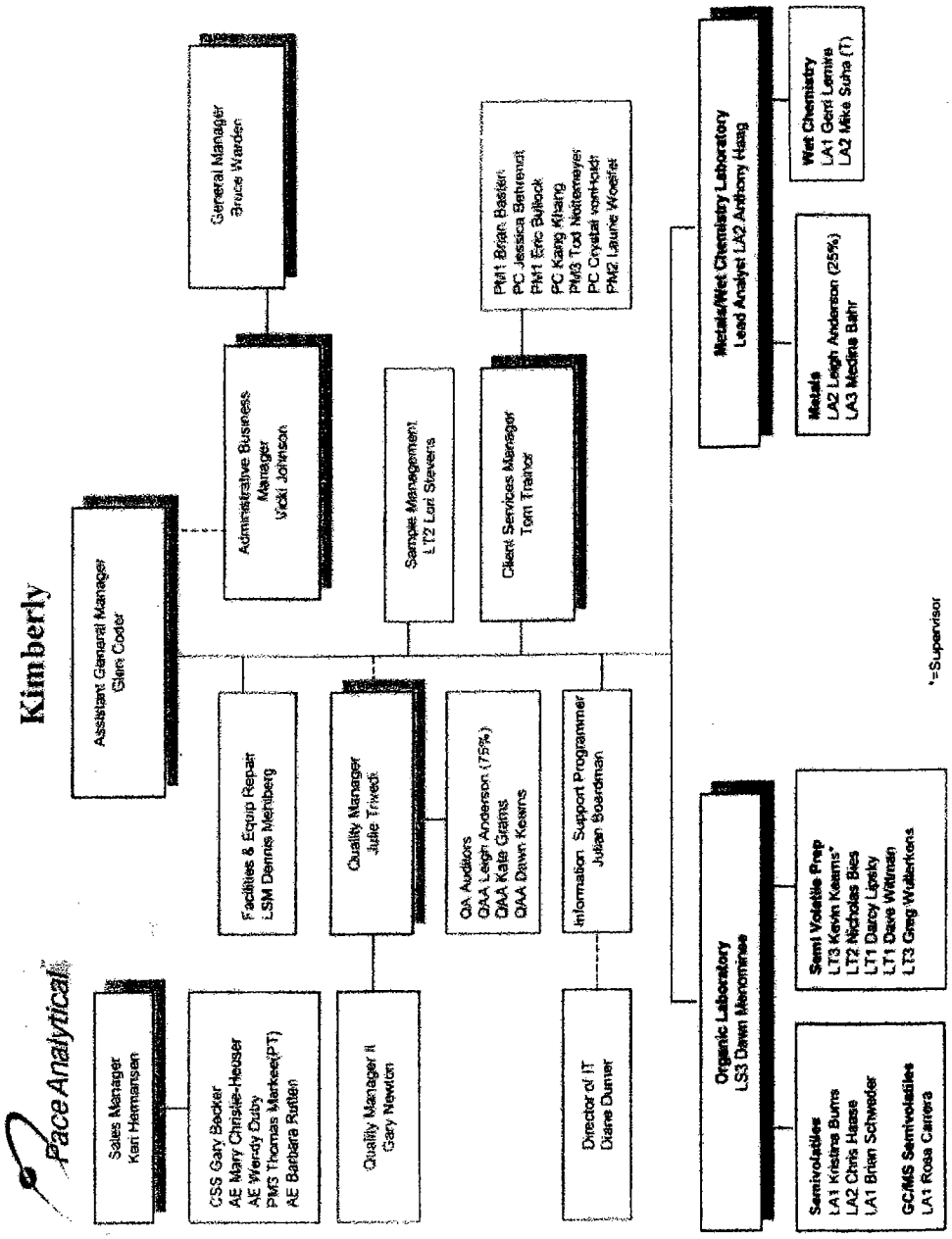

Attachment 5 (page 1 of 3)

Pace Analytical™

Method	Description	MN	GB	KM
%MOISTURE	Percent Moisture			
Ag-List	Organophosphorus Compounds by GC/MS: Capillary Column Technique			
ASTM D1125	Conductivity		x	
ASTM D2974	Moisture, Ash, and Organic Matter of Peat and Other Organic Soils		x	
ASTM D5057	Density by ASTM			
ASTM D3987	Neutral Leaching Procedure, Neutral pH, Aqueous Extraction		x	
ASTM G57	Permeability		x	
CARB 429	Determination of Polycyclic Aromatic Hydrocarbon (PAH) Emissions from Stationary Sources			
EPA 110.2	Color		x	
EPA 120.1	Physical Properties: Conductance, Specific Conductance		x	
EPA 150.1	Physical Properties: pH, Electrometric		x	
EPA 160.1	Physical Properties: Residue, Filterable, Gravimetric, Dried at 180 C o		x	
EPA 160.2	Physical Properties: Residue, Non-Filterable Gravimetric, Dried at 103-105 C o		x	
EPA 160.3	Physical Properties: Residue, Total Gravimetric, Dried at 103-105 C o		x	
EPA 160.4	Physical Properties: Residue, Volatile, Gravimetric, Ignition at 550 C o		x	
EPA 160.5	Physical Properties: Settleable Matter, Volumetric, Imhoff Cone			
EPA 180.1	Turbidity, Nephelometric		x	
EPA 1613	Tetra- through Octa-Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS			
EPA 1613B-DW	2,3,7,8-Tetrachlorodibenzo-p-Dioxin in Drinking Water by Isotope Dilution HRGC/HRMS			
EPA 1614	Brominated diphenyl ethers in Water, Soil, Sediment and Tissue by HRGC/HRMS			
EPA 1653	Chlorinated Phenolics in Wastewater by In Situ Acetylation and GCMS			
EPA 1664 Rev A	N-Hexane Extractable Material (HEM) and Silica Gel Treated N-Hexane Extractable Material (SGT-HEM) by Extraction and Gravimetry (Oil and Grease and Total Petroleum			
EPA 1668	Chlorinated Biphenyl Congeners in Water, Soil, sediment, and Tissue by HRGC/HRMS			
EPA 170.1	Physical Properties: Temperature, Thermometric			
EPA 180.1	Determination of Turbidity by Nephelometry			
EPA 200.7	Determination of Metals and Trace Elements in Water and Wastes by ICP			
EPA 200.8	Determination of Trace Elements in Water and Wastes by ICP-MS			
EPA 245.1	Determination of Mercury in Water by Cold Vapor Atomic Absorption Spectrometry			
EPA 300.0	Determination of Inorganic Anions by Ion Chromatography - Revision 2.1		x	
EPA 305.1	Acidity (Titrimetric)		x	
EPA 310.1	Inorganic, Non-Metallics: Alkalinity, Titrimetic (pH 4.5)		x	
EPA 310.2	Alkalinity, Colorimetric, Automated Methyl Orange		x	
EPA 314.0	Determination of Perchlorate in Drinking Water by Ion Chromatography			
EPA 325.2	Chloride (Colorimetric, Automated Ferricyanide AA II)		x	
EPA 330.2	Inorganic, Non-Metallics: Chlorine, Total Residual, Titrimetric, Back, Iodometric			
EPA 335.2	Inorganic, Non-Metallics: Cyanide, Total, Titrimetric, Spectrphotometric			
EPA 335.4	Determination of Total Cyanide by Semi-Automated Colorimetry		x	
EPA 340.2	Inorganic, Non-Metallics: Fluoride, Potentiometric, Ion Selective Electrode			
EPA 350.1	Determination of Ammonia Nitrogen by Semi-Automated Colorimetry -Revision 2.0		x	
EPA 351.2	Determination of Total Kjeldahl Nitrogen by Semi-Automated Colorimetry -Revision 2.0		x	
EPA 354.1	Inorganic, Non-Metallics: Nitrite, Spectrophotometric		x	
EPA 365.2	Phosphorus, All Forms, Colorimetric, Ascorbic Acid, Single Reagent			
EPA 365.3	Phosphorus, All Forms, Colorimetric, Ascorbic Acid, Two Reagents		x	
EPA 365.4	Phosphorus, Total(Colorimetric, Automated Block Digester AA II)		x	
EPA 376.1	Inorganic, Non-Metallics: Sulfide, Titrimetric, Iodine		x	
EPA 3810 (mod)	Methane,Ethane, Ethene in Water by Headspace Analysis			
EPA 410.2	Organics: Chemical Oxygen Demand, Titrimetric, Low-Level			
EPA 410.4	Determination of Chemical Oxygen Demand by Semi-Automated Colorimetry - Revision 2.0		x	
EPA 415.2	Total Organic Carbon (UV Promoted, Persulfate Oxidation)			x
EPA 420.1	Organics: Phenolics, Total Recoverable, Spectrophotometric, Manual 4-AAP with Distillation			
EPA 420.2	Phenolics (Colorimetric, Automated 4-AAP with Distillation)		x	
EPA 420.4	Determination of Total Recoverable Phenolics by Semi-Automated Colorimetry			
EPA 524.2	Measurement of Purgeable Organic Compounds in Water by GC/MS		x	

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Method	Description	MN	GB	KM
EPA 602	Purgeable Aromatics		X	
EPA 610	Polynuclear Aromatic Hydrocarbons	X		
EPA 624	Chlorinated Hydrocarbons-Purgeables by Low Resolution GC/MS	X	X	
EPA 625	Base/Neutrals and Acids by Low Resolution GC/MS	X	X	
EPA 1631E	Mercury in Water by Oxidation, Purge and Trap and CVAFS			X
HACH 8146	Chlorine, Free		X	
Method 23	Determinatin of Polychlorinated, Polybrominated and Brominated/Chlorinated Dibenzo-p-Dioxins and Dibenzofurans in Ambient Air	X		
Method 26	Determination of Anions and Cations from Ambient Air	X		
Method 29	Determination of Metals Emissions from Stationary Sources	X		
Method 308	Methanol and Ethanol from Stationary Sources	X		
Method 3C	Determination of Carbon Dioxide, Methane, Nitrogen, and Oxygen from Stationary Sources	X		
Method 5	EPA5, Air Filter, Cyclone Wash, Wet Catch, Probe Wash	X		
Molds	Various molds identification	X		
NIOSH 1500	Hydrocarbons	X	X	
NIOSH 7300 (mod)	Metals, ICP, NIOSH 7300 - MOD	X		
NWTPH-Dx	Semi-volatile Petroleum Products Method for Soil and Water	X		
NWTPH-Gx	Volatile Petroleum Products Method for Soil and Water	X		
OA1	Gasoline Range Organics in Water and Soil		X	
OA2	Diesel Products in Water and Soil		X	
PM10	PM 10, Air Filter, Cyclone Wash, Wet Catch, Probe Wash	X		
REDOX	Oxidation/Reduction Potential	X		
SM 2110	Appearance		X	
SM 2160	Taste		X	
SM 2320B	Alkalinity, Water	X	X	
SM 2340B	Hardness, Ca & Mg as Carbonates by ICP	X	X	X
SM 2540	Solids		X	
SM 2580	Oxidation-Reduction Potential (ORP)		X	
SM 2710F	Sludge Specific Gravity		X	
SM 3500-Cr-D	Chromium, Hexavalent (Colorimetric)	X	X	
SM 4500	Chloride (Silver Nitrate)	X		
SM 4500-CN-E	Cyanide (Colorimetric Method)	X		
SM 4500-CN-G	Cyanides Amenable to Chlorination after Distillation	X	X	
SM 4500-CN-I	Weak Acid Dissociable Cyanide	X	X	
SM 4500-CL	Chlorine		X	
SM 4500-CN	Cyanide		X	
SM 4500-F-C	Fluoride by Ion-Selective Electrode Mode	X		
SM 4500-O	Dissolved Oxygen		X	
SM 4500-P-E	Phosphorous- Ascorbic Acid Method	X		
SM 4500-SO3-B	Sulfide	X		
SM 5210B	5-Day Biochemical Oxygen Demand (BOD) Test	X	X	
SM 5220C	Chemical Oxygen Demand (COD) by Closed Reflux, Titrimetic Method	X		
SM 5220D	Chemical Oxygen Demand (COD) by Closed Reflux, Colormetric Method	X		
SM 9215A	Heterotrophic Plate Count	X	X	
SM 9222D	Fecal Coliform in Water	X	X	
SM 9223B	Total Coliform in Water	X	X	
SM2540C	Total Dissolved Solids	X		
SM2540D	Total Suspended Solids	X		
SPC	Standard Plate Count	X		
SW 1311	Toxicity Characteristic Leaching Procedure	X	X	
SW 1312	Synthetic Precipitation Leaching Procedure	X	X	
SW 3005A	Total Recoverable or Dissolved metals		X	X
SW 3010A	Acid Digestion of Aqueous Samples and Extracts for Total Metals for Analysis by FLAA or ICP Spectroscopy	X	X	
SW 3015	Microwave Assisted Acid Digestion of Aqueous Samples and Extracts			X

Attachment 5 (page 3 of 3)

Pace Analytical™

Method	Description	MN	GB	KM
SW 3020A	Total Metals for GFAA		x	
SW 3050B	Acid Digestion of Sediments, Sludges, and Soils		x	
SW 3051	Microwave Assisted Acid Digestion of Sediments, Sludges, Soils, and Oils			
SW 3510C	Separatory Funnel Liquid-Liquid Extraction		x	
SW 3520C	Continuous Liquid-Liquid Extraction			
SW 3535	Solid-Phase Extraction (SPE)			
SW 3540C	Soxhlet Extraction			
SW 3541	Automated Soxhlet Extraction			
SW 3545	Pressurized Fluid Extraction (PFE)		x	
SW 3550B	Ultrasonic Extraction			
SW 3580A	Waste Dilution		x	
SW 3640A	GPC			
SW 3620B	Florisil Cleanup			
SW 3630C	Silica Gel Cleanup			
SW 3660B	Copper Cleanup			
SW 3665A	Sulfuric Acid Cleanup			
SW 5030B	Purge-and-Trap for Aqueous Samples		x	
SW 5035	Closed-System Purge-and-Trap and Extraction for Volatile Organics in Soil and Waste Samples		x	
SW 6010B	Inductively Coupled Plasma-Atomic Emission Spectrometry		x	
SW 6020	Determination of Trace Elements in Water and Wastes by ICP-MS		x	
SW 7196A	Chromium, Hexavalent (Colorimetric)		x	
SW 7470A	Mercury in Liquid Waste (Manual Cold-Vapor Technique)		x	
SW 7471A	Mercury in Solid or Semisolid Waste (Manual Cold-Vapor Technique)		x	
SW 8015B	Nonhalogenated Organics Using GC/FID		x	
SW 8021B	Aromatic and Halogenated Volatiles by Gas Chromatography Using Photoionization and/or Electrolytic Conductivity Detectors		x	
SW 8081A	Organochlorine Pesticides by Gas Chromatography			
SW 8082	Polychlorinated Biphenyls (PCBs) by Gas Chromatography			
SW 8260B	Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)		x	
SW 8270C	Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)		x	
SW 8270C SIM	Semivolatile Organic Compounds by GC/MS-utilizing selective ion monitoring		x	
SW 8280A	The Analysis of Polychlorinated Dibenzo-p-Dioxins and Polychlorinated Dibenzofurans by HRGC/LRMS			
SW 8290	Polychlorinated Dibenzodioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs) by HRGC/HRMS			
SW 8310	Polynuclear Aromatic Hydrocarbons		x	
SW 8330	Nitroaromatics and Nitramines by HPLC			
SW 9010	Total and Amenable Cyanide: Distillation			
SW 9012A	Total and Amenable Cyanide (Automated Colorimetric, with Off-line Distillation)		x	
SW 9040B	pH Electrometric Measurement		x	
SW 9045C	Soil and Waste pH		x	
SW 9050A	Conductivity		x	
SW 9056	Determination of Inorganic Anions by Ion Chromatography		x	
SW 9071B	HEM in Soil			
SW 9095A	Paint Filter Liquids Test		x	
SW 9251	Chloride (Colorimetric, Automated Ferricyanide AAII)		x	
TO-13	Determination of Semi-Volatile Organics in Ambient Air			
TO-14	Determination of VOCs in Ambient Air utilizing a Summa Canister and GC/MS			
TO-15	The Determination of VOCs in Air Collected in Summa Canisters and Analyzed by GC/MS			
TO-15 SIM	The Determination of VOCs in Air Collected in Summa Canisters and Analyzed by GC/MS utilizing SIM			
TO-3	TO3, in Air Source			
TO-4 (PCB)	Determinatin of Polychlorinated Biphenyl in Ambient Air			
TO-4 (Pesticides)	Determinatin of Polychlorinated Pesticide in Ambient Air			
TO-9A	Determinatin of Polychlorinated, Polybrominated and Brominated/Chlorinated Dibenzo-p-Dioxins and Dibenzofurans in Ambient Air			
WIDRO	Determination of Diesel Range Organics in water and soil		x	
WIGRO	Determination of Gasoline Range Organics in water and soil		x	

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STANDARD OPERATING PROCEDURE

DETERMINATION OF SEMI-VOLATILE ORGANICS BY GC/MS

REFERENCE METHODS: Methods SW-846 8270C / EPA 625

LOCAL SOP NUMBER:	S-ALL-GB-O-001-Rev.00
EFFECTIVE DATE:	Date of Final Signature
SUPERSEDES:	ALL-O-001-rev.1, S-ALL-GB-O-001-rev.3
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LOCAL APPROVAL

Nils Melberg, Laboratory General Manager — Date: 06/06/08

Kate Grams, Laboratory Quality Manager — Date: 6/6/08

Glen Coder, Department Manager — Date: 6/6/08

ANNUAL REVIEW

SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE APPROVAL. SOP IS VALID FOR ONE YEAR FROM DATE OF LAST SIGNATURE.

Signature	Title	Date

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1. PURPOSE

This Standard Operating Procedure (SOP) documents the procedures used by PASI – Green Bay to determine the concentration of Semi-Volatile Organic Compounds (SVOCs) in environmental samples. The laboratory utilizes GC/MS and bases these documented procedures on those listed Methods SW-846 8270C / EPA 625. Samples for analysis are prepared by SW846 Method 3510C and SW846 Method 3546 following Pace SOPs S-ALL-GB-O-003 Separatory Funnel Extraction of Water Samples for Semivolatile Analysis, and S-GB-O-045 Microwave Extraction for the Determination of Polynuclear Aromatic Hydrocarbons and Base/Neutral/Acids in Solid Matrices.

The Green Bay laboratory currently processes Methods 625/8270C water samples by automated separatory funnel using Method SW846 3510C, processes Method 8270C soil samples by Microwave Extraction using Method SW846 3546 and processes Method 8270C biota samples by soxhlet extractor using Method SW846 3540C. The latest revision of Pace's SOPs S-ALL-GB-O-003 Separatory Funnel Extraction of Water Samples for Semivolatile Analysis, S-GB-O-046 Microwave Extraction for the Determination of Semivolatile Base/Neutral/Acids-Full Scan, and GB-O-033 Extraction of Biolgical Samples for Base Neutral/Acid and PAH-SIM Analysis for these extraction techniques are available from the quality office.

2. SCOPE AND APPLICATION

2.1 This procedure may be used to determine concentrations of neutral, acidic, and basic semivolatile organic compounds in extracts prepared from many types of water samples, soil samples and wastes. Analytes must be soluble in dichloromethane and amenable to capillary gas chromatography. Specific compound classes include polynuclear aromatic hydrocarbons, chlorinated hydrocarbons and pesticides, phthalate esters, organophosphate esters, nitrosamines, haloethers, aldehydes, ethers, ketones, anilines, pyridines, quinolines, aromatic nitro compounds, and phenols. A list of applicable compounds is shown herein. Pace Reporting Levels (PRLs) are also shown for water and soil samples. PRLs are subject to change based on current analytical system performance and actual sample matrices.

2.2 This method is applicable to most water and solid samples, regardless of moisture content. Common matrices are ground and surface water, wastewater, aqueous sludge, sediment, soils, and other solid samples. Procedures may need to be adapted to address limits in the method or equipment that might hinder or interference with sample analysis. All adaptations made to address matrix related modifications must be documented within the analytical data

2.3 This procedure is restricted to use by, or under the supervision of, analysts experienced in the use of semi-volatile configured GC/MS systems and interpretation of GC/MS data. Each analyst must demonstrate the capability to generate acceptable results with this method to be considered qualified to report sample results.

2.4 This method cannot be substituted for other similar published methods where permit or regulatory compliance is required.

3. SUMMARY OF METHOD

Sample extracts are prepared for analysis by an appropriate sample preparation method. The semivolatile organic compounds are introduced into the gas chromatograph (GC) by injecting an aliquot of the sample extract. The GC conditions are programmed to separate the analytes. The GC effluent is directly introduced to a mass spectrometer (MS) for both identification and quantification of analytes. Analytes are identified by comparison of their mass spectra with

spectra of authentic standards. Analytes are quantified by comparing the response of a selected major (quantitation) ion relative to an internal standard using a multi-point calibration curve.

4. INTERFERENCES

4.1 Interferences may be introduced into sample extracts by contaminants in solvents, reagents, glassware, and any other material that comes in contact with the sample or extract during extract preparation. These interferences must be closely monitored by analyzing Method Blank samples and taking corrective action as required.

4.2 Matrix interferences may result from materials co-extracted from some samples.

4.3 Significant phthalate contamination may result at any time if consistent quality control is not practiced. Plastics, in particular, must be avoided because phthalates are commonly used as plasticizers and are easily extracted from plastic materials.

4.4 Contamination by carryover can occur when high concentration extracts are analyzed prior to low concentration extracts. The contamination may also cause degradation of labile analytes. Whenever carryover is suspected, the affected extracts should be re-analyzed. If significant degradation of the GC/MS systems is suspected, system performances samples should be analyzed and corrective action taken as needed.

4.5 The extent of matrix interference's will vary considerably from source to source. The laboratory utilizes the Gel Permeation Chromatography (GPC) clean-up procedure to clean up the sample extract following the latest revision of Pace's SOP S-GB-O-032 *Gel Permeation Chromatography*. The extraction personnel initially determine the need for GPC cleanup. The analyst can request that the sample extracts have GPC cleanup prior to the addition of Internal Standards. This is usually determined by visual inspection of the sample extract or by historical data. Tissue samples must be cleaned by GPC and silica gel cleanup procedures.

5. SAFETY

5.1 Standards and Reagents

5.2 The toxicity and carcinogenicity of standards and reagents used in this method have not been fully defined. Each chemical compound should be treated as a potential health hazard. Reduce exposure by the use of gloves, lab coats and safety glasses. Material Safety Data Sheets (MSDSs) are on file in the laboratory and available to all personnel. Standard solutions should be prepared in a hood.

5.3 Samples

5.4 Take precautions when handling samples. Samples should always be treated as potentially hazardous "unknowns". The use of personal protective equipment (gloves, lab coats and safety glasses) is required when handling samples. In the event a sample container must be opened, it is recommended to perform this in a hood whenever possible.

5.5 Equipment

5.6 Portions of the analytical instrumentation operate at high temperatures and under positive pressure. Care must be taken to minimize accidents and injuries when working on or with this equipment. Instruments should be turned off or the heated zone temperatures lowered to reduce the risk of thermal burns. Allow adequate time for the equipment to cool prior to working on these specific zones.

5.7 The GC pneumatic system uses gas under high pressure. These high pressures introduce the risk of injury due to flying objects should a vessel or line rupture. Safety glasses are

highly recommended at all times when working in, on or around these pieces of equipment. Even instrumentation that is not operating may contain portions of the system under pressure.

6. DEFINITIONS

6.1 Refer to Glossary section of the Pace Quality Assurance Manual (QAM) for a comprehensive list of terms and definitions. In addition to those listed in the QAM, the following are additional terms found in this SOP.

6.2 **Run Sequence Log** – A logbook that lists all injections and analyses performed on a particular piece of equipment regardless of the use of the data collected from each analysis.

6.3 **Toxicity Characteristic Leaching Procedure (TCLP)** – An extraction procedure used to determine if a sample is acceptable for upland disposal. The extraction procedure is meant to simulate the leaching of contaminants under the environmental conditions typically found in a landfill.

6.4 **Tune Period –** The period after the DFTPP instrument tune check within which analyses may be performed.

7. SAMPLE COLLECTION, PRESERVATION, AND HANDLING

Table 7.1 – Sample Collection, Preservation, Storage and Hold time.

Sample type	Collection per sample	Preservation	Storage	Hold time
Aqueous	One (1) 1-Liter Amber Glass Samples to be analyzed by EPA 625 must be checked for residual chlorine. If residual chlorine is present, add 80 mg of sodium thiosulfate per liter of sample and mix well.	None	4 ± 2°C	7 days
Soil/Solid (non-aqueous)	One (1) 8-oz Glass Jar	None	4 ± 2°C	14 days
Biota	-	None	= 0°C until extraction	-
Extracts	2-5mL Glass vials, same as used for standard storage	None	=-10°C	40 days

8. EQUIPMENT AND SUPPLIES

8.1 Instrumentation

Analytical Instrument/Peripherals	EPIC Pro Name	Serial Number
HP 5890 Series II GC	40MSS1	3336A57925
HP 5972 Mass Selective Detector	40MSS1	3501A02320
HP 7673 AutoSampler Tray	40MSS1	3526A39072
HP 7673 Injector	40MSS1	3009A20936
HP Controller	40MSS1	3526A02233
Alcatel 2005 Rough Pump	40MSS1	265402
HP 5890 Series II GC	40MSS5	3022A29174
HP 5972 Mass Selective Detector	40MSS5	3501A02209
HP 7673 AutoSampler Tray	40MSS5	3319A32067
HP 6890 Injector	40MSS5	DE64502673
HP Controller	40MSS5	3018A22346
Varian DS302 Rough Pump	40MSS5	244968
HP 5890E GC	40MSS6	3310A49571
HP 5972A Mass Selective Detector	40MSS6	3524A03107
HP 18596A AutoSampler Tray	40MSS6	2920A10670
HP 6890 Injector	40MSS6	US0000692
HP 7673 Controller	40MSS6	3113A25880
Edwards E2M2 Rough Pump	40MSS6	53747

8.2 Chromatography Supplies

Item	Vendor	Model / ID	Catalog #	Description
Analytical Column	Restek	XTI-5 w/ Integraguard	12223-124	30 m, 0.25 mm ID, 0.25 df
Fluorocarbon O-rings	Restek		20377	
Vespel/Graphite Ferrules	Restek		20229	1/16” x 0.4 mm ID
Gooseneck Splitless Liner	Restek		20800	4 mm x 6.5 x 78.5 for Aligent GCs
Guard Column	Restek		20231	0.5 MID
Ferrules	Fisher Scientific		5-5	

8.3 Glassware

Glassware	Description	Vendor / Item # / Description
Volumetric Flasks	10mL, 25mL, 50mL	Class A
Glass Storage Vials	5mL, 10mL, 12mL, with Teflon-lined screw caps	MG Scientific / T102-3-INV, T102-1-INV V138-19, B510-1
Glass Autosampler Vials	2.0 mL with Teflon-lined crimp caps	MG Scientific / V300-3 / V300-20N

8.4 General Supplies

Glassware	Description	Vendor/ Item # / Description
Gas tight syringes	10-µL, 25-µL, 50-µL, 100-µL, 250-µL, 500-µL, and 1,000-µL, as needed, Hamilton or equivalent.	Fisher Scientific / Various
Pipettes	Borosilicate Glass 9" Pipette	MG Scientific / D200-9

9. REAGENTS AND STANDARDS

9.1 Reagents

Reagent	Concentration/ Description	Requirements/ Vendor/ Item #
Dichloromethane		Pesticide Grade or equivalent

9.2 Analytical Standards

9.2.1 **Definitions**

Standards are required for mass spectrometer tuning, initial calibration, calibration verification standards, second source verification, internal standards, surrogates, and for preparing LCS, MS, and MSD samples. Table 9.1 describes the standards used.

Table 9.1 Standard Definitions and vendors

Standard	Description	Comments
Tune Standard	Decafluorotriphenylphosphine (DFTPP), 4,4'-DDT, pentachlorophenol, and benzidine solution in dichloromethane used to verify ion response ratios and system inertness prior to analysis.	Must inject no more than 50 ng on column
Initial Calibration Standards	Standards prepared at varying levels to determine response and retention characteristics of instrument	Method requires a minimum of 5 levels
Continuing Calibration Verification Standard	A calibration standard prepared at mid-level concentration for all target compounds. This standard is used to verify that the instrument response has not changed significantly since the initial calibration was performed.	
Second Source Verification Standard	A standard prepared from a source other than that used for the initial calibration. This mid-level standard verifies the accuracy of the calibration curve.	
Internal Standard	A solution added all standards, samples, spikes, control samples, and method blanks prior to analysis. This standard is used to adjust response ratios to account for instrument drift.	1,4 Dichlorobenzene-d4 Naphthalene-d_8 Acenaphthene-d_{10} Phenanthrene-d_{10} Chrysene-d_{12} Perylene-d_{12}
Surrogate Standard	A solution added to all samples, spikes, control samples, and method blanks prior to analysis.	Nitrobenzene-d_5 2-Fluorobiphenyl Terphenyl-d_{14} Phenol-d_6 2-Fluorophenol 2,4,6-Tribromophenol
Spiking Standard	This solution contains all target analytes and should not be prepared from the same standards as the calibration standards.	

9.2.2 **Storage Conditions**

Table 9.2 – Analytical Standard Storage Conditions

Standard Type	Description	Expiration	Storage
Stock Solutions	▪ Concentrated reference solution purchased directly from approved vendor	▪ Manufacturer's recommended expiration date for unopened ampulated standards. ▪ All other stock standards must be replaced 1 year after ampule is opened or on expiration date, whichever is sooner.	▪ Manufacturer's recommended storage conditions ▪ When standard is opened, record all information in the standard logbook.
Intermediate and Working Standard Solutions	▪ Reference solutions prepared by dilutions of the stock solution	▪ 1 year from preparation or the expiration date listed for the stock source, whichever is sooner. ▪ Working solutions must be checked frequently and replaced if degradation or evaporation is suspected.	▪ Store in amber vials with Teflon lined caps ▪ Manufacturer's recommended storage conditions for stock source solution. ▪ If stock source conditions conflict, store according to method requirements.

9.2.3 **Standard Sources**

Standards are prepared from commercially available multi-compound stock solutions and neat materials by multiple dilutions. The sources of the stock solutions and neat materials, recipes for preparing dilutions and working standards, and concentrations for all compounds are presented in Section 10.2.4. All intermediate standards are prepared using dichloromethane and stored in glass vials with Teflon lined caps or Mininert valves or as recommended by the standard manufacturer.

9.2.4 Preparation Procedures

9.2.4.1 **Internal Standard Stock solution**: Restek brand Internal Standard Mix, 4000ug/mL, catalog # 31006 (contains six internal standards: acenaphthene-d10; chrysene-d12; 1,4-dichlorobenzene-d4; naphthalene-d8; perylene-d12; and phenanthrene-d10), or equivalent.

9.2.4.2 **Surrogate Standard stock solutions:** Restek brand Base Neutral surrogate mix, 5000ug/mL, catalog # 31082 (contains four surrogate standards: 2-fluorobiphenyl; nitrobenzene-d5; p-terphenyl-d14; 1,2-Dichlorobenzene-d4(advisory)). Restek brand Acid surrogate mix, 7500ug/mL, catalog # 31083 (contains four surrogate standards 2-fluorophenol; phenol-d6; 2,4,6-tribromophenol; 2-chlorophenol-d4(advisory)), or equivalent.

9.2.4.3 **Surrogate Standard working solution (for extractions):** dilute 5.0mL of both the Restek Base Neutral stock surrogate solution (# 31082) and theRestek Acid stock surrogate solution (#31083) to 50mL with Dichloromethane, or equivalent. This gives a final concentration of 500ug/mL per Base Neutral surrogate compound and 750ug/mL per Acid surrogate compound. The extraction analyst spikes each water and soil sample with 100uL of this working solution.

9.2.4.4 **DFTPP tuning solution**: dilute 500uL of Supelco DFTPP stock standard (catalog # 47548-U; 1000ug/mL) to a total volume of 10mL with methylene chloride for a final concentration of 50ug/mL, or equivalent. The stock standard also contains 4,4'-DDT, benzidine, and pentachlorophenol for assessing column degradation.

9.2.4.5 **Initial Calibration curve standards**: the following three stock standards, or equivalent, are used to prepare the initial calibration curve:

9.2.4.5.1 8270 Custom Mix 1, Supelco, 400ug/mL, Quote# 20447738

9.2.4.5.2 n-Nitrosodiphenylamine, Supelco, 5000ug/mL, catalog # 46702-U

9.2.4.5.3 1,4-Dioxane, Restek, 2000ug/mL, catalog # 30287

9.2.4.5.4 2,3,4,6-Tetrachlorophenol, Accustandard, 2000ug/mL, catalog # A-029S-D-10X

9.2.4.5.5 **Initial Calibration Intermediate Standard**: 2.5mL of 400ug/mL Supelco 8270 Custom Mix 1 plus 200uL of the 5000ug/mL n-Nitrosodiphenylamine solution plus 500uL of the 2000ug/mL 1,4-Dioxane solution plus 500 uL of the 2000 ug/mL 2,3,4,6-Tetrachlorophenol solution are diluted to 5.0mL with dichloromethane, or equivalent. The resulting intermediate standard has a concentration of 200mg/L for each compound.

9.2.4.5.6 **Initial Calibration Working Standards**: The following working calibration standards are prepared by using the intermediate mix listed above (9.2.4.5):

Standard Concentration*	Amount of Intermediate Standard added	Amount of Stock internal standard added	Dilution Solvent Used	Final Volume
5PPM	25uL	10uL	Dichloromethane	1010uL
10ppm	50uL	10uL	Dichloromethane	1010uL
25ppm	125uL	10uL	Dichloromethane	1010uL
50ppm	250uL	10uL	Dichloromethane	1010uL
80ppm	400uL	10uL	Dichloromethane	1010uL
100ppm	500uL	10uL	Dichloromethane	1010uL
120ppm	600uL	10uL	Dichloromethane	1010uL

9.2.4.6 **Initial Calibration Verification stock standards (second-source):** Restek, custom 8270,catalog # 52939, 200ug/mL per compound. Supelco 1,4-Dioxane, catalog #48367, 2000ug/mL. Restek 2,3,4,6-tetrachlorophenol, catalog #560028, 2000ug/mL, or equivalent.

9.2.4.7 **Initial Calibration Verification working standard (second source):** Dilute 250uL of the custom 8270 second source standard #52939, 25ul of 2,3,4,6-Tetrachlorophenol #560028, 25uL of 1,4-Dioxane #48367 and 10uL of the stock internal standard solution (9.2.4.1) to 1mL with methylene chloride, or equivalent. This gives a final concentration of 50ppm.

9.2.4.8 **LCS/MS Standard working solution**: Supelco 70 Component Custom LCS Mix catalog # 861389-U, 200ug/mL. Supelco n-Nitrosodiphenylamine, catalog # 46702-U, 5000ug/mL, or equivalent. The extraction analyst spikes each LCS/LCSD and matrix spike sample with 250uL of the LCS mix and 10uL of the n-NDPA solution. This produces a concentration of 50ug/mL.

9.2.4.9 **Other calibrations:** Other compounds are analyzed per client requests. Curves are prepared at levels similar to those of the standards above. The calibration standards and the second source standards are as follows: Calibration Standards, Benzidine, Supelco, catalog # 40005, 5000ug/mL; EPA CLP SOW OLM4 mix, Supelco. catalog # 47514-U, 2000ug/mL (contains Acetophenone, Atrazine, Benzaldehyde, Biphenyl and Caprolactam). Second Source standards, Benzidine, Restek, catalog# 31441, 1000ug/mL; EPA CLP SOW OLM4 mix, Absolute Standards, catalog #19253, 2000ug/mL, or equivalent. Minnesota Phenols Samples required Calibration Standard Supelco, catalog #20858688, 500 ppm for initial calibration and Accustandard, catalog # 5-8126-R3, 500 ppm for second source standard.

10. CALIBRATION

10.1 Tune Verification

10.2 The mass spectrometer tune status must be verified prior to initial calibration and at the beginning of each analytical sequence. If the current tune status does not meet the ion ratio criteria in the method (see section 10.2), take corrective actions as outlined in section 11.2.1. Otherwise, follow the equipment manufacturers' instructions for re-tuning the mass spectrometer. The tune status must be re-verified after the tuning procedures.

Refer to section **11.2 Procedures** for details on the analysis and evaluation of this standard.

10.3 Initial Calibration (ICAL)

10.3.1 Analysis of Standards

10.3.2 An initial calibration curve using a minimum of five points is analyzed prior to analyzing client samples. The lowest concentration must be at or below the equivalence of the standard reporting limit. The lowest calibration point reflects the practical quantitation limit for that compound, a level below which all reported results must be qualified as estimated values. Refer to table 10.1 for compound concentrations.

10.3.3 An analyte must be present and calibration curve in control in order to be reported on the target analyte list. Analytes identified by mass spectral match but not present and in control in the calibration table may be reported as Tentatively Identified Compounds (TICs). Guidelines for identification are listed in Section 10.6.3. Results for these TICs should be reported only on a present/absent basis. However, quantitative results may be reported provided they are qualified as estimated values.

Table 10.1 – Calibration standard compound concentrations

Analyte	CAS Number	PQL water (ug/L)	PQL soil (ug/kg)	PQL Biota (ug/kg)	Std 1 ug/ml	Std 2 ug/ml	Std 3 ug/ml	Std 4 ug/ml	Std 5 ug/ml	Std 6 ug/ml	Std 7 ug/ml
Acenaphthene	83-32-9	5.0	167	330	5.0	10	25	50	80	100	120
Acenaphthylene	208-96-8	5.0	167	330	5.0	10	25	50	80	100	120
Aniline	62.53.3	5.0	167		5.0	10	25	50	80	100	120
Anthracene	120.12.7	5.0	167	330	5.0	10	25	50	80	100	120
Benz(a)anthracene	56-55-3	5.0	167	330	5.0	10	25	50	80	100	120
Benzo(a)pyrene	50-32.8	5.0	167	330	5.0	10	25	50	80	100	120
Benzo(b)fluoranthene	205-99-2	5.0	167	330	5.0	10	25	50	80	100	120
Benzo(g,h,i)perylene	191-24-2	5.0	167	330	5.0	10	25	50	80	100	120
Benzo(k)fluoranthene	207-08-9	5.0	167	330	5.0	10	25	50	80	100	120
Benzoic acid	65-85-0	10	167		5.0	10	25	50	80	100	120
Benzyl alcohol	100.51-6	10	167		5.0	10	25	50	80	100	120
4-Bromophenylphenyl ether	101.55.3	5.0	167	330	5.0	10	25	50	80	100	120
Butylbenzylphthalate	85-68-7	5.0	167	330	5.0	10	25	50	80	100	120
Carbazole	86-74-8	5.0	167	330	5.0	10	25	50	80	100	120
4-Chloro-3-methylphenol	59-50-7	5.0	167	330	5.0	10	25	50	80	100	120
4-Chloroaniline	106-47-8	10	333	330	5.0	10	25	50	80	100	120
bis(2-Chloroethoxy)methane	111-91-1	5.0	167	330	5.0	10	25	50	80	100	120
Bis(2-Chloroethyl) ether	114-44-4	5.0	167	330	5.0	10	25	50	80	100	120
bis(2-Chloroisopropyl) ether	108-60-1	5.0	167	330	5.0	10	25	50	80	100	120
2-Chloronaphthalene	91-58-7	5.0	167	330	5.0	10	25	50	80	100	120
2-Chlorophenol	95-57-8	5.0	167	330	5.0	10	25	50	80	100	120
4-Chlorophenylphenyl ether	7005-72-3	5.0	167	330	5.0	10	25	50	80	100	120
1,2-Diphenylhydrazine	122-66-7	5.0	167		5.0	10	25	50	80	100	120
Chrysene	218-01-9	5.0	167	330	5.0	10	25	50	80	100	120
Dibenz(a,h)anthracene	53-70-3	5.0	167	330	5.0	10	25	50	80	100	120
Dibenzofuran	132-64-9	5.0	167	330	5.0	10	25	50	80	100	120
1,2-Dichlorobenzene	95-50-1	5.0	167	330	5.0	10	25	50	80	100	120
1,3-Dichlorobenzene	541-73-1	5.0	167	330	5.0	10	25	50	80	100	120
1,4-Dichlorobenzene	106-46-7	5.0	167	330	5.0	10	25	50	80	100	120
3,3'-Dichlorobenzidine	91-94-1	10	167	330	5.0	10	25	50	80	100	120
2,4-Dichlorophenol	120-83-2	5.0	167	330	5.0	10	25	50	80	100	120
Diethylphthalate	84-66-2	5.0	167	330	5.0	10	25	50	80	100	120
2,4-Dimethylphenol	105-67-9	5.0	167	330	5.0	10	25	50	80	100	120
Dimethylphthalate	131-11-3	5.0	167	330	5.0	10	25	50	80	100	120
Di-n-butylphthalate	84-74-2	5.0	167	330	5.0	10	25	50	80	100	120
4,6-Dinitro-2-methylphenol	534-52-1	5.0	333	670	5.0	10	25	50	80	100	120
2,4-Dinitrophenol	51-28-5	10	333	670	5.0	10	25	50	80	100	120
2,4-Dinitrotoluene	121-14-2	5.0	167	330	5.0	10	25	50	80	100	120
2,6-Dinitrotoluene	606-20-2	5.0	167	330	5.0	10	25	50	80	100	120
Di-n-octylphthalate	117-84-0	5.0	167	330	5.0	10	25	50	80	100	120
bis(2-Ethylhexyl)phthalate	117-81-7	5.0	167	330	5.0	10	25	50	80	100	120
Fluoranthene	206-44-0	5.0	167	330	5.0	10	25	50	80	100	120
Fluorene	86-73-1	5.0	167	330	5.0	10	25	50	80	100	120
Hexachloro-1,3-butadiene	87-68-3	10	333	330	5.0	10	25	50	80	100	120
Hexachlorobenzene	118-74-1	5.0	167	330	5.0	10	25	50	80	100	120
Hexachlorocyclopentadiene	77-47-4	5.0	167	330	5.0	10	25	50	80	100	120
Hexachloroethane	57-72-1	5.0	167	330	5.0	10	25	50	80	100	120
Indeno(1,2,3-cd)pyrene	193-39-5	5.0	167	330	5.0	10	25	50	80	100	120
Isophorone	78-59-1	5.0	167	330	5.0	10	25	50	80	100	120
2-Methylnaphthalene	91-57-6	5.0	167	330	5.0	10	25	50	80	100	120
2-Methylphenol	95-48-7	10	333	330	5.0	10	25	50	80	100	120
3&4-Methylphenol	106-44-5	5.0	167	330	5.0	10	25	50	80	100	120
Naphthalene	91-20-3	5.0	167	330	5.0	10	25	50	80	100	120
2-Nitroaniline	88-74-4	5.0	167	330	5.0	10	25	50	80	100	120
3-Nitroaniline	99-09-2	5.0	167	670	5.0	10	25	50	80	100	120
4-Nitroaniline	100-01-6	10	333	670	5.0	10	25	50	80	100	120

Nitrobenzene	98-95-3	5.0	167	330	5.0	10	25	50	80	100	120
2-Nitrophenol	88-75-5	5.0	167	330	5.0	10	25	50	80	100	120
4-Nitrophenol	100-02-7	10	333	670	5.0	10	25	50	80	100	120
N-Nitrosodimethylamine	62-75-9	5.0	333	330	5.0	10	25	50	80	100	120
N-Nitroso-di-n-propylamine	621-64-7	5.0	167	330	5.0	10	25	50	80	100	120
N-Nitrosodiphenylamine	86-30-6	10	333	330	5.0	10	25	50	80	100	120
Pentachlorophenol	87-86-5	5.0	167	670	5.0	10	25	50	80	100	120
Phenanthrene	85-01-8	5.0	167	330	5.0	10	25	50	80	100	120
Phenol	108-95-2	5.0	167	330	5.0	10	25	50	80	100	120
Pyrene	129-00-0	5.0	167	330	5.0	10	25	50	80	100	120
1,2,4-Trichlorobenzene	120-82-1	5.0	167	330	5.0	10	25	50	80	100	120
2,4,5-Trichlorophenol	95-95-4	5.0	167	670	5.0	10	25	50	80	100	120
2,4,6-Trichlorophenol	88-06-2	5.0	167	330	5.0	10	25	50	80	100	120
1,4-Dioxane	123-91-1	10	167		5.0	10	25	50	80	100	120
2,3,4,6-Tetrachlorophenol	58-90-2	10	167		5.0	10	25	50	80	100	120
Acetophenone	98-86-2	10	333		5.0	10	25	50	80	100	120
Atrazine	1912-24-9	10	333		5.0	10	25	50	80	100	120
Benzaldehyde	100-52-7	10	333		5.0	10	25	50	80	100	120
Benzidine	92-87-5	50	1670		5.0	10	25	50	80	100	120
Caprolactam	105-60-2	10	333		5.0	10	25	50	80	100	120
Biphenyl	92-52-4	10	333		5.0	10	25	50	80	100	120

10.3.4 Calibration Response Factors

10.3.5 Response factors (RF) establish the relationship of the instruments response in comparison with the concentration of any given analyte. The RF includes the concentration and response of the internal standard as well. By relating the IS concentration and response in an inverse manner, the target analyte concentration is adjusted to account for drift in the instrument on a per injection basis. As instrument response increases as indicated by the response of the internal standard, the concentration of the target is mathematically decreased, and vice versa.

10.3.6 To calculate the RF for any given calibration standard (or calibration verification standard), tabulate the area response of the characteristic ions against concentration for each compound and each internal standard. Calculate response factors (RF) for each compound relative to one of the internal standards. The internal standard selected for the calculation of the RF for a compound should be the internal standard that has a retention time closest to the compound being measured. Response factors are calculated using the following equation.

$$RF = \frac{A_x C_{is}}{A_{is} C_x}$$

Where:
A_x = Area of the characteristic ion for the compound being measured.
A_{is} = Area of the characteristic ion for the specific internal standard.
C_{is} = Concentration of the specific internal standard (µg/L).
C_x = Concentration of the compound being measured (µg/L).

Most, if not all modern chromatography data systems are capable of calculating this factor and using it to quantify analyte concentrations. The 8270C method has minimum requirements that these response factors must meet in order to be considered valid. The method uses a subset of the target analyte list to evaluate the performance of the system. These compounds are referred to as the System Performance Check Compounds or the SPCCs. The SPCCs serve as an indicator of instrument sensitivity and, by meeting a minimum value, ensure that the laboratory has adequate sensitivity to analyze and reliably report data for environmental samples.

10.3.7 Calibration Curve Fit

10.3.8 The calibration curve is a representation of the relationship of the instrument response and analyte concentration. The curve is used to quantitate the concentration of an unknown based on its response and this known relationship. The curve is produced in several ways depending on the nature of the "goodness of fit".

Average Response Factor (ARF): The average response factor is determined by averaging the response factors calculated for each calibration level for each target analyte. The average RF can be used to calculate the concentration of target analytes in samples provided the criteria are met for consistency in the RFs for any given analyte. An average response factor is the default curve fitting option for calibrations. It is in the most basic sense, a linear regression that is forced through zero at the origin. Because of its simplicity and the interception of the y axis at the origin, this is the preferred technique for curve fitting. A calculation of the percent relative standard deviation (%RSD) is used to determine the acceptability of the use of the ARF (see Table 9.2).

The % RSD is calculated as follows: %RSD = SD*100 / ARF

Where: SD = Standard deviation of the averaged RFs for a given compound

The average response factor is also used to diagnose the integrity of the chromatography system as it relates to calibration linearity. The ***Calibration Check Compounds (CCCs)*** are a subset of the target analyte list that must meet specific criteria (see Table 10.2) for the calibration to be acceptable. For the CCCs, the %RSD for each is compared to the method criteria. If that of any CCC exceeds the criteria, the system needs to be inspected for potential sources of errors and recalibrated.

Linear Regression: The linear regression calibration curve is derived from a least squares regression analysis of the calibration points. A calibration curve based on this technique will have the format of y=ax+b where "a" is the slope of the line and "b" is the y intercept. In order to use this curve fit technique, a minimum of 5 calibration points must be available and the origin cannot be included as one of the points. This technique works well for calibrations where the response of the instrument is linear in nature but does not necessarily intercept the y axis at the origin. However, because the linear regression is not forced through the origin, very low levels of contaminants below the response of the lowest calibration point may generate erroneous reportable results. A calculation of the correlation coefficient "r" is used to determine the acceptability of a linear regressed curve (see Table 10.2).

Non-linear Regression: The non-linear regression calibration curve is derived from a least squares regression analysis of the calibration points. A calibration curve based on this technique will have the format of $y= ax^2+bx+c$. In order to use this curve fit technique, a minimum of 6 calibration points must be available and the origin cannot be included as one of the points. This technique works well for calibrations where the response of the instrument gradually decreases with increasing concentrations. Using this technique, an analyst may be able to generate calibration curves with correlation coefficients very close or equivalent to 1.000. However, because the non-linear regression is not forced through the origin, very low levels of contaminants below the response of the lowest calibration point may generate erroneous reportable results. Likewise, high levels of contamination may not be able to be calculated due to regression equations with multiple intercepts of either axis on the calibration plot.

A calculation of the coefficient of determination (COD) is used to determine the acceptability of a non-linear regressed curve (see Table 10.2). Either the low or high calibration points may be dropped to meet linearity criteria provided the laboratory meets the minimum 5 calibration point requirements. Points within the center of the curve may not be dropped unless an obvious problem is discovered and documented. The point must be dropped in its entirety or reanalyzed. Re-analysis should be within the same 12-hour time window and must occur within 8 hours of the original analysis.

10.4 Calibration Verification

10.4.1 Second Source Verification (SCV)

In addition to meeting the linearity criteria, any new calibration curve must be assessed for accuracy in the values generated. Accuracy is a function of both the "fit" of the curve to the points used and the accuracy of the standards used to generate the calibration points. By meeting the fit criteria, the accuracy relative to the goodness of fit is addressed. However, because all calibration points are from the same source, it is possible that the calibration points may meet linearity criteria but not be accurately made in terms of their true value.

Therefore, to assess the accuracy relative to the purity of the standards, a single standard from a secondary source must be analyzed and the results obtained must be assessed relative to the known true value. This step is referred to as ***Secondary Source Verification*** or, alternatively as ***Initial Calibration Verification***. This secondary source must be from an alternative vendor or, in the event an alternative vendor is not available, from a different lot from the same vendor. The accuracy of the standard is assessed as a percent difference from the true value according to the following equation:

$$\% \text{ Difference} = [\text{Result}_{SCV} - \text{TrueValue}_{SCV}] / \text{TrueValue}_{SCV} * 100$$

See Table 9.3 for details on the preparation of this standard. See Table 10.2 for control criteria

10.4.2 Continuing Calibration Verification (CCV)

As part of the analytical process, the instrumentation must be checked periodically to determine if the response has changed significantly since the initial calibration was established. This verification process is known as ***Continuing Calibration Verification***. The validity of the initial calibration is checked at the beginning of every analytical sequence and every 12 hours thereafter for as long as the instrument is analyzing samples and is accomplished by analyzing a midpoint calibration standard (CCV).

The values obtained from the analysis of the CCV are compared to the true values and a percent change calculated. The percent change must meet the method specified criteria for the analysis to proceed for an additional 12 hours.

The actual determination of change in instrument response is based on the type of curve fit used for each analyte. Calibration curves based on an average response factor are assessed based on the percent difference of the RF calculated for the CCV from the average RF established in the initial calibration. Calibration curves based on a linear or non-linear regression are assessed based on the percent drift of the calculated result from the known true value of the standard. The equations for these calculations are as follows:

$$\% \text{ Difference: } [RF_{CCV} - AvgRF_{CAL}] / AvgRF_{CALl} \times 100$$

$$\% \text{ Drift: } [\text{Result}_{CCV} - \text{TrueValue}_{CCV}] / \text{TrueValue}_{CCV} \times 100$$

Table 10.2 – Calibration Acceptance and Verification Criteria

Calibration Metric	Parameter / Frequency	Criteria	Comments
Calibration Curve Fit	Average Response Factor Linear Regression Non-linear Regression	%RSD = 15% r = 0.99 COD = 0.99	If not met, try linear regression fit If not met, try non-linear regression fit If not met, remake standards and recalibrate
System Performance Check Compounds (SPCCs)	N-Nitroso-di-n-propylamine Hexachlorocyclopentadiene 2,4-Dinitrophenol 4-Nitrophenol	Avg RF = 0.05 Avg RF = 0.05 Avg RF = 0.05 Avg RF = 0.05	Some possible problems are standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, poor purging efficiency, and active sites in the column or chromatographic system.
Calibration Check Compounds (CCCs)	Acenaphthene 1,4-Dichlorobenzene Hexachlorobutadiene N-Nitrosodiphenylamine Di-n-octylphthalate Fluoranthene Benzo[a]pyrene 4-Chloro-3-methylphenol 2,4-Dichlorophenol 2-Nitrophenol Phenol Pentachlorophenol 2,4,6-Trichlorphenol	%RSD < 30%	%RSD for the calibration check compounds (CCC's) must be £30% regardless of curve fit used. If the CCCs are not included on a list of analytes for a project, and therefore not included in the calibration standards, then all compounds of interest must meet a ≤30% RSD criterion.
Second Source Verification Standard	Immediately after each initial calibration	% Diff ±30%	Acceptance criteria are ±30% for all analytes, with allowances for 5% of compounds @ ±40%. See current revision of S-ALL-Q-025.
Continuing Calibration Verification	Prior to the analysis of any samples and every 12 hours thereafter		If the requirements for continuing calibration are not met, these corrective actions must be taken prior to reanalysis of standards. Only two injections of the same standard are permitted back to back.
	SPCCs	Must meet response criteria listed above	
	Internal Standard RT Internal Standard Response	RT ± 30 sec 50 – 200%	Use midpoint calibration standard as reference Use midpoint calibration standard as reference
	CCCs	RF ± 20% Diff. Result ± 20% Drift	Use for Avg RF calibration curves Use for linear and non-linear calibration curves
	Non-CCC Targets	RF ± 50% Diff. Result ±50% Drift	Some programs may require control over non-CCC target analytes. In the absence of specified criteria, use those listed

10.5 Calibration Corrective Actions

10.5.1 Calibration Linearity Problems

10.5.1.1 Check instrumentation/equipment condition.

10.5.1.2 Enter maintenance in instrument maintenance logbook.

10.5.1.3 Perform another initial calibration.

10.5.1.4 No data can be reported.

10.5.1.5 Generate on Non-Conformance Memo.

10.5.2 Secondary Verification Problems

10.5.2.1 Check instrumentation/equipment condition.

10.5.2.2 Enter maintenance in instrument maintenance logbook.

10.5.2.3 Perform another initial calibration.

10.5.2.4 No data can be reported.

10.5.2.5 Generate on Non-Conformance Memo

10.5.3 Continuing Verification Problems

10.5.3.1 Reanalyze the original CCV standard to determine instrument consistency.

10.5.3.2 Prepare and analyze a new CCV standard to determine preparation consistency / standard integrity.

10.5.3.3 Document instrument maintenance

10.5.3.4 Reanalyze CCV standard to determine if maintenance was effective in restoring performance.

10.5.3.5 Complete recalibration of instrument.

10.5.3.6 If samples were analyzed in spite of verification failures, note the following exceptions for addressing those results. Deviations from this requirement must be noted on the injection log with a thorough explanation for the deviation from policy.

Exceptions: If calibration verification is above the upper control limit, samples non-detected for those analytes may be reported without reanalysis.

10.5.4 General Comment: When constructing a linear initial calibration curve, the analyst can drop curve points as follows:

- The lowest curve point can be dropped as long as there is a standard that can meet the necessary reporting limits of the associated samples (or the reporting limits would have to be raised accordingly).
- The highest curve point, or points, can be dropped but this decreases the upper calibration range, thereby limiting the analyst to reporting data within this new calibration range (this may cause more dilutions).
- Any other curve point can only be deleted if it can be proven that it was a bad injection, instrument failure, etc. A supervisor or the Quality Manager is required to approve any such instance

11. PROCEDURES

11.1 GC/MS System Preparation

11.1.1 Operating Parameters

Configure the GC/MS system to match the following operating parameters based on instrument configuration. The parameters themselves are saved as a method on the chromatography data system. By loading the last method used, the instrument will auto-configure to match the parameters from the last time the system was operated under that method. Verify that the settings in the software match the appropriate configuration.

Table 11.1 –Instruments and Operating Parameters

GC/MS Instrument 40MSS1	
GC: Hewlett Packard model 5890	MS: Hewlett Packard model 5972A
Operating Parameters:	Operating Parameters:
Initial Temp: 40°C	Acquisition mode: SCAN
Temp Program: hold 1.0 min at 40°C, ramp at 18°C/min to 100°C, then ramp at 15°C/min to 290°C, hold 5.95min, then ramp at 40°C/min to 320°C and hold for 1 min	Mass Range: 35-500
Final Temp: 320°C	
Transfer Line Temp: 300°C	
Column: Restek XTI-5 (30m; 0.25mm ID and 0.25um film thickness)w/Integraguard	
Purge Flow: 40mL/min	

GC/MS Instrument 40MSS5 – Screen Instrument only	
GC: Hewlett Packard model 5890	MS: Hewlett Packard model 5972A
Operating Parameters:	Operating Parameters:
Initial Temp: 75°C	Acquisition mode: SCAN
Temp Program: hold 0.3 min at 75°C, ramp at 34°C/min to 320°C, then ramp at 40°C/min to 340°C, hold 1.20min	Mass Range: 35-500
Final Temp: 340°C	
Transfer Line Temp: 300°C	
Column: Restek XTI-5 (30m; 0.25mm ID and 0.25um film thickness)w/Integraguard	
Purge Flow: 40mL/min	

GC/MS Instrument 40MSS6 used for Minnesota Phenols Samples	
GC: Hewlett Packard model 5890	MS: Hewlett Packard model 5972A
Operating Parameters:	Operating Parameters:
Initial Temp: 40°C	Acquisition mode: SCAN
Temp Program: hold 1.00 min at 40°C, ramp at 18°C/min to 100°C, then ramp at 5°C/min to 200°C , then ramp at 40°C/min to 300°C and hold for 1.0 min	Mass Range: 35-500
Final Temp: 300°C	
Transfer Line Temp: 300°C	
Column: Restek XTI-5 w/Integra Guard (30m; 0.25um dia)	
Split Flow: 50mL/min	

GC/MS Instrument 40MSS6 used for Biota Samples	
GC: Hewlett Packard model 5890	MS: Hewlett Packard model 5972A
Operating Parameters:	Operating Parameters:
Initial Temp: 40°C	Acquisition mode: SCAN
Temp Program: hold 1.0 min at 40°C, ramp at 18°C/min to 100°C, then ramp at 15°C/min to 290°C, hold 5.95min, then ramp at 40°C/min to 320°C and hold for 1 min	Mass Range: 35-500
Final Temp: 320°C	
Transfer Line Temp: 300°C	
Column: Restek XTI-5 (30m; 0.25mm ID and 0.25um film thickness)w/Integraguard	
Purge Flow: 40mL/min	

11.2 Tune Verification

At the beginning of each analytical sequence, prior to the analysis of any standards or samples, the mass spectrometer tune conditions must be verified. This is done by analyzing a standard containing DFTPP (refer to table 9.3). The tune verification standard can be combined with the CCV standard provided that the amount of DFTPP introduced into the system meets the criteria in Table 9.1. For semi-volatile analysis, the system must also be verified for inertness. This is done simultaneously by the inclusion of DDT, benzidine and pentachlorophenol. DDT is used to verify breakdown conditions; benzidine and pentachlorophenol are used to check for tailing due to system activity.

11.2.1 Ion Ratio Verification

After the analysis of this standard, the mass spectrum of DFTPP must be evaluated against the following criteria.

Table 11.2

Mass (m/z)	Ion Abundance criteria
51	30.0-80.0% of m/z 198
68	<2.0% of m/z 69
69	Present
70	<2.0% of m/z 69
127	25.0-75.0% of m/z 198
197	<1.0% of m/z 198
198	Base peak, 100% relative abundance
199	5.0-9.0% of m/z 198
275	10.0-30.0% of m/z 198
365	>0.75% of m/z 198
441	Present, but less than m/z 443
442	40.0-110.0% of m/z 198
443	15.0-24.0% of m/z 442

To evaluate the tune spectra, following the operating instructions for the chromatography data system to access the data file and obtain mass spectra for DFTPP. If the software has a program or macro for automatically selecting the spectra and evaluating the response ratios, use this option. Otherwise, the spectra must be obtained in one the following manners, in the listed order.

1. **Take one scan for DFTPP; or**
2. **Using an average of three scans, centered on the apex of the peak; or,**
3. **Using an average of all scans across the width of the peak, taken at half height; or,**

4. Using an average of all scans taken across the width of the peak from baseline to baseline.

A background scan taken immediately before but not including the peak must be subtracted.

Once obtained, evaluate the ion ratios against the criteria listed above. If the ratios meet the criteria, then analysis may proceed for 12 hours. The window for analysis is 12 hours from the injection date / time for the DFTPP tune verification. After that, the tune must be verified again to establish a new analytical window. The same Ion Abundance Criteria used for the DFTPP tune coupled with the initial calibration must be used for all subsequent analyses associated with that initial calibration.

If the ratios do not meet the criteria, refer to the following corrective actions to address the problem. Any changes made to the system must be followed with the reanalysis of a tune verification standard. Any maintenance performed on the physical mass spec components requires recalibration. "Autotunes" may be performed as long as the following CCV meets all criteria for response, retention time and sensitivity.

11.2.2 Tailing Factor Verification

The laboratory has no procedure at the present time to judge tailing.

11.2.3 Breakdown Verification

The GC/MS system must be sufficiently inert such that DDT will not breakdown excessively while in the injection port. The inertness is assessed by calculating the percent breakdown of DDT into the products DDD and DDE. The calculation is performed as follows:

% DDT Breakdown = (Sum of responses for DDD and DDE) / (Sum of responses for DDT, DDD and DDE) *100

The % breakdown must not exceed 20% unless all required compounds are within 20% on the CCV. If the breakdown of DDT exceeds this amount, samples may be analyzed if all requested analytes are within +/- 20% in the CCV (documented on an out-of-control form), otherwise corrective action must be taken prior to analysis of samples. The breakdown must be verified by the analysis of another breakdown standard after corrective action is taken. Follow the following steps to return the system to an acceptable operating condition.

- Perform front-end maintenance on the GCMS System.
- Begin the run again by re-analyzing the DFTPP tune solution.

11.3 Calibration Verification

After the instrument tune conditions are verified and the system meets tune criteria, the instrument must undergo calibration verification. If it has already been determined that the instrument needs to be recalibrated, follow the procedures listed in section 10.2.1 (Analysis of Standards). Otherwise, analyze a Continuing Calibration Verification Standard to determine the current calibration status.

If the CCV meets control criteria, the system is deemed to be in control and analysis of samples may commence. If the CCV does not meet control criteria, follow the corrective action procedures listed section 10.4.3 (Continuing Verification Problems). If the tune verification has been combined with the CCV, the 12 hour analysis window begins from the analysis date / time of the CCV.

Note: In situations where the instrument will run unattended (i.e. overnight), the analyst may load sequential (back-to-back) CCVs in anticipation of that the first in the series may fail due to carry over from a previous sample. If so, both CCVs must be evaluated according to the protocol set forth in the Quality Assurance Manual within Section 6 – Equipment and Measurement Traceability.

11.4 Sample Preparation

11.4.1 Samples

11.5.2.1 Water Samples

Aqueous samples are prepared according to EPA Method 3510C. These procedures are contained in a separate standard operating procedure. Refer to S-ALL-GB-O-003 *Separatory Funnel Extraction of Water Samples for Semivolatile Analysis* for details on the preparation of aqueous samples.

Prior to analysis, each sample, MB, LCS, MS, and MSD is spiked with 10uL of the internal standard solution (9.2.4.1).

11.5.2.2 Soil Samples

Solid samples are prepared according to EPA Method 3546. These procedures are contained in a separate standard operating procedure. Refer to S-GB-O-045 *Microwave Extraction for the Determination of Polynuclear Aromatic Hydrocarbons and Base/Neutral/Acids in Solid Matrices* for details on the preparation of soil or solid samples.

Prior to analysis, each sample, MB, LCS, MS, and MSD is spiked with 10uL of the internal standard solution (9.2.4.1).

11.5.2.3 Biota Samples

Biota samples are prepared according to EPA Method 3540C. These procedures are contained in a separate standard operating procedure. Refer to S-GB-O-033 *Extraction of Biological Samples for Base Neutral/Acid and PAH-SIM Analysis* for details on the preparation of biota samples.

Prior to analysis, each sample, MB, LCS, MS, and MSD is spiked with 10uL of the internal standard solution (9.2.4.1).

11.5.2.4 Dilutions

Dilutions on sample extracts must be prepared in a volumetric fashion. Sample aliquots should be taken in volumetric syringes and brought to volume by the addition of solvent via an appropriate syringe. In the event a dilution is made to bring a target analyte into calibration range, the analyst should make a dilution such that the target analyte is roughly the equivalent of the mid calibration point whenever possible.

If dilutions are made on extracts that already contain internal standards, a proportional aliquot of internal standard solution must be added to the diluted extract based on the volume of diluent used.

11.5 Sample Analysis

11.5.1 GC/MS System Preparation

11.5.2.1 **Operating Parameters** – Set up the instrument parameters shown in Table 11.1.

11.5.2.2 **System Tuning and GC Performance Checks** – Analyze the Tuning Solution and tune the mass spectrometer to meet the criteria shown in Section 10.2.1. Verify acceptable GC system performance as described in Section 10.2.1. Print out a tune report.

11.5.2 Batch Sequence – Generate a sequence to run a batch of samples.

11.5.2.1 **Initial Calibration –** The typical batch for initial calibration should include:

Tune Standard
Calibration Level 1
Calibration Level 2
Calibration Level 3
Calibration Level 4
Calibration Level 5
Calibration and System Performance Solution

11.5.2.2 **Sample Analysis –** The typical batch for sample analysis should include the following. Preparation of LCS, MS, MSD, and Duplicate sample extracts is described in the appropriate sample preparation SOP.

Tune Standard
Calibration and System Performance Solution
Instrument Blank
Method Blank
Laboratory Control Sample
Laboratory Control Sample Duplicate
20 samples
Matrix Spike
Matrix Spike Duplicate

11.5.3 Autosampler – Load the autosampler with standards and samples for the batch created above.

11.5.4 Analyze Samples – Analyze all standards, quality control samples, and environmental samples.

11.6 Data Reduction

11.6.1 Qualitative Analysis

Retention Time Comparison: The relative retention time (RRT) of the sample component must be within ±0.06 RRT units of the component in the calibration verification standard. Extracted Ion Current Plots (EICPs) may be used to provide a more reliable assignment of RT in the presence of coeluting components.

Mass Spectrum Comparison: The characteristic ions from the reference mass spectrum are defined as the three ions of greatest relative intensity, or any ions over 30% relative intensity if less than three such ions occur in the reference spectrum. Compounds are identified as present when the following criteria are met.

- The intensities of the characteristic ions of a compound maximize in the same scan or within one scan of each other.
- The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum.
- Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times.
- Due to limitations of the “Target” software, analyst discretion is advised.

Table 11.3 Primary and Secondary quantitation ions for target compounds[2]

Analyte	Primary Ion	Secondary Ions
Phenol	94	65, 66
Bis (2-Chloroethyl) ether	93	63, 95
2-Chlorophenol	128	64, 130
1,3-Dichlorobenzene	146	148, 111
1,4-Dichlorobenzene	46	148, 111
Benzyl Alcohol	108	79, 107
1,2-Dichlorobenzene	146	148, 111
2-Methylphenol	108	107, 79
Bis (2-Chloroisopropyl)ether	45	77, 121
3&4-Methylphenol	108	107, 79
N-Nitroso-di-n-propylamine	70	43, 101
Hexachloroethane	117	200.8, 198.8
1,4-Dioxane	88	58, 43
Benzaldehyde	77	106, 105
N-Nitrosodimethylamine	42	74
Aniline	93	66, 65
Acetophenone	105	77, 51
Nitrobenzene	77	123, 65
Isophorone	82	95, 138
2-Nitrophenol	139	109, 65
2,4-Dimethylphenol	107	122, 121
Benzoic acid	122	105, 77
Bis(2-Chloroethoxy)methane	93	95, 123
2,4-Dichlorophenol	162	164, 98
1,2,4-Trichlorobenzene	180	182, 145
Naphthalene	128	129
4-Chloroaniline	127	129
Hexachlorobutadiene	224.9	118, 190
4-Chloro-3-methylphenol	107	144, 142
2-Methylnaphthalene	142	141
Caprolactam	113	56, 55
Hexachlorocyclopentadiene	237	234.9
2,4,6-Trichlorophenol	196	198, 200
2,4,5-Trichlorophenol	196	198, 200
2-Chloronaphthalene	162	127, 164
2-Nitroaniline	65	92, 138
Dimethylphthalate	163	194, 164
Acenaphthylene	152	153
2,6-Dinitrotoluene	165	63, 89
3-Nitroaniline	138	108, 92
Acenaphthene	154	153, 152
2,4-Dinitrophenol	184	63, 154
4-Nitrophenol	109	139, 65
Dibenzofuran	168	139
2,4-Dinitrotoluene	165	63, 89
Diethylphthalate	149	177, 150
4-Chlorophenyl-phenylether	204	206, 141
Fluorene	166	165, 167
4-Nitroaniline	138	108, 92
2,3,4,6-Tetrachlorophenol	232	131, 230
4,6-Dinitro-2-methylphenol	198	51, 105
N-Nitrosodiphenylamine	169	168, 167
4-Bromophenyl-phenylether	248	250, 141

Hexachlorobenzene	283.8	142, 248.8
Atrazine	200	173, 215
Pentachlorophenol	265.8	263.8, 267.8
Phenanthrene	178	179, 176
Anthracene	178	176, 179
Di-n-butylphthalate	149	150, 104
Fluoranthene	202	101, 203
Benzidine	184	185, 92
Pyrene	202	200, 203
Butylbenzylphthalate	149	91, 206
3,3'-Dichlorobenzidine	252	254, 126
Benzo(a)anthracene	228	229, 226
Chysene	228	226, 229
Bis(2-ethylhexyl)phthalate	149	167, 279
Di-n-octylphthalate	149	43
Benzo(b)fluoranthene	251.99	253, 125
Benzo(k)fluoranthene	252	253, 125
Benzo(a)pyrene	252	253, 25
Indeno(1,2,3-cd)pyrene	276	138, 277
Dibenz(a,h)anthracene	278	139, 279
Benzo(g,h,i)perylene	276	138, 277
Carbazole	167	

[2] The information in this table was taken from Method 8270C. Please refer to the method for additional compounds and their applicable ions.

Analyte	Primary Ion	Secondary Ions
Internal Standards		
1,4-Dichlorobenzene-d_4	152	150, 115
Naphthalene-d_8	136	68
Acenaphthene-d_{10}	164	162, 160
Phenanthrene-d_{10}	188	94, 80
Chrysene-d_{12}	240	120, 236
Perylene-d_{12}	264	260, 265
Surrogates		
2-Fluorophenol (acid)	112	64
Phenol-d_6 (acid)	99	42, 71
Nitrobenzene-d_5 (BN)	82	128, 54
2-Fluorobiphenyl (BN)	172	171
2,4,6-Tribromophenol (acid)	330	332, 141
Terphenyl-d_{14} (BN)	244	122, 212

[2] The information in this table was taken from Method 8270C. Please refer to the method for additional compounds and their applicable ions.

11.6.2 Internal Standard Assignment List (from Method SW-846 8270C- Table 5): this section lists the internal standard compounds and all of the target compounds that are assigned to each internal for quantitation:

1,4-Dichlorobenzene-d4

Aniline
Benzyl alcohol
Bis(2-chloroethyl)ether
Bis(2-chloroisopropyl)ether
2-Chlorophenol
1,3-Dichlorobenzene
1,4-Dichlorobenzene
1,2-Dichlorobenzene
2-Fluorophenol (surrogate)
Hexachloroethane
2-Methylphenol
4-Methylphenol
N-Nitroso-dimethylamine Nitrobenzene
N-Nitroso-di-n-propylamine
Phenol
Phenol-d6 (surrogate)
1,4-Dioxane
Pyridine
2-Chlorophenol-d4(advisory surrogate)
Benzaldehyde
1,2-Dichlorobenzene-d4(advisory surrogate)

Naphthalene-d8

Acetophenone
Benzoic acid
Bis(2-chloroethoxy)methane
4-Chloroaniline
4-Chloro-3-methylphenol
2,4-Dichlorophenol
2,6-Dichlorophenol
2,4-Dimethylphenol
Hexachlorobutadiene
Isophorone
2-Methylnaphthalene
Naphthalene

Nitrobenzene-d8 (surrogate)
2-Nitrophenol
1-Methylnaphthalene
1,2,4-Trichlorobenzene

Acenaphthene-d10

Acenaphthene
Acenaphthylene
1,2-Diphenylhydrazine
2-Chloronaphthalene
4-Chlorophenyl phenyl ether
Dibenzofuran
Diethyl phthalate
Dimethyl phthalate
2,4-Dinitrophenol
2,4-Dinitrotoluene
2,6-Dinitrotoluene
Fluorene
2-Fluorobiphenyl (surrogate)
Hexachlorocyclopentadiene
2-Nitroaniline
3-Nitroaniline
4-Nitroaniline
4-Nitrophenol
Biphenyl
2,4,6-Tribromophenol (surrogate)
2,4,6-Trichlorophenol
2,4,5-Trichlorophenol

Phenanthrene-d10

Atrazine
Anthracene
4-Bromophenyl phenyl ether
Di-n-butyl phthalate
4,6-Dinitro-2-methylphenol
Carbazole
Fluoranthene
Hexachlorobenzene
N-Nitroso-diphenylamine
Pentachlorophenol
Phenanthrene

Chrysene-d12

Benzidine
Benzo(a)anthracene
Bis(2-ethylhexyl)phthalate
Butyl benzyl phthalate
Chrysene
3,3'-Dichlorobenzidine
Pyrene
Terphenyl-d6 (surrogate)
Di-n-octyl phthalate
Indeno(123,cd)pyrene

Perylene-d12

Benzo(b)fluoranthene
Benzo(k)fluoranthene
Benzo(g,h,i)perylene
Benzo(a)pyrene
Dibenz(a,h)anthracene

11.6.3 Quantitative Analysis – Quantitation is based on the integrated abundance of the target analyte's quantitation ion using the internal standard technique.

Raw Data Results: The GC/MS data system will calculate the concentration of each analyte in the sample extract. If supplied with the preparation parameters, the system may be able to calculate the results back to the original matrix. The calculation for the concentration of the target analyte in the original matrix is listed below and is based on the calibration table in units of ppm (ug/mL).

If the initial analysis of the sample or a dilution of the sample has a concentration that exceeds the calibration range, the sample must be analyzed at a higher dilution. All dilutions should keep the response of the major constituents near the middle of the linear range of the curve.

11.5.2.1 Results Calculation – Aqueous Sample:

$$\text{Concentration } (mg/L) = \frac{(C_x)(V_x)(DF)}{(V_s)}$$

Where:

C_x = Concentration in extract (µg/mL).
V_v = Volume of final extract (mL).
DF = Dilution factor.
V_s = Volume of water sample extracted (mL).

11.5.2.2 Results Calculation – Soil / Solid calculations:

$$\text{Concentration } (mg/kg) = \frac{(C_x)(V_x)(1000)(DF)}{(W_s)}$$

Where:

C_x = Concentration in extract (µg/mL).
V_v = Volume of final extract (mL).
DF = Dilution factor.
W_s = Weight of soil sample extracted (g). The wet weight or dry weight may be used, depending upon the specific applications of the data.

11.5.2.3 Results Calculation – Biota calculations:

$$\text{Concentration } (mg/kg) = \frac{(C_x)(V_x)(1000)(DF)}{(W_s)}$$

Where:

C_x = Concentration in extract (µg/mL).
V_v = Volume of final extract (mL).
DF = Dilution factor.
W_s = Weight of biota sample extracted (g).

11.6.4 Tentatively Identified Compounds (TICs) – For some samples, identification may be desired for non-target compounds. A mass spectral library search may be conducted to attempt assignment of tentative identifications. Only after visual comparison of sample spectra with the nearest library searches may the analyst assign a tentative identification. Use the following guidelines for making tentative identifications.

- Relative intensities of major ions in the reference spectrum (ions greater than 10% of the most abundant ion) should be present in the sample spectrum.
- The relative intensities of the major ions should agree within ± 20%.
- Molecular ions present in the reference spectrum should be present in the sample spectrum.
- Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of co-eluting compounds.
- Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or co-eluting peaks. Data system library reduction programs can sometimes create these discrepancies.

12. QUALITY CONTROL

12.1 Instrument Quality Control: Refer to Table 10.2 for initial and continuing calibration criteria and corrective actions.

12.1.1 South Carolina requires the use of a linear calibration model. Either the %RSD is less than 15% and the average RF is used for quantitation or a linear regression with a correlation coefficient greater than or equal to 0.99 must be used for all analytes listed in SW 846 Method 8270C.

12.2 **Batch Quality Control**

Table 12.1 – Batch Quality Control Criteria

QA Sample	Components	Frequency	Acceptance Criteria	Corrective Action
Method Blank (MB)	Reagent water	One (1) per 20 samples	1) Target analytes must be less than reporting limit. 2) If results are reported to MDL, target analytes in MB should be non-detect	1) Qualify results and / or re-extract associated samples. ***Exceptions:*** 1) If sample ND, report sample without qualification 2) If sample result <20x MB detects, report sample with appropriate qualifier to indicate an estimated value. Client must be alerted and authorize this condition.
Laboratory Control Sample (LCS)	Method specified compounds: Base / Neutrals 1,2,4-Trichlorobenzene Acenapthene 2,4-Dinitrotoluene Pyrene N-Nitroso-di-n-propylamine 1,4-Dichlorobenzene *OR (alternative)* Full Target List	One (1) per batch of up to 20 samples. LCSD is performed for water samples where no volume provided for Ms/MSD. Acids Pentachlorophenol Phenol 2-Chlorophenol 4-Chloro-3-methylphenol 4-Nitrophenol	Laboratory derived limits Method Specified List: All compounds must pass control criteria, with no exceptions. Full Target List: Marginal exceedances allowed according to NELAC 2003 Chap 5 D.1.1.2.1.e	1) If LCS passes, review samples for potential injection problems 2) If problem persists, check spike solution 3) Re-extract samples where possible ***Exceptions:*** 1) If LCS rec > QC limits and these compounds are non-detect in the associated samples, the sample data may be reported with appropriate data qualifiers.

Matrix Spike (MS)	Method specified compounds: Base / Neutrals 1,2,4-Trichlorobenzene Acenapthene 2,4-Dinitrotoluene Pyrene N-Nitroso-di-n-propylamine 1,4-Dichlorobenzene *OR (alternative)* Full Target List	One pair per batch of up to 20 samples Acids Pentachlorophenol Phenol 2-Chlorophenol 4-Chloro-3-methylphenol 4-Nitrophenol	Laboratory derived limits	1) If LCS and MBs are acceptable, the MS/MSD chromatogram should be reviewed and it may be reported with appropriate footnote indicating matrix interferences
MSD / Duplicate	MS Duplicate *OR (alternative)* Sample Dup	One (1) for every 5% of all environmental samples	Laboratory Derived Limits	1) Report results with an appropriate footnote.

12.3 Sample Quality Control

Table 12.2 – Sample Quality Control criteria

QA Sample	Components	Frequency	Acceptance Criteria	Corrective Action
Internal Standard	1,4 Dichlorobenzene-d4 Naphthalene-d8 Acenaphthene-d10 Phenanthrene-d10 Chrysene-d12 Perylene-d12	Added to all standards, samples, spikes, control samples, and method blanks prior to analysis	**Retention Time:** RT must be ± 30 seconds from last calibration check on all samples	**Retention Time Failure:** 1) If matrix interference is NOT probable, the analytical system must be checked for source of retention time shifting. 2) Affected samples should be reanalyzed in the absence of an obvious instrument or matrix related interference.
Surrogate Standards	Nitrobenzene-d5 2-Fluorobiphenyl Terphenyl-d14 Phenol-d6 2-Fluorophenol 2,4,6-Tribromophenol	Added to all samples, spikes, control samples and method blanks prior to extraction	Laboratory derived limits	1) Assess impact of sample matrix 2) In the absence of obvious matrix interference (high background, extremely dark extract), re-extract sample. ***Exceptions:*** 1) Surr rec above criteria and target compounds < RL, result may be reported with appropriate footnote. 2) Surr rec out of control due to obvious sample matrix interference (i.e. co-elution), report results with appropriate footnote. 3) One acid and one base surrogate compound is allowed to be out of control. If two or more acid or base surrogate compounds are out of control, the samples must be re-extracted and reanalyzed. If there is insufficient sample available for re-extraction, the data must be appropriately qualified.

13. METHOD PERFORMANCE

13.1 Method Detection Limit (MDL) Study: An MDL study must be conducted annually per S-ALL-Q-004, Method Detection Limit Studies for each matrix per instrument.

13.2 Demonstration of Capability (DOC): Every analyst who performs this method must first document acceptable accuracy and precision by passing a demonstration of capability study (DOC) per S-ALL-Q-020, Orientation and Training Procedures.

13.3 Method Modifications

Method modifications for EPA method 8270C are as follows:

- Modifications should be targeted to improve quality, efficiency or the cost effectiveness of the procedure.
- All major modifications to the procedure that may directly affect data quality must be thoroughly documented. A new demonstration of capability and equivalency must be performed and kept on record.

- Procedures identified as "Best Practices" by the PACE 3P Program will be incorporated into this document as minimum requirements for Pace laboratories.

14. POLLUTION PREVENTION AND WASTE MANAGEMENT

14.1 Procedures for handling waste generated during this analysis are addressed in ALL-S-002, Waste Handling.

14.2 In order to minimize the amount of waste generated during this procedure, analyst should prepare reagents in an amount which may be used in a reasonable amount of time (i.e. before a reagent expires)

14.3 The company wide Chemical Hygiene and Safety Manual contains additional information on pollution prevention.

15. REFERENCES

15.1 USEPA, SW-846, Method 8270C, "Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS), December 1996.

15.2 USEPA, SW-846, Method 8000B, "Determinative Chromatographic Separations", December 1996.

15.3 USEPA, EPA 625, "Base/Neutrals and Acids".

16. TABLES, DIAGRAMS, FLOWCHARTS, ATTACHMENTS, APPENDICES, ETC.

17. REVISIONS

Document Number	Reason for Change	Date
SOT-ALL-O-001-Rev.00	Restructured document format. Added tables and other content to create an "SOP Template" in which local edits are allowed. Modified signature page to include department manager and SOP template number. Updated SOP template number. Made the tuning criteria red so edits can be made to reflect local tuning criteria used. Updated calibration sections with new calibration policies described in the PASI Quality Manual revision 10.0.	28Nov2006
S-ALL-GB-O-001-Rev.00	First Issue using Corporate Template	04Jun2008

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STANDARD OPERATING PROCEDURE

Determination of Volatile Organics by GC/MS

Reference Methods: EPA Method SW-846 8260B with 5030B and 5035; and EPA Method 624

LOCAL SOP NUMBER:	S-GB-ALL-O-002-Rev.01
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LOCAL APPROVAL

Nils Melberg, Laboratory General Manager — Date: 12/22/08

Kate Grams, Laboratory Quality Manager — Date: 12/22/08

Jeff Bushner, Department Manager — Date: 12/19/2008

ANNUAL REVIEW

SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE APPROVAL. SOP IS VALID FOR ONE YEAR FROM DATE OF LAST SIGNATURE.

Signature	Title	Date

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1. Purpose

This Standard Operating Procedure (SOP) documents the procedures used by PASI – Green Bay to determine the concentration of Volatile Organic Compounds (VOCs) in environmental samples. The laboratory utilizes purge-and-trap GC/MS and bases these documented procedures on those listed SW-846 Methods 5030B, 5035 and 8260B; and EPA 624.

2. Summary of Method

Volatile organic compounds are introduced into the gas chromatograph by a purge-and trap method. The analytes are purged from a sample aliquot or extract by purging with helium. The purged analytes are collected in a trap. At the completion of the purge time, the trap is rapidly heated and back flushed with helium to drive out the trapped analytes. The analytes are transferred into the inlet of a capillary gas chromatography column. The carrier gas flow through the column is controlled and the temperature is increased according to a set program to achieve optimum separation of purged analytes. The mass spectrometer is operated in a repetitive scan mode. Analytes are identified by the GC/MS retention times and by a comparison of their mass spectra with spectra of authentic standards. Analytes are quantified by comparing the response of a selected primary ion relative to an internal standard against a calibration curve.

3. Scope and Application

3.1. This method is applicable to most organic compounds that have boiling points below 200 ºC and are insoluble or slightly soluble in water. Volatile water-soluble compounds may also be determined although quantitation limits are typically higher due to their hydrophilic properties (e.g. ketones, oxygenates).

3.2. This method is applicable to most water and solid samples, regardless of moisture content. Common matrices are ground and surface water, wastewater, aqueous sludge, sediment, soils, and other solid samples. Procedures may need to be adapted to address limits in the method or equipment that might hinder or interference with sample analysis. All adaptations made to address matrix related modifications must be documented within the analytical data

3.3. This procedure is restricted to use by, or under the supervision of, analysts experienced in the use of purge-and-trap GC/MS systems and interpretation of GC/MS data. Each analyst must demonstrate the capability to generate acceptable results with this method to be considered qualified to report sample results.

3.4. This method cannot be substituted for other similar published methods where permit or regulatory compliance is required.

4. Interferences

4.1. Major contaminant sources are volatile materials in the laboratory and impurities in the inert purging gas and in the absorbent trap. The use of polytetrafluoroethylene (PTFE, Teflon) as thread sealants, tubing, or in flow controllers is highly recommended since other materials can be sources of contamination which may concentrate in the trap during the purging.

4.2. A common source of interfering contamination is carryover. This may occur when a sample containing low concentrations of volatile organic compounds is analyzed immediately after a sample containing high concentrations of volatile organic compounds. The preventive action to this condition is rinsing the purging apparatus and sample syringes with two or more portions of organic free water between samples. Analyze one or more blanks to check for cross contamination prior to sample analysis.

4.3. Since methylene chloride and acetone are common laboratory solvents, special precautions must

be taken. The volatiles analysis and sample storage area should be located as far as possible from areas where these solvents are used or stored. Where possible, the volatiles analysis and sample storage area should be served by a separate HVAC system and maintained under positive pressure to prevent intrusion of contaminants. Laboratory clothing previously exposed to methylene chloride fumes during extraction procedures can contribute to sample contamination.

5. Safety

5.1. Standards and Reagents

The toxicity and carcinogenicity of standards and reagents used in this method have not been fully defined. Each chemical compound should be treated as a potential health hazard. Reduce exposure by the use of gloves, lab coats and safety glasses. Material Safety Data Sheets (MSDSs) are on file in the laboratory and available to all personnel. Standard solutions should be prepared in a hood whenever possible.

5.2. Samples

Take precautions when handling samples. Samples should always be treated as potentially hazardous "unknowns". The use of personal protective equipment (gloves**,** lab coats and safety glasses) is required when handling samples. In the event a sample container must be opened, it is recommended to perform this in a hood whenever possible.

5.3. Equipment

Portions of the analytical instrumentation operate at high temperatures and under positive pressure. Care must be taken to minimize accidents and injuries when working on or with this equipment. Instruments should be turned off or the heated zone temperatures lowered to reduce the risk of thermal burns. Allow adequate time for the equipment to cool prior to working on these specific zones.

The purge and trap concentrator and autosampler use gas under pressure to purge samples and, in some cases, drive the robotic assemblies. These high pressures introduce the risk of injury due to flying glass and other objects should a vessel or line rupture. Safety glasses are highly recommended at all times when working in, on or around these pieces of equipment. Even instrumentation that is not operating may contain portions of the system under pressure.

6. Definitions

Refer to Glossary section of the Pace Quality Assurance Manual (QAM) for a comprehensive list of terms and definitions. In addition to those listed in the QAM, the following are additional terms found in this SOP.

6.1. **Run Sequence Log** – A logbook that lists all injections and analyses performed on a particular piece of equipment regardless of the use of the data collected from each analysis.

6.2. **Toxicity Characteristic Leaching Procedure (TCLP)** – An extraction procedure used to determine if a sample is acceptable for upland disposal. The extraction procedure is meant to simulate the leaching of contaminants under the environmental conditions typically found in a landfill.

6.3. **Tune Period** – The period after the BFB instrument tune check within which analyses may be performed.

7. Sample Collection, Preservation, and Handling

Table 7.1 – Sample Collection, Preservation, Storage and Hold time.

Sample type	Collection per sample	Preservation	Storage	Hold time
Aqueous	Two (2) VOA vials	Acidified w/ 1:1 HCl (1-2 drops) to pH<2, no headspace *Note:* 2-CLEVE requires an unpreserved sample.	4 ± 2°C	Unpreserved: 7 days pH Preserved: 14 days
Low Level Aliquot Soil/Solid (non-aqueous)	One (1) 2-4 oz. wide mouth jar for % moisture **AND** Two (2) 5-g aliquots in vials with magnetic stir bar, 5.0 mL reagent water and 1.0 g sodium bisulfate as needed. *OR (alternative):* Two (2) EnCore, TerraCore or similar sampling tubes.	No preservation *OR* sodium bisulfate **Note:** If sample effervesces on contact with the preservative, the sodium bisulfate should be eliminated for that sample.	With sodium bisulfate: 4 ± 2°C Without preservation (including EnCore, TerraCore or similar): 4 ± 2°C for up to 48 hours before storing between -7°C and -20°C, inclusive, until analysis.	Unpreserved or not stored frozen: 48 hours Preserved with sodium bisulfate or stored frozen: 14 days
High Level Aliquot Soil/Solid (non-aqueous)	One (1) 10-g aliquot in vial with 10.0 mL purge and trap grade MeOH. *OR (alternative)* One (1) 10-g aliquot in empty vial	Methanol - if sample was collected in empty vial it must be transferred into 10 mL of purge & trap grade MeOH within 48 hours of collection	With methanol: 4 ± 2°C	Unpreserved: 48 hours Preserved with methanol: 14 days
TCLP Leachates	Tedlar bag or THREE (3) VOA vials.	Filled and capped to eliminate any headspace. Vials with bubbles larger than 5 mm should be discarded.	4 ± 2°C	14 days from end of leaching procedure

Table 7.2 - Trip Blank Requirements

Aqueous	Low Level Aliquot Soil/Solid	High Level Aliquot Soil/Solid
One (1) 40mL VOA vial w/ reagent DI water	One (1) 40mL VOA vial w/ 5mL sodium bisulfate (or reagent DI water) and magnetic stir bar	One (1) 40mL VOA vial w/ 5mL purge and trap grade MeOH

8. Equipment and Supplies

Table 8.1 Equipment

Analytical Instrument/Peripherals	EPIC Pro Name	Serial Number
HP 5890 Series II GC	40MSV1	3235A46437
HP 5972 MSD	40MSV1	3306A00154
Archon Autosampler	40MSV1	11948-696A
Tekmar 3000 Purge and Trap Concentrator	40MSV1	94104001
HP 6890 GC	40MSV2	US00032794
HP 5973 MSD	40MSV2	US90460014
Archon Autosampler	40MSV2	11768-695A
Tekmar 3000 Purge and Trap Concentrator	40MSV2	9535005
Agilent 6850 GC	40MSV3	CN10719006
Agilent 5975 MSD	40MSV3	US71216198
Dynatech PTA-30 Autosampler	40MSV3	11153-593E
Tekmar 3000 Purge and Trap Concentrator	40MSV3	94104006
HP 5890 Series II GC	40MSV4	3336A53831
HP 5972 MSD	40MSV4	3341A01395
Dynatech PTA-30 Autosampler	40MSV4	11647-1194
Tekmar 3000 Purge and Trap Concentrator	40MSV4	98197002
HP 6890 GC	40MSV5	US00025885
HP 5973 MSD	40MSV5	US82322154
Archon Autosampler	40MSV5	11894-396A
Tekmar 3000 Purge and Trap Concentrator	40MSV5	94067011
HP 5890 Series II GC	40MSV6	3336A59437
HP 5972 MSD	40MSV6	3341A01384
Archon Autosampler	40MSV6	11851-195A
Tekmar 3000 Purge and Trap Concentrator	40MSV6	95039012
HP 6890 GC	40MSV7	US00040707
HP 5973 MSD	40MSV7	US03950358
Archon Autosampler	40MSV7	11931-596A
Tekmar 3000 Purge and Trap Concentrator	40MSV7	93217001
Agilent Technologies 6850 Network GC System	40MSV8	CN1065-1003
Agilent Technologies 5975B MSD	40MSV8	US65115041
EST 8100 Autosampler	40MSV8	15048
Teledyne Tekmar 14-9800-100 Stratum Purge and Trap System	40MSV8	US07152010
HP 6890 GC	40MSV9	US00002310
HP 5973 MSD	40MSV9	US63810274
Archon Autosampler	40MSV9	11365-196A
Tekmar 3000 Purge and Trap Concentrator	40MSV9	98205001

Table 8.2 Supplies

Supplies	Manufacturer	Vendor	Catalog #
10ul Gastight 1701	Hamilton	Fisher Scientific	14-815-1
25ul Gastight 1702	Hamilton	Fisher Scientific	14-815-29
50ul Gastight 1705	Hamilton	Fisher Scientific	14-824-30
100ul Gastight 1710	Hamilton	Fisher Scientific	13-684-100
250ul Gastight 1725	Hamilton	Fisher Scientific	13-684-102
500ul Gastight 1750	Hamilton	Fisher Scientific	13-684-106
1ml Gastight 1001	Hamilton	Fisher Scientific	14-824-25
5ml Gastight 1005	Hamilton	Fisher Scientific	13-684-96
50ml Gastight 1050	Hamilton	Fisher Scientific	14-815-195
DB-624 Capillary column, 20mX0.18 mm i.d.X1.0 um	J&W Scientific	VWR Scientific	121-1324
K-Trap, Vocarb3000, Tekmar3000	Supelco	Supelco	24920-U
Fritless 5-ml Sparge Tube	Supelco	Supelco	22780
IceBlue Septa, 11mm	Restek	Restek	22392
Single Gooseneck Injection port liners (4mm)	Restek	Restek	20799
Gold-plated inlet seals	Restek	Restek	21306
Viton O-rings	Restek	Restek	20377
0.4mm Vespel/Graphite ferrules	Restek	Restek	20211
GCMS Filaments	Agilent Technologies	Agilent Technologies	05972-60053
Stir Bar	Fisher Brand	Fisher Brand	14-511-60A
40 ml VOA vials	QEC	QEC	3112-40ml
10 ml volumetric	Kimax Brand	Fisher Scientific	10-212AA
25 ml volumetric	Kimax Brand	Fisher Scientific	10-212BB
50 ml volumetric	Kimax Brand	Fisher Scientific	10-212A
100 ml volumetric	Kimax Brand	Fisher Scientific	10-212B
200 ml volumetric	Kimax Brand	Fisher Scientific	10-212C
500 ml volumetric	Kimax Brand	Fisher Scientific	10-218D
Pasteur Pipettes	Fisher Scientific	Fisher Scientific	13-678-20A
Pipette bulb	Fisher Scientific	Fisher Scientific	14-065B
0.1-2.5 ml Repipetter	Brinkmann	Fisher Scientific	13-688-130
1-5 ml Repipetter	Brinkmann	Fisher Scientific	13-688-131
2-10 ml Repipetter	Brinkmann	Fisher Scientific	13-688-133
5-25 ml Repipetter	Brinkmann	Fisher Scientific	13-688-134
1.8 ml amber vials & caps	Restek	Restek	24637
10 ml graduate cylinder	Kimex Brand	Fisher Scientific	08-554B "to deliver"
40 ml VOA vials HCl preserved	QEC	QEC	3112-40HCL
2 oz. jars with teflon lids	QEC	QEC	2114-0002
Spatulas	Fisher Scientific	Fisher Scientific	14-511-60A

9. Reagents and Standards

9.1. Reagents

Table 9.1 Reagents

Reagent	Conc.	Purity	Manufacturer	Vendor	Catalog #
Methanol	100%	Purge and Trap grade	Burdick & Jackson	VWR Scientific	232-1
Sodium Bisulfate	Granular	Certified grade	Fisher Scientific	Fisher Scientific	S-240-3
Helium gas		99.999%	Michigan Airgas	Michigan Airgas	
OFW		ASTM Type II	Barnstead-Nanopure	VWR Scientific	D8961
Ottawa Sand, 20-30 mesh		ASTM C190	Fisher Scientific	Fisher Scientific	S23-3

9.2. Analytical Standards

9.2.1. Definitions

Standards are required for mass spectrometer tuning, initial calibration, calibration verification standards, second source verification, internal standards, surrogates, and for preparing LCS, MS, and MSD samples. Table 9.2 describes the standards used. Table 9.3 lists the stock standards used. Table 9.4 lists the compounds in each stock standard.

Table 9.2 Standard Definitions

Standard	Description	Comments
Tune Standard	4-Bromofluorobenzene (BFB) solution used to verify ion response ratios prior to analysis	Must purge between 5 and 50ng
Initial Calibration Standards	Standards prepared at varying levels to determine response and retention characteristics of instrument	Method requires a minimum of 5 levels
Continuing Calibration Verification Standard	A calibration standard prepared at mid-level concentration for all target compounds. This standard is used to verify that the instrument response has not changed significantly since the initial calibration was performed.	
Second Source Verification Standard	A standard prepared from a source other than that used for the initial calibration. This mid-level standard verifies the accuracy of the calibration curve.	For volatiles analysis, this may be used as the LCS if analyzed once every 20 samples.
Internal Standard	A solution added all standards, samples, spikes, control samples, and method blanks prior to analysis. This standard is used to adjust response ratios to account for instrument drift.	Pentafluorobenzene 1,4-Difluorobenzene Chlorobenzene-d5 1,4-Dichlorobenzene-d4
Surrogate Standard	A solution added to all samples, spikes, control samples, and method blanks prior to analysis.	Dibromofluoromethane Toluene-d8 4-Bromofluorobenzene
Spiking Standard	This solution contains all target analytes and should not be prepared from the same standards as the calibration standards.	For volatiles analysis, this can be used as the second source verification standard.

9.2.2. Stock Standards

Table 9.3 Stock Standards

Standard	Conc.	Purity	Manufacturer	Vendor	Catalog #
4-BFB Tuning Standard	5000 ug/mL	99%	Restek	Restek	30003-520
502.2 Calibration Mix#1	2000 ug/mL	99%	Restek	Restek	30042
502.2 Calibration Mix#1 – ICV	2000 ug/mL	99%	Accustandard	Accustandard	M-502B-10X
502.2 Cal 2000 Megamix	2000 ug/mL	99%	Restek	Restek	30431
502.2 Cal 2000 Megamix – ICV	2000 ug/mL	99%	Accustandard	Accustandard	M-502A-R-10X
Vinyl Acetate	Neat	99+%	Chem Service	Chem Service	F718
Vinyl Acetate	Neat	99+%	Aldrich Chemical	Aldrich Chemical	V150-3
VOA Calibration Mix #1	5000 ug/mL	99%	Restek	Restek	30006
VOA Calibration Mix #1 – ICV	5000 ug/mL	99%	Accustandard	Accustandard	CLP-022K-25X
Pace GB Custom Mix	2000 ug/mL	99+%	Restek	Restek	56230
Pace GB Custom Mix – ICV	2000 ug/mL	99%	Accustandard	Accustandard	S-13659
Pace GB Custom Mix – Cyclohexanes	10000 ug/mL	99+%	Restek	Restek	58314
Pace GB Custom Mix – Cyclohexanes – ICV	10000 ug/mL	99%	Accustandard	Accustandard	S-7134-R1-5X
Pace GB Custom Mix – NELAP	Various	99+%	Restek	Restek	553772
Pace GB Custom Mix – NELAP – ICV	Various	99%	Accustandard	Accustandard	S-13661
Pace GB Custom Mix – Acrolein	20000 ug/mL	99+%	Restek	Restek	52995
Pace GB Custom Mix – Acrolein – ICV	20000 ug/mL	99%	Accustandard	Accustandard	QM-8015B/5031-03-2X
Pace GB Custom Mix – 2-Chloroethylvinyl Ether	2000 ug/mL	99+%	Restek	Restek	30265
Pace GB Custom Mix – 2-Chloroethylvinyl Ether – ICV	2000 ug/mL	99%	Accustandard	Accustandard	M-601C-10X
Pace GB Custom Revised Volatiles Standard Mix	Various	98+%	Restek	Restek	560395
Pace GB Custom Appendix 9 Standard Mix – ICV	Various	98.9%	Accustandard	Accustandard	S-13660-R1
8260 Internal Standard	2500 ug/mL	99%	Restek	Restek	30173
8260 Surrogate Standard	2500 ug/mL	99%	Restek	Restek	30174
Cal 2000 Mix A/B	2000 ug/mL	99%	Restek	Restek	30438
VOA Cal Mix # 5	2000 ug/mL	99%	Restek	Restek	30010
502.2 Mix #1	2000 ug/mL	99%	Restek	Restek	30042
Michigan GRO Mix	2000 ug/mL	99%	Restek	Restek	30468

9.2.3. Standard Mixes

Table 9.4 Standard Mixes

Vendor	Standard Name	Catalog#	Compound list	Concentration (ug.mL)
Restek	**502.2 Cal Mix 1**	**30042**	Bromomethane	2000
			Chloroethane	2000
			Chloromethane	2000
			Dichlorodifluoromethane	2000
			Trichlorofluoromethane	2000
			Vinyl Chloride	2000
Accustandard	**502.2 Cal Mix 1 - ICV**	**M-502B-10X**	Bromomethane	2000
			Chloroethane	2000
			Chloromethane	2000
			Dichlorodifluoromethane	2000
			Trichlorofluoromethane	2000
			Vinyl Chloride	2000
Restek	**502.2 MegaMix**	**30431**	1,1,1,2-Tetrachloroethane	2000
			1,1,1-Trichloroethane	2000
			1,1,2,2-Tetrachloroethane	2000
			1,1,2-Trichloroethane	2000
			1,1-Dichloroethane	2000
			1,1-Dichloropropene	2000
			1,1-Dichlroethene	2000
			1,2,3-Trichlorobenzne	2000
			1,2,3-Trichloropropane	2000
			1,2,3-Trimethylbenzene	2000
			1,2,4-Trimethylbenzene	2000
			1,2-Dibromo-3-chloropropane	2000
			1,2-Dibromoethane	2000
			1,2-Dichlorethane	2000
			1,2-Dichlorobenzene	2000
			1,2-Dichloropropane	2000
			1,3,5-Trimethylbenzene	2000
			1,3-Dichlorobenzene	2000
			1,3-Dichloropropane	2000
			1,4-Dichlorobenzene	2000
			2,2-Dichloropropane	2000
			2-Chlorotoluene	2000
			4-Chlorotoluene	2000
			4-Isopropyltoluene	2000
			Benzene	2000
			Bromobenzene	2000
			Bromochloromethane	2000

Vendor	Standard Name	Catalog#	Compound list	Concentration (ug.mL)
			Bromodichloromethane	2000
			Bromoform	2000
			Carbon Tetrachloride	2000
			Chlorobenzene	2000
			Chloroform	2000
			cis-1,2-Dichloroethene	2000
			cis-1,3-Dichloropropene	2000
			Dibromochloromethane	2000
			Dibromomethane	2000
			Ethylbenzene	2000
			Hexachloro-1,3-butadiene	2000
			Isopropylbenzene	2000
			Methylene Chloride	2000
			m-Xylene	2000
			Naphthalene	2000
			n-Butylbenzene	2000
			n-Propylbenzene	2000
			o-Xylene	2000
			p-Xylene	2000
			sec-Butylbenzene	2000
			Styrene	2000
			tert-Butylbenzene	2000
			Tetrachloroethene	2000
			Toluene	2000
			trans-1,2-Dichloroethene	2000
			trans-1,3-Dichloropropene	2000
			Trichloroethene	2000
Accustandard	**502.2 MegaMix - ICV**	**M-502A-R-10X**	1,1,1,2-Tetrachloroethane	2000
			1,1,1-Trichloroethane	2000
			1,1,2,2-Tetrachloroethane	2000
			1,1,2-Trichloroethane	2000
			1,1-Dichloroethane	2000
			1,1-Dichloropropene	2000
			1,1-Dichlroethene	2000
			1,2,3-Trichlorobenzne	2000
			1,2,3-Trichloropropane	2000
			1,2,3-Trimethylbenzene	2000
			1,2,4-Trimethylbenzene	2000
			1,2-Dibromo-3-chloropropa	2000
			1,2-Dibromoethane	2000
			1,2-Dichlorethane	2000
			1,2-Dichlorobenzene	2000
			1,2-Dichloropropane	2000
			1,3,5-Trimethylbenzene	2000

Vendor	Standard Name	Catalog#	Compound list	Concentration (ug.mL)
			1,3-Dichlorobenzene	2000
			1,3-Dichloropropane	2000
			1,4-Dichlorobenzene	2000
			2,2-Dichloropropane	2000
			2-Chlorotoluene	2000
			4-Chlorotoluene	2000
			4-Isopropyltoluene	2000
			Benzene	2000
			Bromobenzene	2000
			Bromochloromethane	2000
			Bromodichloromethane	2000
			Bromoform	2000
			Carbon Tetrachloride	2000
			Chlorobenzene	2000
			Chloroform	2000
			cis-1,2-Dichloroethene	2000
			cis-1,3-Dichloropropene	2000
			Dibromochloromethane	2000
			Dibromomethane	2000
			Ethylbenzene	2000
			Hexachloro-1,3-butadiene	2000
			Isopropylbenzene	2000
			Methylene Chloride	2000
			m-Xylene	2000
			Naphthalene	2000
			n-Butylbenzene	2000
			n-Propylbenzene	2000
			o-Xylene	2000
			p-Xylene	2000
			sec-Butylbenzene	2000
			Styrene	2000
			tert-Butylbenzene	2000
			Tetrachloroethene	2000
			Toluene	2000
			trans-1,2-Dichloroethene	2000
			trans-1,3-Dichloropropene	2000
			Trichloroethene	2000
Restek	**Vinyl Acetate**	**30216**	Vinyl Acetate	2000
Aldrich	**Vinyl Acetate - ICV**	**V150-3**	Vinyl Acetate	Neat
Restek	**VoaCalMix 1**	**30006**	2-Butanone	5000
			2-Hexanone	5000
			4-Methyl-2-pentanone	5000

Vendor	Standard Name	Catalog#	Compound list	Concentration (ug.mL)
			Acetone	5000
Accustandard	**VoaCalMix 1 - ICV**	**CLP-022K-25X**	2-Butanone	5000
			2-Hexanone	5000
			4-Methyl-2-pentanone	5000
			Acetone	5000
Restek	**Pace-GB Custom**	**56230**	1 1 2-TRICHLOROTRIFLUOROETHANE	2000
	Mix		1 2 3-TRIMETHYLBENZENE	2000
			2 3-DICHLOROPROPENE	2000
			2-METHYLNAPHTHALENE	2000
			ACRYLONITRILE	2000
			ALLYL CHLORIDE	2000
			CARBON DISULFIDE	2000
			CIS-1 4-DICHLORO-2-BUTENE	2000
			DICHLOROFLUOROMETHANE	2000
			DIETHYL ETHER	2000
			DIISOPROPYL ETHER	2000
			ETHYL METHACRYLATE	2000
			HEXACHLOROETHANE	2000
			IODOMETHANE	2000
			METHYL METHACRYLATE	2000
			METHYL T-BUTYL ETHER	2000
			N-HEXANE	2000
			TETRAHYDROFURAN	2000
			TRANS-1 4-DICHLORO-2-BUTENE	2000
Accustandard	**Pace-GB Custom**	**S-13659**	1 1 2-TRICHLOROTRIFLUOROETHANE	2000
	Mix - ICV		1 2 3-TRIMETHYLBENZENE	2000
			2 3-DICHLOROPROPENE	2000
			2-METHYLNAPHTHALENE	2000
			ACRYLONITRILE	2000
			ALLYL CHLORIDE	2000
			CARBON DISULFIDE	2000
			CIS-1 4-DICHLORO-2-BUTENE	2000
			DICHLOROFLUOROMETHANE	2000
			DIETHYL ETHER	2000
			DIISOPROPYL ETHER	2000
			ETHYL METHACRYLATE	2000
			HEXACHLOROETHANE	2000
			IODOMETHANE	2000

Vendor	Standard Name	Catalog#	Compound list	Concentration (ug.mL)
			METHYL METHACRYLATE	2000
			METHYL T-BUTYL ETHER	2000
			N-HEXANE	2000
			TETRAHYDROFURAN	2000
			TRANS-1 4-DICHLORO-2-BUTENE	2000
Restek	**Pace-GB Custom**	**58314**	CYCLOHEXANE	10000
	Mix - Cyclohexanes		METHYL ACETATE	10000
			METHYLCYCLOHEXANE	10000
Accustandard	**Pace-GB Custom**	**S-7134-R1-5X**	CYCLOHEXANE	10000
	Mix - Cyclohexanes - ICV		METHYL ACETATE	10000
			METHYLCYCLOHEXANE	10000
Restek	**Pace-GB Custom**	**553772**	1 4-DIOXANE	100000
	Mix - Nelap		1-PROPANOL	100000
			AMYL ACETATE	2000
			BUTYL ACETATE	2000
			CYCLOHEXANONE	20000
			ETHYL ACETATE	20000
			ISOAMYL ACETATE	2000
			ISOPROPANOL	20000
			N-BUTANOL	100000
			N-HEPTANE	2000
			N-PROPYL ACETATE	2000
			ISOPROPYL ACETATE	2000
Accustandard	**Pace-GB Custom**	**S-13661**	1 4-DIOXANE	100000
	Mix - Nelap - ICV		1-PROPANOL	100000
			AMYL ACETATE	2000
			BUTYL ACETATE	2000
			CYCLOHEXANONE	20000
			ETHYL ACETATE	20000
			ISOAMYL ACETATE	2000
			ISOPROPANOL	20000
			N-BUTANOL	100000
			N-HEPTANE	2000
			N-PROPYL ACETATE	2000
			ISOPROPYL ACETATE	2000

Vendor	Standard Name	Catalog#	Compound list	Concentration (ug.mL)
Restek	**Pace-GB Custom**	**52995**	ACROLEIN	20000
	Acrolein			
Accustandard	**Pace-GB Custom**	**QM-8015B/5031-03-2X**	ACROLEIN	20000
	Acrolein - ICV			
Restek	**Pace-GB Custom**	**30265**	2-CHLOROETHYLVINYL ETHER	2000
	2-chloroethylvinyl ether			
Accustandard	**Pace-GB Custom**	**M-601C-10X**	2-CHLOROETHYLVINYL ETHER	2000
	2-chloroethylvinyl ether - ICV			
Restek	**Pace-GB Custom**	**560395**	ACETONITRILE	5000
	Revised Volatiles		CHLOROPRENE	5000
	Standard Mix		ETHANOL	200000
			ETHYL TERT BUTYL ETHER	2000
			ISOBUTANOL	20000
			METHACRYLONITRILE	5000
			PROPIONITRILE	5000
			TERT AMYL METHYL ETHER	2000
			TERT BUTYL ALCOHOL	10000
Accustandard	**Pace-GB Custom**	**S-13660-R1**	ACETONITRILE	5000
	Appendix 9 Standard		CHLOROPRENE	5000
	Mix		ETHANOL	200000
			ETHYL TERT BUTYL ETHER	2000
			ISOBUTANOL	20000
			METHACRYLONITRILE	5000
			PROPIONITRILE	5000
			TERT AMYL METHYL ETHER	2000
			TERT BUTYL ALCOHOL	10000

9.2.4. Standard Storage Conditions

Table 9.5 – Analytical Standard Storage Conditions

Standard Type	Description	Expiration	Storage
Stock Solutions	Concentrated reference solution purchased directly from approved vendor	Manufacturer's recommended expiration date for unopened ampulated standards. Gas standards must be replaced 6 months after ampule is opened. All other stock standards must be replaced 6 months after ampule is opened or on expiration date, whichever is sooner.	Manufacturer's recommended storage conditions When standard is opened, record all information in the standard logbook.
Intermediate and Working Standard Solutions	Reference solutions prepared by dilutions of the stock solution	6 months from preparation or the expiration date listed for the stock source, whichever is sooner. 6 months for gas working standards. Working solutions must be checked frequently and replaced if degradation or evaporation is suspected.	Store in amber vials with Teflon lined screw caps Manufacturer's recommended storage conditions for stock source solution. If stock source conditions conflict, store standard at coldest condition of any source.

9.2.5. Standard Sources

Standards are prepared from commercially available multi-compound stock solutions and neat materials by multiple dilutions. The sources of the stock solutions and neat materials are listed in Table 9.3. The recipes for preparing dilutions and all working and intermediate standards, and concentrations for all compounds are presented in Tables 9.6 and 9.7. All intermediate standards are prepared using purge and trap grade methanol and stored frozen in glass vials with Teflon lined screw caps or Mininert valves or as recommended by the standard manufacturer.

9.2.6. Preparation Procedures

Table 9.6 Intermediate Standard Preparation

Standard	Acronym	Concentration	Direction found in Section:
Level 1 Calibration Standard	VSTD001	1.0 ug/L all compounds except as follows: 2.5 ug/L acetonitrile, chloroprene, propionitrile, methacrylonitrile; 5.0 ug/L tert butyl alcohol; 10 ug/l acrolein, cyclohexanone, ethyl acetate, isopropanol, isobutanol; 50 ug/L 1,4-dioxane, 1-propanol, n-butanol; 100 ug/L ethanol	Table 9.7
Level 2 Calibration Standard	VSTD005	5.0 ug/L all compounds except as follows: 12.5 ug/L acetonitrile, chloroprene, propionitrile, methacrylonitrile; 25 ug/L tert butyl alcohol; 50 ug/l acrolein, cyclohexanone, ethyl acetate, isopropanol, isobutanol; 250 ug/L 1,4-dioxane, 1-propanol, n-butanol; 200 ug/L ethanol.	Table 9.7
Level 3 Calibration Standard	VSTD020	20 ug/L all compounds except as follows: 50 ug/L acetonitrile, chloroprene, propionitrile, methacrylonitrile; 100 ug/L tert butyl alcohol; 200 ug/l acrolein, cyclohexanone, ethyl acetate, isopropanol, isobutanol; 1000 ug/L 1,4-dioxane, 1-propanol, n-butanol; 2000 ug/L ethanol.	Table 9.7
Level 4 Calibration Standard	VSTD050	50 ug/L all compounds except as follows: 125 ug/L acetonitrile, chloroprene, propionitrile, methacrylonitrile; 250 ug/L tert butyl alcohol; 500 ug/l acrolein, cyclohexanone, ethyl acetate, isopropanol, isobutanol; 2500 ug/L 1,4-dioxane, 1-propanol, n-butanol; 5000 ug/L ethanol	Table 9.7
Level 5 Calibration Standard	VSTD100	100 ug/L all compounds except as follows: 250 ug/L acetonitrile, chloroprene, propionitrile, methacrylonitrile; 500 ug/L tert butyl alcohol; 1000 ug/l acrolein, cyclohexanone, ethyl acetate, isopropanol, isobutanol; 5000 ug/L 1,4-dioxane, 1-propanol, n-butanol; 10000 ug/L ethanol.	Table 9.7
Level 6 Calibration Standard	VSTD200	200 ug/L all compounds except as follows: 500 ug/L acetonitrile, chloroprene, propionitrile, methacrylonitrile; 1000 ug/L tert butyl alcohol; 2000 ug/l acrolein, cyclohexanone, ethyl acetate, isopropanol, isobutanol; 10000 ug/L 1,4-dioxane, 1-propanol, n-butanol; 20000 ug/L ethanol.	Table 9.7

Standard	Acronym	Concentration	Direction found in Section:
Level 7 Calibration Standard	VSTD0005	0.50 ug/L all compounds except as follows: 1.25 ug/L acetonitrile, chloroprene, propionitrile, methacrylonitrile; 2.5 ug/L tert butyl alcohol; 5.0 ug/l acrolein, cyclohexanone, ethyl acetate, isopropanol, isobutanol; 25 ug/L 1,4-dioxane, 1-propanol, n-butanol; 50 ug/L ethanol	Table 9.7
Level 8 Calibration Standard	VSTD0004	0.40 ug/L all compounds except as follows: 1.0 ug/L acetonitrile, chloroprene, propionitrile, methacrylonitrile; 2.0 ug/L tert butyl alcohol; 4.0 ug/l acrolein, cyclohexanone, ethyl acetate, isopropanol, isobutanol; 20 ug/L 1,4-dioxane, 1-propanol, n-butanol; 40 ug/L ethanol	Table 9.7
Level 9 Calibration Standard (Water Curve only)	VSTD300	300 ug/L all compounds except as follows: 750 ug/L acetonitrile, chloroprene, propionitrile, methacrylonitrile; 1500 ug/L tert butyl alcohol; 3000 ug/l acrolein, cyclohexanone, ethyl acetate, isopropanol, isobutanol; 15000 ug/L 1,4-dioxane, 1-propanol, n-butanol; 30000 ug/L ethanol.	Table 9.7
Independent Calibration Verification Standard	ICV050	50 ug/L all compounds except as follows: 125 ug/L acetonitrile, chloroprene, propionitrile, methacrylonitrile; 250 ug/L tert butyl alcohol; 500 ug/l acrolein, cyclohexanone, ethyl acetate, isopropanol, isobutanol; 2500 ug/L 1,4-dioxane, 1-propanol, n-butanol; 5000 ug/L ethanol.	Table 9.7
Calibration Verification Standard	VSTD050	50 ug/L all compounds except as follows: 125 ug/L acetonitrile, chloroprene, propionitrile, methacrylonitrile; 250 ug/l tert butyl alcohol; 500 ug/l acrolein, cyclohexanone, ethyl acetate, isopropanol, isobutanol; 2500 ug/L 1,4-dioxane, 1-propanol, n-butanol; 5000 ug/L ethanol	Table 9.7
Surrogate Standard	SS	50 ug/L	Table 9.7
Internal Standard	IS	50 ug/L	Table 9.7
Method Blank	MB	< Reporting Limit	Table 9.7
BFB	Vtunxxx	50 ng injection	Table 9.7
Matrix Spike/Blank Spike Stock Solution - TCL 3.4 List for Water and Low Level Soil Samples	MS/BS TCL 3.4 List Stock Solution for Water and Low Level Soil Samples	100 ug/mL for all comounds	Table 9.7

Standard	Acronym	Concentration	Direction found in Section:
Matrix Spike/Blank Spike Stock Solution - TCL 3.4 List for Methanol Preserved Soil Samples	MS/BS TCL 3.4 List Stock Solution for Methanol Preserved Soil Samples	500 ug/mL for all comounds	Table 9.7
Matrix Spike/Blank Spike Stock Solution - Full List for Water and Low Level Soil Samples	MS/BS Stock Solution - Full List for Water and Low Level Soil Samples	100 ug/mL all compounds except as follows: 1000 ug/mL Acrolein	Table 9.7
Matrix Spike/Blank Spike Stock Solution - Full List for Methanol Preserved Soil Samples	MS/BS Stock Solution – Full List for Methanol Preserved Soil Samples	500 ug/mL all compounds except as follows: 5000 ug/mL Acrolein	Table 97
MS/MSD – BS/BSD Spike for Water Samples	MS/MSD BS/BSD	50 ug/L for most compounds, Various for others.	Table 9.7
MS/MSD – BS/BSD Spike for Low Level Soil Samples	MS/MSD BS/BSD	50 ug/kg for most compounds, Various for others.	Table 9.7
MS/MSD – BS/BSD Spike for Methanol Preserved Soil Samples	MS/MSD BS/BSD	2500 ug/kg for most compounds, Various for others.	Table 9.7
Extraction Blank	EBLK	< Reporting Limit	

Table 9.7 Preparation of Standards

Standard	Acronym	Concentration of Intermediate	Reagents Used	Final Volume
4-Bromofluorobenzene	BFB	50 ug/mL	100µL of 5000 ug/mL BFB into methanol	10 mL
Internal Standard	IS	250 ug/mL	5000 µL of 2500 ug/mL IS into methanol	50 mL
Surrogate Standard	SS	250 ug/mL	5000 µL of 2500 ug/mL SS into methanol	50 mL
Internal/Surrogate Std.	IS/SS	250 ug/mL	5000 µL of 2500 ug/mL IS/SS into MeOH	50 mL
100 ug/mL Calibration Std. 250 ug/mL acetonitrile, chloroprene, propionitrile, methacrylonitrile; 500 ug/mL tert butyl alcohol; 1000 ug/mL arrolein, cyclohexanone, ethyl acetate, isopropanol, isobutanol; 5000 ug/mL 1,4-dioxane, 1-propanol, n-butanol; 10000 ug/mL ethanol.	CAL Stock Standard	100 ug/mL all compounds except as follows: 250 ug/mL acetonitrile, chloroprene, propionitrile, methacrylonitrile; 500 ug/mL tert butyl alcohol; 1000 ug/mL acrolein, cyclohexanone, ethyl acetate, isopropanol, isobutanol; 5000 ug/mL 1,4-dioxane, 1-propanol, n-butanol; 10000	1250 µL of 2000 ug/mL 502.2 Calibration Mix #1 1250 µL of 2000 ug/mL 502.2 Cal 2000 Megamix 1250 µL of 2000 ug/mL Vinyl Acetate 500 µL of 5000 ug/mL VOA Calibration Mix #1 1250 µL of 2000 ug/mL Pace GB Custom Mix 250 µL of 10000 ug/mL Pace GB Custom Mix - Cyclohexanes 1250 µL of 20000 ug/mL Pace GB	25 mL

		ug/mL ethanol	Custom Mix - Acrolein 1250 µL of 2000 ug/mL Pace GB Custom Mix - 2-Chloroethylvinyl ether 1250 µL of Various Concentration Pace GB Custom Mix - NELAP 1250 µL of Pace GB Custom Revised Volatiles Standard Mix. Diluted into methanol	
100 ug/mL Calibration Std. 250 ug/mL acetonitrile, chloroprene, propionitrile, methacrylonitrile; 500 ug/mL tert butyl alcohol; 1000 ug/mL acrolein, cyclohexanone, ethyl acetate, isopropanol, isobutanol; 5000 ug/mL 1,4-dioxane, 1-propanol, n-butanol; 10000 ug/mL ethanol.	ICV Stock Standard	100 ug/mL all compounds except as follows: 250 ug/mL acetonitrile, chloroprene, propionitrile, methacrylonitrile; 500 ug/mL tert butyl alcohol; 1000 ug/mL acrolein, cyclohexanone, ethyl acetate, isopropanol, isobutanol; 5000 ug/mL 1,4-dioxane, 1-propanol, n-butanol; 10000 ug/mL ethanol.	1250 µL of 2000 ug/mL 502.2 Calibration Mix #1 - ICV 1250 µL of 2000 ug/mL 502.2 Cal 2000 Megamix - ICV 500 µL of 5000 ug/mL VOA Calibration Mix #1 - ICV 1250 µL of 2000 ug/mL Pace GB Custom Mix - ICV 250 µL of 10000 ug/mL Pace GB Custom Mix – Cyclohexanes - ICV 1250 µL of 20000 ug/mL Pace GB Custom Mix – Acrolein - ICV 1250 µL of 2000 ug/mL Pace GB Custom Mix - 2-Chloroethylvinyl ether - ICV 263 µL of 9520 ug/mL Vinyl Acetate 1250 µL of Various Concentration Pace GB Custom Mix – NELAP - ICV 1250 µL of Pace GB Custom Appendix 9 Standard Mix – ICV Diluted into methanol	25 mL
Vinyl Acetate	VA	9520 ug/mL	0.238 mg of neat Vinyl Acetate Diluted into methanol	25 mL
Level 1 Calibration Standard	VSTD001	1.0 ug/L all compounds except as follows: 2.5 ug/L acetonitrile, chloroprene, propionitrile, methacrylonitrile; 5.0 ug/L tert butyl alcohol; 10 ug/l acrolein, cyclohexanone, ethyl acetate, isopropanol, isobutanol; 50 ug/L 1,4-dioxane, 1-propanol, n-butanol; 100 ug/L ethanol.	Dilute 0.5 uL 100 ug/mL all compounds except as follows: 250 ug/mL acetonitrile, chloroprene, propionitrile, methacrylonitrile; 500 ug/mL tert butyl alcohol; 1000 ug/mL acrolein, cyclohexanone, ethyl acetate, isopropanol, isobutanol; 5000 ug/mL 1,4-dioxane, 1-propanol, n-butanol; 10000 ug/mL ethanol CAL Stock Standard into 50 mL reagent water. If for a methanol curve, use 49 mL reagent water and 1 mL methanol.	50 mL
Level 2 Calibration Standard	VSTD005	5.0 ug/L all compounds except as follows: 12.5 ug/L acetonitrile, chloroprene, propionitrile, methacrylonitrile; 25 ug/L tert butyl alcohol; 50 ug/l acrolein, cyclohexanone, ethyl acetate, isopropanol, isobutanol; 250 ug/L 1,4-dioxane, 1-	Dilute 2.5 uL 100 ug/mL all compounds except as follows: 250 ug/mL acetonitrile, chloroprene, propionitrile, methacrylonitrile; 500 ug/mL tert butyl alcohol; 1000 ug/mL acrolein, cyclohexanone, ethyl acetate, isopropanol, isobutanol; 5000 ug/mL 1,4-dioxane, 1-propanol, n-butanol; 10000 ug/mL ethanol CAL Stock Standard into 50 mL reagent	50 mL

		propanol, n-butanol; 200 ug/L ethanol.	water. If for a methanol curve, use 49 mL reagent water and 1 mL methanol.	
Level 3 Calibration Standard	VSTD020	20 ug/L all compounds except as follows: 50 ug/L acetonitrile, chloroprene, propionitrile, methacrylonitrile; 100 ug/L tert butyl alcohol; 200 ug/l acrolein, cyclohexanone, ethyl acetate, isopropanol, isobutanol; 1000 ug/L 1,4-dioxane, 1-propanol, n-butanol; 2000 ug/L ethanol	Dilute 10 uL 100 ug/mL all compounds except as follows: 250 ug/mL acetonitrile, chloroprene, propionitrile, methacrylonitrile; 500 ug/mL tert butyl alcohol; 1000 ug/mL axcrolein, cyclohexanone, ethyl acetate, isopropanol, isobutanol; 5000 ug/mL 1,4-dioxane, 1-propanol, n-butanol; 10000 ug/mL ethanol CAL Stock Standard into 50 mL reagent water. If for a methanol curve, use 49 mL reagent water and 1 mL methanol.	50 mL
Level 4 Calibration Standard	VSTD050	50 ug/L all compounds except as follows: 125 ug/L acetonitrile, chloroprene, propionitrile, methacrylonitrile; 250 ug/L tert butyl alcohol; 500 ug/l acrolein, cyclohexanone, ethyl acetate, isopropanol, isobutanol; 2500 ug/L 1,4-dioxane, 1-propanol, n-butanol; 5000 ug/L ethanol	Dilute 25 uL 100 ug/mL all compounds except as follows: 250 ug/mL acetonitrile, chloroprene, propionitrile, methacrylonitrile; 500 ug/mL tert butyl alcohol; 1000 ug/mL acrolein, cyclohexanone, ethyl acetate, isopropanol, isobutanol; 5000 ug/mL 1,4-dioxane, 1-propanol, n-butanol; 10000 ug/mL ethanol CAL Stock Standard into 50 mL reagent water. If for a methanol curve, use 49 mL reagent water and 1 mL methanol.	50 mL
Level 5 Calibration Standard	VSTD100	100 ug/L all compounds except as follows: 250 ug/L acetonitrile, chloroprene, propionitrile, methacrylonitrile; 500 ug/L tert butyl alcohol; 1000 ug/l acrolein, cyclohexanone, ethyl acetate, isopropanol, isobutanol; 5000 ug/L 1,4-dioxane, 1-propanol, n-butanol; 10000 ug/L ethanol	Dilute 50 uL 100 ug/mL all compounds except as follows: 250 ug/mL acetonitrile, chloroprene, propionitrile, methacrylonitrile; 500 ug/mL tert butyl alcohol; 1000 ug/mL acrolein, cyclohexanone, ethyl acetate, isopropanol, isobutanol; 5000 ug/mL 1,4-dioxane, 1-propanol, n-butanol; 10000 ug/mL ethanol CAL Stock Standard into 50 mL reagent water. If for a methanol curve, use 49 mL reagent water and 1 mL methanol.	50 mL
Level 6 Calibration Standard	VSTD200	200 ug/L all compounds except as follows: 500 ug/L acetonitrile, chloroprene, propionitrile, methacrylonitrile; 1000 ug/L tert butyl alcohol; 2000 ug/l acrolein, cyclohexanone, ethyl acetate, isopropanol, isobutanol; 10000 ug/L 1,4-dioxane, 1-propanol, n-butanol; 20000 ug/L ethanol	Dilute 100 uL 100 ug/mL all compounds except as follows: 250 ug/mL acetonitrile, chloroprene, propionitrile, methacrylonitrile; 500 ug/mL tert butyl alcohol; 1000 ug/mL acrolein, cyclohexanone, ethyl acetate, isopropanol, isobutanol; 5000 ug/mL 1,4-dioxane, 1-propanol, n-butanol; 10000 ug/mL ethanol CAL Stock Standard into 50 mL reagent water. If for a methanol curve, use 49 mL reagent water and 1 mL methanol.	50 mL
Level 7 Calibration Standard	VSTD0005	0.50 ug/L all compounds except as follows: 1.25 ug/L	Dilute 0.25 uL 100 ug/mL all compounds except as follows: 250	50 mL

		acetonitrile, chloroprene, propionitrile, methacrylonitrile; 2.5 ug/L tert butyl alcohol; 5.0 ug/l acrolein, cyclohexanone, ethyl acetate, isopropanol, isobutanol; 25 ug/L 1,4-dioxane, 1-propanol, n-butanol; 50 ug/L ethanol	ug/mL acetonitrile, chloroprene, propionitrile, methacrylonitrile; 500 ug/mL tert butyl alcohol; 1000 ug/mL acrolein, cyclohexanone, ethyl acetate, isopropanol, isobutanol; 5000 ug/mL 1,4-dioxane, 1-propanol, n-butanol; 10000 ug/mL ethanol CAL Stock Standard into 50 mL reagent water. If for a methanol curve, use 49 mL reagent water and 1 mL methanol.	
Level 8 Calibration Standard	VSTD0004	0.40 ug/L all compounds except as follows: 1.0 ug/L acetonitrile, chloroprene, propionitrile, methacrylonitrile; 2.0 ug/L tert butyl alcohol; 4.0 ug/l acrolein, cyclohexanone, ethyl acetate, isopropanol, isobutanol; 20 ug/L 1,4-dioxane, 1-propanol, n-butanol; 40 ug/L ethanol	Dilute 0.20 uL 100 ug/mL all compounds except as follows: : 250 ug/mL acetonitrile, chloroprene, propionitrile, methacrylonitrile; 500 ug/mL tert butyl alcohol; 1000 ug/mL acrolein, cyclohexanone, ethyl acetate, isopropanol, isobutanol; 5000 ug/mL 1,4-dioxane, 1-propanol, n-butanol; 10000 ug/mL ethanol CAL Stock Standard into 50 mL reagent water. If for a methanol curve, use 49 mL reagent water and 1 mL methanol.	50 mL
Level 9 Calibration Standard (Water Curve only)	VSTD300	300 ug/L all compounds except as follows: 750 ug/L acetonitrile, chloroprene, propionitrile, methacrylonitrile; 1500 ug/L tert butyl alcohol; 3000 ug/l acrolein, cyclohexanone, ethyl acetate, isopropanol, isobutanol; 15000 ug/L 1,4-dioxane, 1-propanol, n-butanol; 30000 ug/L ethanol	Dilute 150 uL 100 ug/mL all compounds except as follows: 250 ug/mL acetonitrile, chloroprene, propionitrile, methacrylonitrile; 500 ug/mL tert butyl alcohol; 1000 ug/mL acrolein, cyclohexanone, ethyl acetate, isopropanol, isobutanol; 5000 ug/mL 1,4-dioxane, 1-propanol, n-butanol; 10000 ug/mL ethanol CAL Stock Standard into 50 mL reagent water.	50 mL
Independent Calibration Verification Standard	ICV050	50 ug/L all compounds except as follows: 125 ug/L acetonitrile, chloroprene, propionitrile, methacrylonitrile; 250 ug/L tert butyl alcohol; 500 ug/l acrolein, cyclohexanone, ethyl acetate, isopropanol, isobutanol; 2500 ug/L 1,4-dioxane, 1-propanol, n-butanol; 5000 ug/L ethanol.	Dilute 25 uL 100 ug/mL all compounds except as follows: 250 ug/mL acetonitrile, chloroprene, propionitrile, methacrylonitrile; 500 ug/mL tert butyl alcohol; 1000 ug/mL acrolein, cyclohexanone, ethyl acetate, isopropanol, isobutanol; 5000 ug/mL 1,4-dioxane, 1-propanol, n-butanol; 10000 ug/mL ethanol ICV Stock Standard into 50 mL reagent water. If for a methanol curve, use 49 mL reagent water and 1 mL methanol.	50 mL
Calibration Verification Standard	VSTD050	50 ug/L all compounds except as follows: 125 ug/L acetonitrile, chloroprene, propionitrile, methacrylonitrile; 250 ug/L tert butyl alcohol; 500 ug/l acrolein,	Dilute 25 uL 100 ug/mL all compounds except as follows: 250 ug/mL acetonitrile, chloroprene, propionitrile, methacrylonitrile; 500 ug/mL tert butyl alcohol; 1000 ug/mL acrolein, cyclohexanone, ethyl acetate, isopropanol, isobutanol;	50 mL

		cyclohexanone, ethyl acetate, isopropanol, isobutanol; 2500 ug/L 1,4-dioxane, 1-propanol, n-butanol; 5000 ug/L ethanol.	5000 ug/mL 1,4-dioxane, 1-propanol, n-butanol; 10000 ug/mL ethanol CAL Stock Standard into 50 mL reagent water. If for a methanol curve, use 49 mL reagent water and 1 mL methanol.	
Matrix Spike/Blank Spike Stock Solution - TCL 3.4 List for Water and Low Level Soil Samples	MS/BS TCL 3.4 List Stock Solution for Water and Low Level Soil Samples	100 ug/mL for all comounds	1250 µL of 2000 ug/mL Cal 2000 Mix A/B 1250 µL of 2000 ug/mL VOA Cal Mix #5 1250 µL of 2000 ug/mL 502.2 Cal. Mix #1 Dilute into methanol.	25 mL
Matrix Spike/Blank Spike Stock Solution - TCL 3.4 List for Methanol Preserved Soil Samples	MS/BS TCL 3.4 List Stock Solution for Methanol Preserved Soil Samples	500 ug/mL for all comounds	6250 µL of 2000 ug/mL Cal 2000 Mix A/B 6250 µL of 2000 ug/mL VOA Cal Mix #5 6250 µL of 2000 ug/mL 502.2 Cal. Mix #1 Dilute into methanol.	25 mL
Matrix Spike/Blank Spike Stock Solution - Full List for Water and Low Level Soil Samples	MS/BS Stock Solution - Full List for Water and Low Level Soil Samples	100 ug/mL all compounds except as follows: 250 ug/mL acetonitrile, chloroprene, propionitrile, methacrylonitrile; 500 ug/mL tert butyl alcohol; 1000 ug/mL acrolein, cyclohexanone, ethyl acetate, isopropanol, isobutanol; 5000 ug/mL 1,4-dioxane, 1-propanol, n-butanol; 10000 ug/mL ethanol.	1250 µL of 2000 ug/mL 502.2 Calibration Mix #1 - ICV 1250 µL of 2000 ug/mL 502.2 Cal 2000 Megamix - ICV 500 µL of 5000 ug/mL VOA Calibration Mix #1 - ICV 1250 µL of 2000 ug/mL Pace GB Custom Mix - ICV 250 µL of 10000 ug/mL Pace GB Custom Mix – Cyclohexanes - ICV 1250 µL of 20000 ug/mL Pace GB Custom Mix – Acrolein - ICV 1250 µL of 2000 ug/mL Pace GB Custom Mix - 2-Chloroethylvinyl ether - ICV 263 µL of 9520 ug/mL Vinyl Acetate 1250 µL of Various Concentration Pace GB Custom Mix – NELAP - ICV 1250 µL of Pace GB Custom Appendix 9 Standard Mix – ICV Diluted into methanol	25 mL
Matrix Spike/Blank Spike Stock Solution - Full List for Methanol Preserved Soil Samples	MS/BS Stock Solution – Full List for Methanol Preserved Soil Samples	500 ug/mL all compounds except as follows: 1250 ug/mL acetonitrile, chloroprene, propionitrile, methacrylonitrile; 2500 ug/mL tert butyl alcohol; 5000 ug/mL acrolein, cyclohexanone, ethyl acetate, isopropanol, isobutanol; 25000 ug/mL 1,4-dioxane,	6250 µL of 2000 ug/mL 502.2 Calibration Mix #1 - ICV 6250 µL of 2000 ug/mL 502.2 Cal 2000 Megamix - ICV 2500 µL of 5000 ug/mL VOA Calibration Mix #1 - ICV 6250 µL of 2000 ug/mL Pace GB Custom Mix - ICV 1250 µL of 10000 ug/mL Pace GB Custom Mix – Cyclohexanes - ICV 6250 µL of 20000 ug/mL Pace GB Custom Mix – Acrolein - ICV	25 mL

		1-propanol, n-butanol; 50000 ug/mL ethanol.	6250 µL of 2000 ug/mL Pace GB Custom Mix - 2-Chloroethylvinyl ether - ICV 1315 µL of 9520 ug/mL Vinyl Acetate 6250 µL of Various Concentration Pace GB Custom Mix – NELAP - ICV 6250 µL of Pace GB Custom Appendix 9 Standard Mix – ICV Diluted into methanol	
100 ug/mL Matrix Spike/Blank Spike Solution for Michigan List	MS/BS Stock Solution for Michigan List	100 ug/mL for all compounds	1250 µL of 2000 ug/mL Michigan GRO Mix Dilute into methanol.	25 mL
MS/MSD – BS/BSD Spike for Water Samples	MS/MSD BS/BSD	50 ug/L for most compounds, Various for others.	Add 21 µL of the appropriate Matrix Spike/Blank Spike Solution to 42 mL of sample for MS/MSD, or 42 mL of reagent water for BS/BSD	42 mL
MS/MSD – BS/BSD Spike for Low Level Soil Samples	MS/MSD BS/BSD	50 ug/kg for most compounds, Various for others.	Add 2.5 µL of the appropriate Matrix Spike/Blank Spike Solution to 5.0 g of sample containing 5 mL of reagent water for MS/MSD, or 5.0 g of Ottawa sand containing 5 mL of reagent water for BS/BSD	5 mL
MS/MSD – BS/BSD Spike for Methanol Preserved Soil Samples	MS/MSD BS/BSD	2500 ug/kg for most compounds, Various for others.	Add 50 µL of the appropriate Matrix Spike/Blank Spike Solution to 10 g of sample containing 10 mL of methanol for MS/MSD, amount of Spike Solution is adjusted according to the initial methanol volume; or 10 g of Ottawa sand containing 10 mL of methanol for BS/BSD	10 mL

10. Calibration

10.1. Tune Verification

The mass spectrometer tune status must be verified prior to initial calibration and at the beginning of each analytical sequence. If the current tune status does not meet the ion ratio criteria in the method (see section 11.2), follow the equipment manufacturers' instructions for re-tuning the mass spectrometer. The tune status must be verified after the tuning procedures.

Refer to section **11.2 Procedures** for details on the analysis and evaluation of this standard.

10.2. Initial Calibration (ICAL)

10.2.1. Analysis of Standards

An initial calibration curve using a minimum of five points is analyzed prior to analyzing client samples. The lowest concentration must be at or below the equivalence of the standard reporting limit. The lowest calibration point reflects the practical quantitation limit for that compound, a level below which all reported results must be qualified as estimated values. Refer to table 10.1 for compound concentrations.

An analyte must be present and calibration curve in control in order to be reported on the target analyte list. Analytes identified by mass spectral match but not present and in control in the calibration table

may be reported as Tentatively Identified Compounds (TICs). Guidelines for identification are listed in Section 11.6.3. Results for these TICs should be reported only on a present/absent basis. However, quantitative results may be reported provided they are qualified as estimated values.

Table 10.1 – Calibration standard compound concentrations

Analyte	PQL water (ug/L)	PQL soil (ug/kg)	PQL 5035 soil (ug/Kg)	Std 1 Ug/L	Std 2 ug/L	Std 3 ug/L	Std 4 ug/L	Std 5 ug/L	Std 6 ug/L	Std 7 ug/L	Std 8 Ug/L	Std 9 ug/L
1,1-Dichloroethane	1	50	5	1	5	20	50	100	200			300
1,1-Dichloroethene	1	50	5	1	5	20	50	100	200			300
1,1-Dichloropropene	1	50	5	1	5	20	50	100	200			300
1,1,1-Trichloroethane	1	50	5	1	5	20	50	100	200			300
1,1,2-Trichloroethane	1	50	5	1	5	20	50	100	200			300
1,1,1,2-Tetrachloroethane	1	50	5	1	5	20	50	100	200			300
1,1,2,2-Tetrachloroethane	1	50	5	1	5	20	50	100	200			300
1,2,4-Trichlorobenzene	1	50	5	1	5	20	50	100	200			300
1,2-Dichlorobenzene	1	50	5	1	5	20	50	100	200			300
1,2-Dibromo-3-chloropropane	5	250	5		5	20	50	100	200			300
1,2-Dichloroethane	1	25	5	1	5	20	50	100	200	0.50	0.40	300
1,2-Dibromoethane	1	50	5	1	5	20	50	100	200	0.50	0.40	300
1,2-Dichloropropane	1	50	5	1	5	20	50	100	200			300
1,2-Dichloroethene (Total)	2	100	10	2	10	40	100	200	400			600
1,2,3-Trimethylbenzene	1	50	5	1	5	20	50	100	200			300
1,2,4-Trimethylbenzene	1	50	5	1	5	20	50	100	200			300
1,2,3-Trichlorobenzene	1	50	5	1	5	20	50	100	200			300
1,2,3-Trichloropropane	1	50	5	1	5	20	50	100	200			300
1,3-Dichlorobenzene	1	50	5	1	5	20	50	100	200			300
1,3-Dichloropropane	1	50	5	1	5	20	50	100	200			300
1,3,5-Trimethylbenzene	1	50	5	1	5	20	50	100	200			300
1,4-Dichlorobenzene	1	50	5	1	5	20	50	100	200			300
1,4-Dioxane (p-Dioxane)	250	12500	250		250	1000	2500	5000	10000			15000
2,2-Dichloropropane	1	50	5	1	5	20	50	100	200			300
2,3-Dichloropropene	1	50	5	1	5	20	50	100	200			300
2-Butanone (MEK)	5	250	5		5	20	50	100	200			300
2-Chlorotoluene	1	50	5	1	5	20	50	100	200			300
2-Chloroethylvinyl ether	1	50	5	1	5	20	50	100	200			300
2-Hexanone	5	250	5		5	20	50	100	200			300
2-Methylnaphthalene	5	250	5		5	20	50	100	200			300
2-Propanol	250	12500	50	10	50	200	500	1000	2000			3000
Allyl chloride	5	50	5		5	20	50	100	200			300
4-Chlorotoluene	1	50	5	1	5	20	50	100	200			300
TOTAL BTEX	1	300	30	1	5	20	50	100	200			300
Carbon disulfide	1	50	5	1	5	20	50	100	200			300
Ethanol	100	5000	500	100	500	2000	5000	10000	20000			30000
Acetone	5	250	5		5	20	50	100	200			300
Acrolein	10	2500	50	10	50	200	500	1000	2000			3000
Acetonitrile	20	1000	20	2.5	12.5	50	125	250	500			750
Acrylonitrile	5	250	5		5	20	50	100	200			3200

Bromochloromethane	1	50	5	1	5	20	50	100	200			300
Benzene	1	25	5	1	5	20	50	100	200	0.50	0.40	300
Bromobenzene	1	50	5	1	5	20	50	100	200			300
Bromodichloromethane	1	50	5	1	5	20	50	100	200			300
Bromomethane	1	50	5	1	5	20	50	100	200			300
Bromoform	1	50	5	1	5	20	50	100	200			300
cis-1,2-Dichloroethene	1	50	5	1	5	20	50	100	200			300
cis-1,3-Dichloropropene	1	50	5	1	5	20	50	100	200			300
cis-1,4-Dichloro-2-butene	5	250	5		5	20	50	100	200			300
Carbon tetrachloride	1	50	5	1	5	20	50	100	200			300
Cyclohexane	5	250	5		5	20	50	100	200			300
Chlorobenzene	1	50	5	1	5	20	50	100	200			300
Chloroprene	20	1000	20	2.5	12.5	50	125	250	500			750
Chloroethane	1	50	5	1	5	20	50	100	200			300
Chloroform	5	250	5		5	20	50	100	200			300
Chloromethane	1	50	5	1	5	20	50	100	200			300
Cyclohexanone	50	12500	50		50	200	500	1000	2000			3000
Dibromochloromethane	1	50	5	1	5	20	50	100	200			300
Dichlorofluoromethane	1	50	5	1	5	20	50	100	200			300
Diethyl ether (Ethyl ether)	1	50	5	1	5	20	50	100	200			300
Dichlorodifluoromethane	1	50	5	1	5	20	50	100	200			300
Diisopropyl ether	1	50	5	1	5	20	50	100	200			300
Dibromomethane	1	50	5	1	5	20	50	100	200			300
Ethyl acetate	50	2500	50		50	200	500	1000	2000			3000
Ethylbenzene	1	25	5	1	5	20	50	100	200	0.50	0.40	300
Ethyl methacrylate	5	250	5		5	20	50	100	200			300
Ethyl-tert-butyl ether	5	250	5		5	20	50	100	200			300
Hexachloro-1,3-butadiene	1	50	5	1	5	20	50	100	200			300
Hexachloroethane	5	50	5		5	20	50	100	200			300
Iodomethane	5	250	5		5	20	50	100	200			300
Isopropylbenzene (Cumene)	1	50	5	1	5	20	50	100	200			300
Isoamyl acetate	5	250	5		5	20	50	100	200			300
Isopropyl acetate	5	250	5		5	20	50	100	200			300
Isobutanol	50	2500	50		50	200	500	1000	2000			3000
Methyl acetate	5	250	5		5	20	50	100	200			300
Methylene Chloride	1	50	5	1	5	20	50	100	200			300
Methyl methacrylate	5	250	5		5	20	50	100	200			300
Methylcyclohexane	5	250	5		5	20	50	100	200			300
Methyl-tert-butyl ether	1	50	5	1	5	20	50	100	200			300
Methacrylonitrile	20	1000	20	2.5	12.5	50	125	250	500			750
4-Methyl-2-pentanone	5	50	5		5	20	50	100	200			300
M&p-Xylene	2	50	10	2	10	40	100	200	400	1.0	0.80	600
n-Amyl acetate	5	250	5		5	20	50	100	200	0.50	0.40	300
Naphthalene	5	50	5		5	20	50	100	200			300
n-Butyl acetate	5	50	5		5	20	50	100	200			300
n-Butanol	250	12500	250	50	250	1000	2500	5000	10000			15000
n-Butylbenzene	1	50	5	1	5	20	50	100	200			300
n-Heptane	5	250	5		5	20	50	100	200			300

n-Hexane	5	250	5		5	20	50	100	200			300
n-Propylbenzene	1	50	5	1	5	20	50	100	200			300
n-Propanol	250	2500	250	50	250	1000	2500	5000	10000			15000
o-Xylene	1	25	5	1	5	20	50	100	200	0.50	0.40	300
p-Isopropyltoluene	1	50	5	1	5	20	50	100	200			300
Propionitrile	20	1000	20		12.5	50	125	250	500			750
Propyl acetate	5	250	5		5	20	50	100	200			300
sec-Butlybenzene	1	50	5	1	5	20	50	100	200			300
Styrene	1	50	5	1	5	20	50	100	200			300
trans-1,2-Dichloroethane	1	50	5	1	5	20	50	100	200			300
trans-1,3-Dichloropropene	1	50	5	1	5	20	50	100	200			300
trans-1,4-Dichloro-2-butene	5	250	5		5	20	50	100	200			300
tert-Amyl-methyl ether	1	250	5	1	5	20	50	100	200			300
tert-Butyl Alcohol	25	1250	25		25	100	250	500	1000			1500
Tetrachloroethene	1	50	5	1	5	20	50	100	200			300
Tetrahydrofuran	5	250	5		5	20	50	100	200			300
1,1,2-Trichlorotrifluoroethane	5	50	5		5	20	50	100	200			300
Toluene	1	50	5	1	5	20	50	100	200			300
Trichloroethene	1	50	5	1	5	20	50	100	200			300
Trichlorofluoromethane	1	50	5	1	5	20	50	100	200			300
tert-Butylbenzene	1	50	5	1	5	20	50	100	200			300
Xylene (Total)	3	75	15	3	15	60	150	300	600	1.5	1.2	900
Vinyl acetate	5	250	5		5	20	50	100	200			300
Vinyl chloride	1	50	5	1	5	20	50	100	200	0.50	0.40	300

10.2.2. **Calibration Response Factors**

Response factors (RF) establish the relationship of the instruments response in comparison with the concentration of any given analyte. The RF includes the concentration and response of the internal standard as well. By relating the IS concentration and response in an inverse manner, the target analyte concentration is adjusted to account for drift in the instrument on a per injection basis. As instrument response increases as indicated by the response of the internal standard, the concentration of the target is mathematically decreased, and vice versa.

To calculate the RF for any given calibration standard (or calibration verification standard), tabulate the area response of the characteristic ions against concentration for each compound and each internal standard. Calculate response factors (RF) for each compound relative to one of the internal standards. The internal standard selected for the calculation of the RF for a compound should be the internal standard that has a retention time closest to the compound being measured. Response factors are calculated using the following equation.

$$RF = \frac{A_x C_{is}}{A_{is} C_x}$$

Where:
A_x = Area of the characteristic ion for the compound being measured.
A_{is} = Area of the characteristic ion for the specific internal standard.
C_{is} = Concentration of the specific internal standard (µg/L).
C_x = Concentration of the compound being measured (µg/L).

Most, if not all modern chromatography data systems are capable of calculating this factor and using it to quantify analyte concentrations. The 8260B method has minimum requirements that these response factors must meet in order to be considered valid. The method uses a subset of the target analyte list to evaluate the performance of the system. These compounds are referred to as the System Performance Check Compounds or the SPCCs. The SPCCs serve as an indicator of instrument sensitivity and, by meeting a minimum value, ensure that the laboratory has adequate sensitivity to analyze and reliably report data for environmental samples.

10.2.3. **Calibration Curve Fit**

The calibration curve is a representation of the relationship of the instrument response and analyte concentration. The curve is used to quantitate the concentration of an unknown based on its response and this known relationship. The curve is produced in several ways depending on the nature of the "goodness of fit".

Average Response Factor (ARF): The average response factor is determined by averaging the response factors calculated for each calibration level for each target analyte. The average RF can be used to calculate the concentration of target analytes in samples provided the criteria are met for consistency in the RFs for any given analyte. An average response factor is the default curve fitting option for calibrations. It is in the most basic sense, a linear regression that is forced through zero at the origin. Because of its simplicity and the interception of the y axis at the origin, this is the preferred technique for curve fitting. A calculation of the percent relative standard deviation (%RSD) is used to determine the acceptability of the use of the ARF (see Table 10.2).

The % RSD is calculated as follows: %RSD = SD*100 / ARF

Where: SD = Standard deviation of the averaged RFs for a given compound

The average response factor is also used to diagnose the integrity of the chromatography system as it relates to calibration linearity. The ***Calibration Check Compounds (CCCs)*** are a subset of the target analyte list that must meet specific criteria (see Table 10.2) for the calibration to be acceptable. For the CCCs, the %RSD for each is compared to the method criteria. If that of any CCC exceeds the criteria, the system needs to be inspected for potential sources of errors and recalibrated.

Linear Regression: The linear regression calibration curve is derived from a least squares regression analysis of the calibration points. A calibration curve based on this technique will have the format of y=ax+b where "a" is the slope of the line and "b" is the y intercept. In order to use this curve fit technique, a minimum of 5 calibration points must be available and the origin cannot be included as one of the points. This technique works well for calibrations where the response of the instrument is linear in nature but does not necessarily intercept the y-axis at the origin. However, because the linear regression is not forced through the origin, very low levels of contaminants below the response of the lowest calibration point may generate erroneous reportable results. A calculation of the correlation coefficient "r" is used to determine the acceptability of a linear regressed curve (see Table 10.2)

Non-linear Regression: The non-linear regression calibration curve is derived from a least squares regression analysis of the calibration points. A calibration curve based on this technique will have the format of $y= ax^2+bx+c$. In order to use this curve fit technique, a minimum of 6 calibration points must be available and the origin cannot be included as one of the points. This technique works well for calibrations where the response of the instrument gradually decreases with increasing concentrations. Using this technique, an analyst may be able to generate calibration curves with correlation coefficients very close or equivalent to 1.000. However, because the non-linear regression is not forced through the origin, very low levels of contaminants below the response of the lowest calibration point may generate erroneous reportable results. Likewise, high levels of contamination may not be able to be calculated due to regression equations with multiple intercepts of either axis on the calibration plot.

Refer to table 10.2.5 for curve fit criteria. Either the low or high calibration points may be dropped to meet linearity criteria provided the laboratory meets the minimum 5 calibration point requirements. Points within the center of the curve may not be dropped unless an obvious problem is discovered and documented. The point must be dropped in its entirety and reanalyzed. Re-analysis should be within the same 12-hour time window and must occur within 8 hours of the original analysis.

10.3. Calibration Verification

10.3.1. Second Source Verification (SCV)

In addition to meeting the linearity criteria, any new calibration curve must be assessed for accuracy in the values generated. Accuracy is a function of both the "fit" of the curve to the points used and the accuracy of the standards used to generate the calibration points. By meeting the fit criteria, the accuracy relative to the goodness of fit is addressed. However, because all calibration points are from the same source, it is possible that the calibration points may meet linearity criteria but not be accurately made in terms of their true value.

Therefore, to assess the accuracy relative to the purity of the standards, a single standard from a secondary source must be analyzed and the results obtained must be assessed relative to the known true value. This step is referred to as ***Secondary Source Verification*** or, alternatively as ***Initial Calibration Verification***. This secondary source must be from an alternative vendor or, in the event an alternative vendor is not available, from a different lot from the same vendor. The accuracy of the standard is assessed as a percent difference from the true value according to the following equation:

% Difference = $[Result_{SCV} - TrueValue_{SCV}] / TrueValue_{SCV} * 100$

See Tables 9.6 and 9.7 for details on the preparation of this standard. See Table 10.2 for control criteria

10.3.2. Continuing Calibration Verification (CCV)

As part of the analytical process, the instrumentation must be checked periodically to determine if the response has changed significantly since the initial calibration was established. This verification process is known as ***Continuing Calibration Verification***. The validity of the initial calibration is checked at the beginning of every analytical sequence and every 12 hours thereafter for as long as the instrument is analyzing samples and is accomplished by analyzing a midpoint calibration standard (CCV).

The values obtained from the analysis of the CCV are compared to the true values and a percent change calculated. The percent change must meet the method specified criteria for the analysis to proceed for an additional 12 hours.

The actual determination of change in instrument response is based on the type of curve fit used for each analyte. Calibration curves based on an average response factor are assessed based on the percent difference of the RF calculated for the CCV from the average RF established in the initial calibration. Calibration curves based on a linear or non-linear regression are assessed based on the percent drift of the calculated result from the known true value of the standard. The equations for these calculations are as follows:

% Difference: $[RF_{CCV} - AvgRF_{CAL}] / AvgRF_{CALI} \times 100$

% Drift: $[Result_{CCV} - TrueValue_{CCV}] / TrueValue_{CCV} \times 100$

Table 10.2 – Calibration Acceptance and Verification Criteria

Calibration Metric	Parameter / Frequency	Criteria	Comments
Calibration Curve Fit	Average Response Factor	%RSD ≤ 15%	If not met, try linear regression fit
	Linear Regression	r ≥ 0.99	If not met, try non-linear regression fit
	Non-linear Regression	COD ≥ 0.99	If not met, remake standards and recalibrate
System Performance Check Compounds (SPCCs)	Chloromethane 1,1-Dichloroethane Bromoform Chlorobenzene 1,1,2,2-Tetrachloroethane	Avg RF ≥ 0.10 Avg RF ≥ 0.10 Avg RF ≥ 0.10 Avg RF ≥ 0.30 Avg RF ≥ 0.30	Some possible problems are standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, poor purging efficiency, and active sites in the column or chromatographic system.
Calibration Check Compounds (CCCs)	1,1-Dichloroethane Toluene Chloroform Ethylbenzene 1,2-Dichloropropane Vinyl Chloride	%RSD < 30%	%RSD for the calibration check compounds (CCC's) must be ≤30% regardless of curve fit used. If the CCCs are not included on a list of analytes for a project, and therefore not included in the calibration standards, then all compounds of interest must meet a ≤15% RSD criterion.
Second Source Verification Standard	Immediately after each initial calibration	% Diff ±30%	Acceptance criteria are ±30% for all analytes, with allowances for 5% of compounds @ ±40%. See ALL_Q_025_Rev.1
Continuing Calibration Verification	Prior to the analysis of any samples and every 12 hours thereafter		If the requirements for continuing calibration are not met, these corrective actions must be taken prior to reanalysis of standards. Only two injections of the same standard are permitted back to back.
	SPCCs	Must meet response criteria listed above	
	Internal Standard RT	RT ± 30 sec	Use midpoint calibration standard as reference
	Internal Standard Response	50 – 200%	Use midpoint calibration standard as reference
	CCCs	RF ± 20% Diff.	Use for Avg RF calibration curves
		Result ± 20% Drift	Use for linear and non-linear calibration curves

10.4. Calibration Corrective Actions

10.4.1. Calibration Linearity Problems

10.4.1.1. Check instrumentation/equipment condition.

10.4.1.2. Enter maintenance in instrument maintenance logbook.

10.4.1.3. Perform another initial calibration.

10.4.1.4. No data can be reported.

10.4.1.5. Generate on Non-Conformance Memo.

10.4.2. Secondary Verification Problems

10.4.2.1. Check instrumentation/equipment condition.

10.4.2.2. Enter maintenance in instrument maintenance logbook.

10.4.2.3. Perform another initial calibration.

10.4.2.4. No data can be reported.

10.4.2.5. Generate on Non-Conformance Memo

10.4.3. Continuing Verification Problems

10.4.3.1. Reanalyze the original CCV standard to determine instrument consistency.

10.4.3.2. Prepare and analyze a new CCV standard to determine preparation consistency / standard integrity.

10.4.3.3. Document instrument maintenance

10.4.3.4. Reanalyze CCV standard to determine if maintenance was effective in restoring performance.

10.4.3.5. Complete recalibration of instrument.

10.4.3.6. If samples were analyzed in spite of verification failures, note the following exceptions for addressing those results. Deviations from this requirement must be noted on the injection log with a thorough explanation for the deviation from policy.

Exceptions: If calibration verification is above the upper control limit, samples non-detected for those analytes may be reported without reanalysis.

11. Procedures

11.1. Purge-Trap GC/MS System Preparation

11.1.1. Operating Parameters

Configure the GC/MS system to match the following operating parameters based on instrument configuration. The parameters themselves are saved as a method on the chromatography data system. By loading the last method used, the instrument will auto-configure to match the parameters from the last time the system was operated under that method. Verify that the settings in the software match the appropriate configuration.

Table 11.1 –Instruments and Operating Parameters

Instrument ID	Component	Settings and Consumables	
40MSV1	Gas Chromatograph	**Column**: J&W Scientific DB-624 Capillary Column, 20m x 0.18 mm, i.d. 1.0 um **Inlet Liner:** Restek 4 mm Single Gooseneck Injection Port Liners **Inlet Seal:** Restek Gold Plated inlet seal **Column Ferrules:** Restek 04.mm Vespel/Graphite	Pressure / Flow: 0.5 mL / min Initial Temperature: 40°C Initial Time: 3 min Final Temperature: 8°C / min to 110°C 0 min hold 20°C / min to 220°C 1 min hold Final Time: 18.25 min Injector Temperature: 220°C Detector Temperature: 240°C

		ferrules	
	Mass Spectrometer	Tune File: Named to date of tune	
	Purge & Trap Concentrator	Prepurge: NO Preheat: 40°C Sample: 20°C Purge: 10 min Dry Purge: NO Desorb Preheat: 245°C Desorb: 250°C	Standby: - Bake: 270°C for 7 min BGB: OFF Valve: 150°C Line: 150°C Mount: N/A Transfer Line Temp: 150°C
	Autosampler	Suringe Flushes: 2 Sparge Tube Flushes: 2	
Instrument ID	**Component**	**Settings and Consumables**	
40MSV2	Gas Chromatograph	**Column**: J&W Scientific DB-624 Capillary Column, 20m x 0.18 mm, i.d. 1.0 um **Inlet Liner:** Restek 4 mm Single Gooseneck Injection Port Liners **Inlet Seal:** Restek Gold Plated inlet seal **Column Ferrules:** Restek 04.mm Vespel/Graphite ferrules	Pressure / Flow: 0.5 mL / min Initial Temperature: 40°C Initial Time: 3 min Final Temperature: 8°C / min to 110°C 0 min hold 20°C / min to 220°C 1 min hold Final Time: 18.25 min Injector Temperature: 220°C Detector Temperature: 240°C
	Mass Spectrometer	Tune File: Named to date of tune	
	Purge & Trap Concentrator	Prepurge: NO Preheat: NO Sample: 20°C Purge: 10 min Dry Purge: NO Desorb Preheat: 245°C Desorb: 250°C	Standby: - Bake: 270°C for 7 min BGB: OFF Valve: 150°C Line: 150°C Mount: N/A Transfer Line Temp: 150°C
	Autosampler	Suringe Flushes: 2 Sparge Tube Flushes: 2	
Instrument ID	**Component**	**Settings and Consumables**	
40MSV3	Gas Chromatograph	**Column**: J&W Scientific DB-624 Capillary Column, 20m x 0.18 mm, i.d. 1.0 um **Inlet Liner:** Restek 4 mm Single Gooseneck Injection Port Liners **Inlet Seal:** Restek Gold Plated inlet seal **Column Ferrules:** Restek 04.mm Vespel/Graphite ferrules	Pressure / Flow: 1.0 mL / min Initial Temperature: 40°C Initial Time: 3 min Final Temperature: 8°C / min to 110°C 0 min hold 20°C / min to 220°C 1 min hold Final Time: 18.25 min Injector Temperature: 220°C Detector Temperature: 240°C
	Mass Spectrometer	Tune File: Named to date of tune	
	Purge & Trap Concentrator	Prepurge: NO Preheat: 40°C Sample: 20°C Purge: 10 min Dry Purge: NO	Standby: - Bake: 270°C for 7 min BGB: OFF Valve: 150°C Line: 150°C

		Desorb Preheat: 245°C Desorb: 250°C	Mount: N/A Transfer Line Temp: 150°C
	Autosampler	Suringe Flushes: 2 Sparge Tube Flushes: 2	
Instrument ID	**Component**	**Settings and Consumables**	
40MSV4	Gas Chromatograph	**Column**: J&W Scientific DB-624 Capillary Column, 20m x 0.18 mm, i.d. 1.0 um **Inlet Liner:** Restek 4 mm Single Gooseneck Injection Port Liners **Inlet Seal:** Restek Gold Plated inlet seal **Column Ferrules:** Restek 04.mm Vespel/Graphite ferrules	Pressure / Flow: 0.5 mL / min Initial Temperature: 40°C Initial Time: 3 min Final Temperature: 8°C / min to 110°C 0 min hold 20°C / min to 220°C 1 min hold Final Time: 18.25 min Injector Temperature: 220°C Detector Temperature: 240°C
	Mass Spectrometer	Tune File: Named to date of tune	
	Purge & Trap Concentrator	Prepurge: NO Preheat: NO Sample: 20°C Purge: 10 min Dry Purge: NO Desorb Preheat: 245°C Desorb: 250°C	Standby: - Bake: 270°C for 7 min BGB: OFF Valve: 150°C Line: 150°C Mount: N/A Transfer Line Temp: 150°C
	Autosampler	Suringe Flushes: 2 Sparge Tube Flushes: 2	
Instrument ID	**Component**	**Settings and Consumables**	
40MSV5	Gas Chromatograph	**Column**: J&W Scientific DB-624 Capillary Column, 20m x 0.18 mm, i.d. 1.0 um **Inlet Liner:** Restek 4 mm Single Gooseneck Injection Port Liners **Inlet Seal:** Restek Gold Plated inlet seal **Column Ferrules:** Restek 04.mm Vespel/Graphite ferrules	Pressure / Flow: 0.5 mL / min Initial Temperature: 40°C Initial Time: 3 min Final Temperature: 8°C / min to 110°C 0 min hold 20°C / min to 220°C 1 min hold Final Time: 18.25 min Injector Temperature: 220°C Detector Temperature: 240°C
	Mass Spectrometer	Tune File: Named to date of tune	
	Purge & Trap Concentrator	Prepurge: NO Preheat: NO Sample: 20°C Purge: 10 min Dry Purge: NO Desorb Preheat: 245°C Desorb: 250°C	Standby: - Bake: 270°C for 7 min BGB: OFF Valve: 150°C Line: 150°C Mount: N/A Transfer Line Temp: 150°C
	Autosampler	Suringe Flushes: 2 Sparge Tube Flushes: 2	
Instrument ID	**Component**	**Settings and Consumables**	
40MSV6	Gas Chromatograph	**Column**: J&W Scientific DB-624 Capillary Column, 20m x 0.18 mm, i.d. 1.0 um **Inlet Liner:** Restek 4 mm	Pressure / Flow: 0.8 mL / min Initial Temperature: 40°C Initial Time: 3 min Final Temperature: 8°C / min to 110°C 0 min hold

		Single Gooseneck Injection Port Liners **Inlet Seal:** Restek Gold Plated inlet seal **Column Ferrules:** Restek 04.mm Vespel/Graphite ferrules	20°C / min to 220°C 1 min hold Final Time: 18.25 min Injector Temperature: 220°C Detector Temperature: 240°C
	Mass Spectrometer	Tune File: Named to date of tune	
	Purge & Trap Concentrator	Prepurge: NO Preheat: NO Sample: 20°C Purge: 10 min Dry Purge: NO Desorb Preheat: 245°C Desorb: 250°C	Standby: - Bake: 270°C for 7 min BGB: OFF Valve: 150°C Line: 150°C Mount: N/A Transfer Line Temp: 150°C
	Autosampler	Suringe Flushes: 2 Sparge Tube Flushes: 2	
Instrument ID	**Component**	**Settings and Consumables**	
40MSV7	Gas Chromatograph	**Column**: J&W Scientific DB-624 Capillary Column, 20m x 0.18 mm, i.d. 1.0 um **Inlet Liner:** Restek 4 mm Single Gooseneck Injection Port Liners **Inlet Seal:** Restek Gold Plated inlet seal **Column Ferrules:** Restek 04.mm Vespel/Graphite ferrules	Pressure / Flow: 0.5 mL / min Initial Temperature: 40°C Initial Time: 3 min Final Temperature: 8°C / min to 110°C 0 min hold 20°C / min to 220°C 1 min hold Final Time: 18.25 min Injector Temperature: 220°C Detector Temperature: 240°C
	Mass Spectrometer	Tune File: Named to date of tune	
	Purge & Trap Concentrator	Prepurge: NO Preheat: 40°C Sample: 20°C Purge: 10 min Dry Purge: NO Desorb Preheat: 245°C Desorb: 250°C	Standby: - Bake: 270°C for 7 min BGB: OFF Valve: 150°C Line: 150°C Mount: N/A Transfer Line Temp: 150°C
	Autosampler	Suringe Flushes: 2 Sparge Tube Flushes: 2	
Instrument ID	**Component**	**Settings and Consumables**	
40MSV8	Gas Chromatograph	**Column**: J&W Scientific DB-624 Capillary Column, 20m x 0.18 mm, i.d. 1.0 um **Inlet Liner:** Restek 4 mm Single Gooseneck Injection Port Liners **Inlet Seal:** Restek Gold Plated inlet seal **Column Ferrules:** Restek 04.mm Vespel/Graphite ferrules	Pressure / Flow: 1.0 mL / min Initial Temperature: 40°C Initial Time: 3 min Final Temperature: 8°C / min to 110°C 0 min hold 20°C / min to 220°C 1 min hold Final Time: 18.25 min Injector Temperature: 220°C Detector Temperature: 240°C
	Mass Spectrometer	Tune File: Named to date of tune	

	Purge & Trap Concentrator	Prepurge: NO Preheat: NO Sample: 20°C Purge: 10 min Dry Purge: NO Desorb Preheat: 245°C Desorb: 250°C	Standby: - Bake: 270°C for 7 min BGB: OFF Valve: 150°C Line: 150°C Mount: 90°C Transfer Line Temp: 150°C
	Autosampler	Suringe Flushes: 2 Sparge Tube Flushes: 2	
Instrument ID	**Component**	**Settings and Consumables**	
40MSV9	Gas Chromatograph	**Column**: J&W Scientific DB-624 Capillary Column, 20m x 0.18 mm, i.d. 1.0 um **Inlet Liner:** Restek 4 mm Single Gooseneck Injection Port Liners **Inlet Seal:** Restek Gold Plated inlet seal **Column Ferrules:** Restek 04.mm Vespel/Graphite ferrules	Pressure / Flow: 0.5 mL / min Initial Temperature: 40°C Initial Time: 3 min Final Temperature: 8°C / min to 110°C 0 min hold 20°C / min to 220°C 1 min hold Final Time: 18.25 min Injector Temperature: 220°C Detector Temperature: 240°C
	Mass Spectrometer	Tune File: Named to date of tune	
	Purge & Trap Concentrator	Prepurge: NO Preheat: NO Sample: 20°C Purge: 10 min Dry Purge: NO Desorb Preheat: 245°C Desorb: 250°C	Standby: - Bake: 270°C for 7 min BGB: OFF Valve: 150°C Line: 150°C Mount: N/A Transfer Line Temp: 150°C
	Autosampler	Suringe Flushes: 2 Sparge Tube Flushes: 2	

11.2. Tune Verification

At the beginning of each analytical sequence, prior to the analysis of any standards or samples, the mass spectrometer tune conditions must be verified. This is done by analyzing a standard containing bromofluorobenzene (refer to table 9.2). The tune verification standard can be combined with the CCV standard provided that the amount of BFB introduced into the system meets the criteria in Table 9.2.

After the analysis of this standard, the mass spectrum of BFB must be evaluated against the following criteria.

Mass (m/z)	Ion Abundance criteria
50	15.00-40.00% of m/z 95
75	30.00-60.00% of m/z 95
95	Base peak, 100% relative abundance
96	5.00-9.00% of m/z 95
173	<2.00% of m/z 174
174	50.00-99.00% of m/z 95
175	5.00-9.00% of m/z 174
176	95.00-101.00% of m/z 174
177	5.00-9.00% of m/z 176

To evaluate the tune spectra, following the operating instructions for the chromatography data system to access the data file and obtain mass spectra for bromofluorobenzene. If the software has a program or macro for automatically selecting the spectra and evaluating the response ratios, use this option. Otherwise, the spectra must be obtained in one the following manners, in the listed order.

Using an average of three scans, centered on the apex of the peak; or,

Using an average of all scans across the width of the peak, taken at half height; or,

Using an average of all scans taken across the width of the peak from baseline to baseline.

A background scan taken immediately before but not including the peak must be subtracted.

Once obtained, evaluate the ion ratios against the criteria listed above. If the ratios meet the criteria, then analysis may proceed for 12 hours. The window for analysis is 12 hours from the injection date / time for the BFB tune verification. After that, the tune must be verified again to establish a new analytical window. The same Ion Abundance Criteria used for the BFB tune coupled with the initial calibration must be used for all subsequent analyses associated with that initial calibration.

If the ratios do not meet the criteria, refer to the following corrective actions to address the problem:

Retune the mass spectrometer following the equipment manufacturers' instructions. The tune status must be verified after the tuning procedures.

If this fails, change filament and retune.

If this fails, take down the mass spectrometer and clean the instrument.

11.3. Calibration Verification

After the instrument tune conditions are verified and the system meets tune criteria, the instrument must undergo calibration verification. If it has already been determined that the instrument needs to be recalibrated, follow the procedures listed in section 10.2 (Analysis of Standards). Otherwise, analyze a Continuing Calibration Verification Standard to determine the current calibration status.

If the CCV meets control criteria, the system is deemed to be in control and analysis of samples may commence. If the CCV does not meet control criteria, follow the corrective action procedures listed section 10.4.3 (Continuing Verification Problems). If the tune verification has been combined with the CCV, the 12 hour analysis window begins from the analysis date / time of the CCV.

Note: In situations where the instrument will run unattended (i.e. overnight), the analyst may load sequential CCVs in anticipation of that the first in the series may fail due to carry over from a previous sample. If so, the CCV must be evaluated according to the protocol set forth in the Quality Assurance Manual within Section 6 – Equipment and Measurement Traceability.

11.4. Sample Preparation

11.4.1. Samples

11.4.1.1. Sample Pre-screening

11.4.1.1.1. Samples are pre-screened using a rapid GC headspace technique. See SOP GB-O-001 *Sample Screening Volatile Organics Prior to Preparation* for the specifics on the pre-screening of samples.

11.4.1.2. Water Samples

After pre-screening, water samples typically do not require any sample preparation unless they require a dilution to bring high-level contaminants within calibration range or to minimize matrix intereference. Dilutions are made following Section 11.4.1.4.1.

After analysis check the residue in the vial following analysis using pH paper. The pH should be <2. Document results in the run sequence log as <2 or >2. Footnote any sample not meeting the pH

requirement. If dilutions are required, pH preservation can be verified at the time the dilution is made using the sample remaining in the original sample container.

11.4.1.3. Soil Samples

11.4.1.3.1. Low concentration soils

Samples received for low level analysis should be contained in pre-weighed VOA vials either with or without Organic Free Water (OFW) and/or sodium bisulfate preservative. NOTE: some samples may be received in coring devices (e.g. Encore™, etc.). These samples must be extruded into a VOA vial either with or without OFW and/or sodium bisulfate and a magnetic stir bar within 48 hours of sample collection. If samples are received that are greater than 10g the PM must be notified and samples will be rejected for analysis.

11.4.1.3.1.1. Weight determination: Prior to preparation or analysis of any soil received in a pre-weighed VOA vial, the sample weight must be determined and recorded. Accurately weigh the VOA vial to 0.01 g in the laboratory; record this amount in the sample preparation logbook. Subtract the tare weight recorded on the vial; this will be the weight of sample in the vial.

11.4.1.3.1.2. Before any coring devices (e.g. Encore™, etc.) are extruded a test for effervescence will be done using soil from the supplied total solids container. Place 5 mLs of 200g/L Sodium Bisulfate solution into a disposable beaker. Scoop out of the total solids container approximately 5g of the sample. Check for effervescence. Drop into the sample a pH strip. Record the pH in the preservation log book. If the pH is >2 an extra gram of solid Sodium Bisulfate must be added to this sample at the time of preservation. If effervescence occurs skip to Section 11.4.1.3.1.4. If no effervescence occurs both coring devices are extruded as follows:

11.4.1.3.1.3. Place 5 mLs of 200g/L Sodium Bisulfate solution into a 40 mL VOA vial containing a disposable magnetic stir bar and, if necessary, the extra 1g of Sodium Bisulfate. Put the vial on an analytical balance capable of weighing to 0.01g and zero the weight. Extrude the sample from the coring devices into the vial and re-cap the vial(s). Re-weigh the vial(s) in order to obtain the sample weight. Record the weight of the sample in a logbook and also record the weight of the sample on the vial. Dispose of the coring devices properly.

11.4.1.3.1.4. If effervescence is observed:

Place 5 mLs of OFW into a 40 mL VOA vial containing a disposable magnetic stir bar. Put the vial on an analytical balance capable of weighing to 0.01g and zero the weight. Extrude the sample from the coring devices into the vial and re-cap the vial(s). Re-weigh the vial(s) in order to obtain the sample weight. Record the weight of the sample in a logbook and also record the weight of the sample on the vial. Dispose of the coring devices properly.

11.4.1.3.1.5. Samples received pre-weighed in the field must be in 40 mL VOA vials and contain a magnetic stir bar, acid preservative and a field tare weight. The analyst will compare the field tare weight to the weight of the sample

before analysis. The weight of the sample should be recorded.

11.4.1.3.1.6. All samples must be extruded from the coring devices within 48 hrs. of collection. If the samples are to also be analyzed within the 48 hr criteria, no acid preservation is required. If analysis is to occur after 48 hrs. but within 14 days, the samples must be preserved with Sodium Bisulfate or if preserved with OFW, stored frozen. The ratio of Sodium Bisulfate to sample weight is 0.2g of preservative to 1g of sample.

11.4.1.3.2. High concentration soils

11.4.1.3.2.1. Methanol-Preserved Samples: Samples received in pre-weighed vials preserved with methanol must be accurately weighed in the laboratory to 0.01 g and the sample weight determined. Subtract the weight written on the VOA vial from the weight determined in the laboratory. This will be the weight of sample in the VOA vial. The volume of methanol in the sample container should be at a 1 to 1 ratio of soil to methanol. See Section 11.4.1.3.2.3.

11.4.1.3.2.2. Unpreserved Samples: Samples received in unpreserved pre-weighed vials must be accurately weighed in the laboratory to 0.01 g. NOTE: some samples may be collected and transported to the laboratory in bulk containers. An accurately weighed ≥5 gram sub-sample must be taken and added to a 40-ml VOA vial. The non-compliant sample collection technique must be recorded in the preparation logbook and a qualifier added to the sample result. The samples are then preserved with 10 ml methanol within 48 hours of sample collection. To determine the sample weight: subtract the weight written on the VOA vial from the weight determined in the laboratory prior to the addition of the 10 ml methanol preservative. This will be the weight of sample in the VOA vial. See Section 11.4.1.3.2.3.

11.4.1.3.2.3. The balance is to be leveled before calibration. Calibration verification of the analytical balance is done with S-class weights. These values are to be noted in the Balance calibration logbook. The frequency of balance calibration verification is once per day before the balance is used or when the balance is moved.

11.4.1.3.2.3.1. Login to NETWORK (click icon “METHANOL MAKEUP”).

11.4.1.3.2.3.2. Click on VOC Methanol make up botton.

11.4.1.3.2.3.3. Type in the following information:

11.4.1.3.2.3.3.1. Prep Batch ID (Will correspond with logbook number).

11.4.1.3.2.3.3.2. Sample Number

11.4.1.3.2.3.3.3. Scan the bar code on the side of the 2-oz jar.

11.4.1.3.2.3.3.4. Methanol weight defaults to 15.8 grams assuming 20 mLs, if methanol amount varies adjust weight accordingly, i.e. 25 mLs equals 19.75 grams

11.4.1.3.2.3.4. Put bottle on the balance, hit <ENTER> or click “Read

Balance" button. The program calculates the amount of Methanol to add to adjust the soil to methanol ratio to 1:1.

11.4.1.3.2.3.5. Write the amount of Methanol to add on the backlog under the "MeOH added (mLs)" column.

11.4.1.3.2.3.6. Save data. Repeat steps 11.4.1.3.2.3.3 to 11.4.1.3.2.3.5 until all sample for prep batch are entered.

11.4.1.3.2.3.7. Click on Print Benchsheet button. Type the prep batch id number to generate a copy of the sample numbers with corresponding amounts of methanol and/or surrogate to be added to each sample.

11.4.1.3.2.3.8. If 1:1 ratio cannot be achieved, write the sample weight and volume of Methanol in the prep logbook and comment in Epic Pro.

11.4.1.3.2.3.9. Add Methanol using a graduated cylinder or syringe.

11.4.1.3.2.3.10. Add appropriate amount of Methanol with the use of the graduated cylinder.

11.4.1.3.2.3.11. Add the calculated amount of 2500 ppm surrogate standard to each soil sample using a 50 µL syringe labeled "SS".

11.4.1.3.2.3.12. Place prep sheet in the VOC SOILS PREP BOOK.

11.4.1.3.2.3.13. Sign over the face of the printout and page to insure removal of page will be noticeable. Date the top of the page of the notebook and sign and date the bottom of the notebook.

11.4.1.3.2.3.14. The QC set includes a Method Blank, a Laboratory Control Sample, and a Laboratory Control Sample Duplicate.

11.4.1.3.2.3.15. Samples and QC set are then shaken on shaker table for two minutes to pre-homogenize the samples

11.4.1.3.2.3.16. Samples are then placed in the sonnicator, which is set at the fifth (5) setting for power and the coldest temperature setting. The samples are sonnicated for 20 minutes to finish the homogenization process

11.4.1.3.2.3.17. Samples are pre-screened using a rapid GC headspace technique. See SOP S-GB-O-001 *Sample Screening Volatile Organics Prior to Preparation* for the specifics on the pre-screening of samples

11.4.1.3.2.3.18. Dilute all samples according to Section 11.4.1.4.2.2.

11.4.1.3.3. Sample Preparation Problems

Missing Tare Weights on VOA vials: Mark the vial to indicate pre-weight must be determined after sample analysis. Record the weight of the full vial with sample. Following sample analysis, transfer any remaining sample into another vial. Clean the original vial and remove all trace of the sample. Add all

contents that were present in the vial that were not sample content (magnetic stir bar, preservative, organic free water, etc). Take care to add the exact amount of contents (weights and volumes) that were originally in the vial when sample was collected. Weigh the vial with all non-sample contents and record this weight as the estimated initial weight of the VOA vial. Subtract this estimated initial vial weight from the full vial weight with sample (recorded prior to sample analysis). Document all steps and weights and include a narrative on sample report indicating action taken to estimate initial vial weight for sample weight determination.

11.4.1.4. Dilutions

11.4.1.4.1. Water

Dilutions on aqueous samples must be prepared in a volumetric fashion. Sample aliquots may be measured in either a volumetric pipette or syringe and brought to volume in a volumetric flask.

11.4.1.4.1.1. All steps must be performed without delays until the diluted sample is in a 40 mL VOA Vial.

11.4.1.4.1.2. Dilutions are made in gastight 50mL syringes.

11.4.1.4.1.3. Calculate the approximate volume of organic-free reagent water added to the syringe and add slightly less than this quantity of organic-free reagent water to the syringe barrel.

11.4.1.4.1.4. Inject the proper aliquot of sample using the appropriate 10uL to 5mL syringes to create the desired dilution in the 50 mL syringe. Dilute the sample to the mark with organic-free reagent water. Invert, and shake three times. Repeat the above procedure for additional dilutions.

11.4.1.4.1.5. Fill a 40-mL VOA vial with the diluted sample from the 50 mL syringe prepared in Section 11.4.1.4.1.4.

11.4.1.4.1.6. Place the VOA vial on the autosampler. All dilutions should keep the response of a major constituent (previously saturated peaks) in the upper half of the linear range of the curve.

11.4.1.4.1.7. The autosampler will add the 1.0 uL of the internal standard and surrogate to the sample and transfer 5 mLs over to the 5 mL sparge tube on the Tekmar 3000 concentrator.

11.4.1.4.2. Soil

11.4.1.4.2.1. Low Level Soils

11.4.1.4.2.1.1. It will be necessary to adjust the sample weight for quantitation purposes. Any analyte hits outside of the calibration range, 200 ug/kg, will be extracted into Methanol and analyzed under High Concentration Sample criteria.

11.4.1.4.2.2. High Concentration Soils

11.4.1.4.2.2.1. Dilute all samples according to the results of the screening data. A standard analytical dilution is 1:50. Add 1.0 mL of the sample extract measured with a microsyringe of appropriate volume to 49 mL of reverse osmosis water in a 50 mL syringe.

11.4.1.4.2.2.2. To make dilutions other than a standard 1:50 dilution, fill a 50

mL syringe to a volume of 49 mL with reverse osmosis water. Using a 1.0 mL syringe, inject methanol into the 50 mL syringe to bring the total volume of sample and methanol to equal 1.0 mL. Using an appropriate volume syringe, inject the sufficient amount of sample to reach desired dilution. See Table 1 for dilutions.

11.4.1.4.2.2.3. The 50 mL syringe contents are place into a 40 mL VOC vial by slowly deploying the plunger and injecting on the side of the vial to eliminate cavitation and loss of analytes to volatilization or sparging. Enough of the contents are injected to created a meniscus at the top of the vial that when capped will produce a no headspace sample.

11.4.1.4.2.2.4. The vial is capped and checked for headspace. If vial is free of headspace, it is ready for analysis as per Section 11.5.3.

11.4.2. Batch QC

Refer to Table 12.1 for details on Batch QC requirements.

11.4.2.1. Method Blank

11.4.2.1.1. Water

11.4.2.1.1.1. Fill a 40ml VOA vial with OFW and place on autosampler rack. The autosampler will add 1.0 uL of the internal standard and surrogate to the sample and transfer 5mLs over to the 5mL sparge tube on the Tekmar 3000 concentrator.

11.4.2.1.2. Low Level Soil

11.4.2.1.2.1. A method blank is prepared with 5 mL of OFW into a 40 mL VOA vial containing a disposable magnetic stir bar. The vial is placed onto the autosampler and 1 uL of IS/SS mix @ 250 ug/mL is added. The blank is preheated to 40°C and purged. The method blank must be analyzed under the same criteria as the samples.

11.4.2.1.3. High Concentration Soil

11.4.2.1.3.1. The method blank (extraction blank) is made by adding 10 µL of the 2500 ppm surrogate standard in 10 mL methanol placed in a 2 oz. jar containing 10g of Ottawa sand. A 1.0 mL portion of this is diluted with 49 mL of OFW for a final concentration on the instrument of 50 ug/L.

11.4.2.2. Laboratory Control Sample

See Table 9.7 for procedure.

11.4.2.3. MS/MSD Samples

See Table 9.7 for procedure

11.5. Analyze Samples

11.5.1. Water Samples

11.5.1.1. Create run sequence log. Place 40-mL VOA vial containing sample (Section 11.4.1.1), or appropriately diluted 40 mL VOA vial containing sample (Section 11.4.1.4.1) onto the autosampler. The autosampler will add the 1.0 uL of the internal standard and surrogate to the sample and transfer 5 mLs over to the 5 mL sparge tube on the Tekmar 3000 concentrator.

11.5.2. Low-level Samples

11.5.2.1. Create run sequence log. Place the already weighed 40 mL VOA vial containing the sample, stir bar and 5 mL of OFW or Sodium Bisulfate solution (Section 11.4.1.3.1) onto the autosampler where another 5 mLs of OFW and 1 uL of IS/SS @ 250 ug/mL will be added by the autosampler. The sample is preheated to 40°C and purged. The stir bar is moving continuously during the purge cycle. This also helps in compound recovery by breaking down any clumps that may remain in the sample.

It will be necessary to adjust the sample weight for quantitation purposes. Any analyte hits outside of the calibration range, 200 ug/kg, will be extracted into Methanol and analyzed under High Concentration Sample criteria.

11.5.3. High Concentration Samples

11.5.3.1. Create run sequence log. Place 40-mL VOA vial containing sample (Section 11.4.3.2), or appropriately diluted 40 mL VOA vial containing sample (Section 11.4.1.4.2) onto the autosampler. The autosampler will add the 1.0 uL of the internal standard to the sample and transfer 5 mLs over to the 5 mL sparge tube on the Tekmar 3000 concentrator

11.6. Data Reduction

11.6.1. Qualitative Analysis

Retention Time Comparison: The relative retention time (RRT) of the sample component must be within ±0.06 RRT units of the component in the calibration verification standard. Extracted Ion Current Plots (EICPs) may be used to provide a more reliable assignment of RT in the presence of coeluting components.

Mass Spectrum Comparison: The characteristic ions from the reference mass spectrum are defined as the three ions of greatest relative intensity, or any ions over 30% relative intensity if less than three such ions occur in the reference spectrum. Compounds are identified as present when the following criteria are met.

- The intensities of the characteristic ions of a compound maximize in the same scan or within one scan of each other.
- The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum.
- Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times.
- Compare computer-matched compounds with reference spectra to accept or reject each identification.
- All ions present in the reference spectrum that are at least 10% of the base peak must be present in the sample background-subtracted spectrum.
- The relative intensities of these ions must agree within +/-30% between the standard and sample spectra.
- While this is a good guideline, acceptance or rejection will depend upon the judgment of the analyst.

11.6.2. **Quantitative Analysis –** Quantitation is based on the integrated abundance of the target analyte's quantitation ion using the internal standard technique.

Raw Data Results: The GC/MS data system will calculate the concentration of each analyte as µg/l (or ng/ml). For water samples, no further calculations are necessary unless a dilution of the sample has been performed. If the initial analysis of the sample or a dilution of the sample has a concentration that exceeds the calibration range, the sample must be analyzed at a higher dilution. All dilutions should keep the response of the major constituents in the upper half of the linear range of the curve.

11.6.2.1. Results Calculation – Aqueous Sample:

$$\text{Concentration } (\mu g/L) = \frac{(A_x)(I_s)}{(A_{is})(RF)(V_o)}$$

Where:

A_x= Area of characteristic ion for compound being measured.
I_s = Amount of internal standard injected (ng).
A_{is} = Area of characteristic ion for the internal standard.
RF = Average Relative Response factor for compound being measured.
V_o = Volume of water purged (ml), taking into consideration any dilutions made.

11.6.2.2. Soil/ Solid calculations:

$$\textit{High}\ \text{Conc. (ug/kg)} = \frac{(A_x)(I_s)(V_t)}{(A_{is})(RF)(V_i)(W_s)}$$

$$\textit{Low}\ \text{Conc. (ug/kg)} = \frac{(A_x)(I_s)}{(A_{is})(RF)(W_s)}$$

Where:

A_x, I_s, A_{is}, RF = Same as in water and water-miscible waste above.
V_t = Volume of total extract (ml).
V_i = Volume of extract added (ml) for purging.
S_v = Volume of diluted extract.
W_s= Weight of sample extracted or purged (g). The wet weight or dry weight may be used, depending upon the specific applications of the data.

11.6.3. **Tentatively Identified Compounds (TICs)** – For some samples, identification may be desired for non-target compounds. A mass spectral library search may be conducted to attempt assignment of tentative identifications. Only after visual comparison of sample spectra with the nearest library searches may the analyst assign a tentative identification. Use the following guidelines for making tentative identifications.

- Relative intensities of major ions in the reference spectrum (ions greater than 10% of the most abundant ion) should be present in the sample spectrum.
- The relative intensities of the major ions should agree within ± 20%.
- Molecular ions present in the reference spectrum should be present in the sample spectrum.
- Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of co-eluting compounds.
- Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or co-eluting peaks. Data system library reduction programs can sometimes create these

discrepancies.

12. Quality Control

12.1. **Instrument Quality Control:** Refer to Table 10.2 for initial and continuing calibration criteria and corrective actions.

12.2. **Batch Quality Control**

Table 12.1 – Batch Quality Control Criteria

QA Sample	Components	Frequency	Acceptance Criteria	Corrective Action
Method Blank (MB)	Reagent water	One (1) per 20 samples or 12 hour window (whichever is most frequent)	Target analytes must be less than reporting limit. If results are reported to MDL, target analytes in MB should be non-detect	Re-analyze associated samples. ***Exceptions:*** If sample ND, report sample without qualification If sample result >20x MB detects and sample cannot be reanalyzed, report sample with appropriate qualifier indicating blank contamination. If sample result <20x MB detects, report sample with appropriate qualifier to indicate an estimated value. Client must be alerted and authorize this condition.
Laboratory Control Sample (LCS)	Method specified compounds: Benzene, Chlorobenzene, 1,1-Dichloroethene, Toluene, Trichloroethene *OR (alternative)* Full Target List compounds	One (1) per batch of up to 20 samples	Laboratory derived limits Method Specified List: All compounds must pass control criteria, with no exceptions. Full Target List: Marginal exceedances allowed according to NELAC 2003 Chap 5 D.1.1.2.1.e	Analyze a new LCS If problem persists, check spike solution Perform system maintenance prior to new LCS run ***Exceptions:*** 1) If LCS rec > QC limits and these compounds are non-detect in the associated samples, the sample data may be reported with appropriate data qualifiers.
Laboratory Control Sample Duplicate (LCSD)	Method specified compounds: Benzene, Chlorobenzene, 1,1-Dichloroethene, Toluene, Trichloroethene *OR (alternative)* Full Target List compounds	One (1) per batch of up to 20 samples	Laboratory derived limits Method Specified List: All compounds must pass control criteria, with no exceptions. Full Target List: Marginal exceedances allowed according to NELAC 2003 Chap 5 D.1.1.2.1.e	Analyze a new LCSD If problem persists, check spike solution Perform system maintenance prior to new LCSD run ***Exceptions:*** 1) If LCSD rec > QC limits and these compounds are non-detect in the associated samples, the sample data may be reported with appropriate data qualifiers.
Matrix Spike (MS)	Method specified compounds: Benzene, Chlorobenzene, 1,1-Dichloroethene, Toluene, Trichloroethene *OR (alternative)* Full Target List compounds	One (1) per batch of up to 20 samples, must include one TCLP MS for any analyzed in sequence	Laboratory derived limits	If LCS/LCSD and MBs are acceptable, the MS/MSD chromatogram should be reviewed and it may be reported with appropriate footnote indicating matrix interferences

MSD / Duplicate	MS Duplicate *OR (alternative)* Sample Dup	One (1) for every 5% of all environmental samples	Laboratory Derived Limits	Report results with an appropriate footnote.

12.3. **Sample Quality Control**

Table 12.2 – Sample Quality Control criteria

QA Sample	Components	Frequency	Acceptance Criteria	Corrective Action
Internal Standard	Pentafluorobenzene 1,4 Difluororobenzene 1,4-Dichlorobenzene-d4 Chlorobenzene-d5	Added to all standards, samples, spikes, control samples, and method blanks prior to analysis	**Retention Time:** RT must be ± 30 seconds from last calibration check on all samples	**Retention Time Failure:** If matrix interference is NOT probable, the analytical system must be checked for source of retention time shifting. Affected samples should be reanalyzed in the absence of an obvious instrument or matrix related interference.
Surrogate Standards	Dibromofluoromethane Toluene-d8 4-Bromofluorobenzene	Added to all samples, spikes, control samples and method blanks prior to analysis	Laboratory derived limits	Check system parameters Identify and correct likely cause Re-run samples ***Exceptions:*** Surr rec above criteria and target compounds < RL, result may be reported with appropriate footnote. Surr rec out of control due to obvious sample matrix interference (i.e. co-elution), report results with appropriate footnote.

13. Method Performance

13.1. **Method Detection Limit (MDL) Study**: An MDL study must be conducted annually per S-ALL-Q-004, *Method Detection Limit Studies* for each matrix per instrument.

13.2. **Demonstration of Capability (DOC)**: Every analyst who performs this method must first document acceptable accuracy and precision by passing a demonstration of capability study (DOC) per S-ALL-Q-020, *Orientation and Training Procedures*.

13.3. **Method Modifications**

Method modifications for EPA method 8260B are as follows:

- Modifications should be targeted to improve quality, efficiency or the cost effectiveness of the procedure.
- All major modifications to the procedure that may directly affect data quality must be thoroughly documented. A new demonstration of capability and equivalency must be performed and kept on record.
- Procedures identified as "Best Practices" by the PACE 3P Program will be incorporated into this document as minimum requirements for Pace laboratories.

14. Pollution Prevention and Waste Management

14.1. Procedures for handling waste generated during this analysis are addressed in ALL-S-002, *Waste Handling.*

14.2. In order to minimize the amount of waste generated during this procedure, analyst should prepare reagents in an amount which may be used in a reasonable amount of time (i.e. before a reagent expires)

14.3. The company wide Chemical Hygiene and Safety Manual contains additional information on pollution prevention.

15. References

15.1. USEPA, SW-846, Method 8260B, "Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS), December 1996.

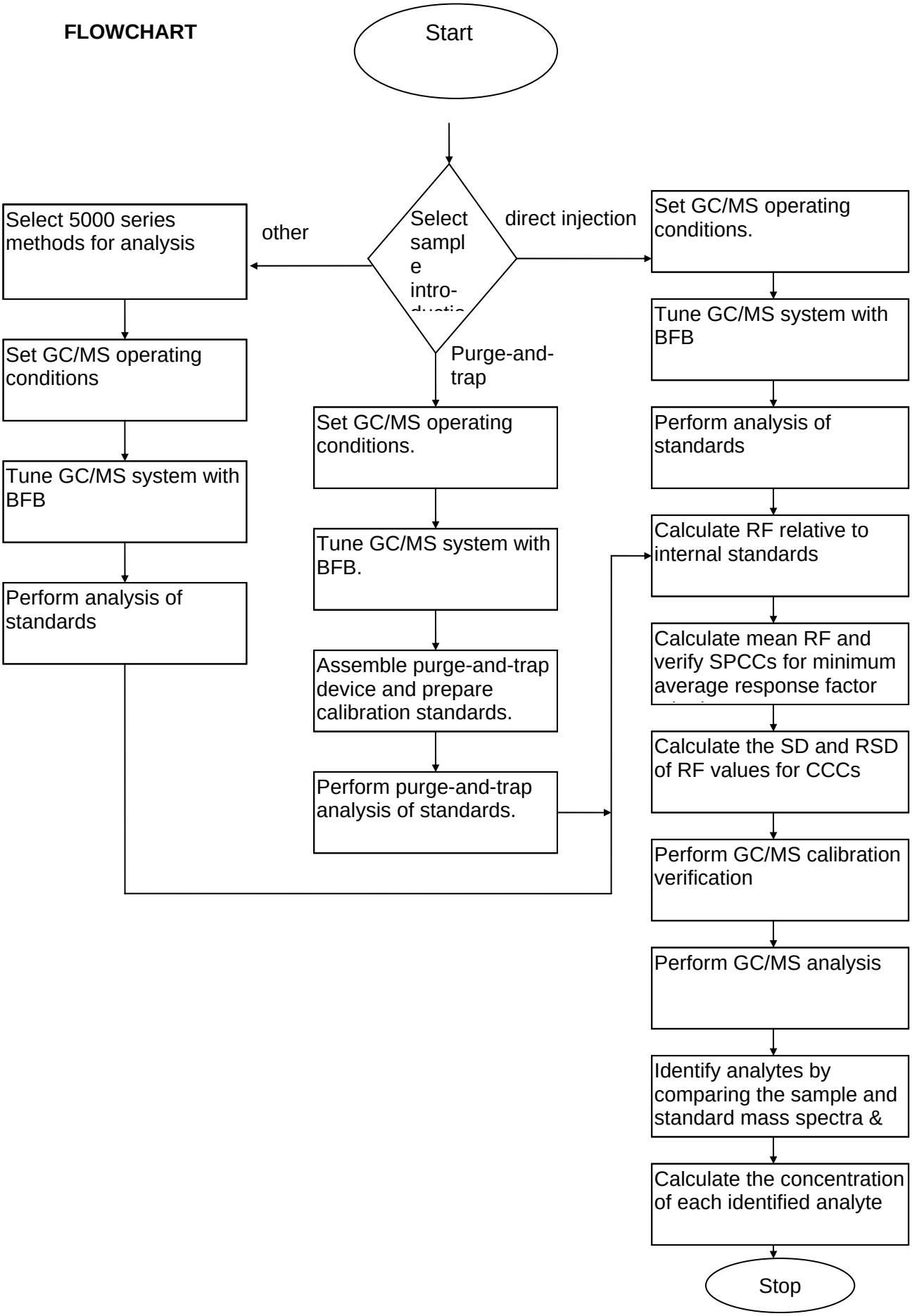
15.2. USEPA, SW-846, Method 5030B, "Purge and Trap for Aqueous Samples," December 1996.

15.3. USEPA, SW-846, Method 5035A, "Closed-System Purge-and-Trap and Extraction for Volatile Organics in Soil and Waste Samples," Draft Revision 1 July 2002.

15.4. USEPA, SW-846, Method 8000B, "Determinative Chromatographic Separations", December 1996.

16. Tables, Diagrams, Flowcharts, Attachments, Appendices, etc.

FLOWCHART



17. Revisions

Document Number	Reason for Change	Date
TMP_ALL_Q_001_Rev.01	Restructured document format. Added tables and other content to create an "SOP Template" in which local edits are allowed. Modified signature page to include department manager and SOP template number. Updated SOP template number. Made the tuning criteria red so edits can be made to reflect local tuning criteria used. Updated calibration sections with new calibration policies described in the PASI Quality Manual revision 10.0.	14July2006
S-GB-ALL-O-002-Rev.00	1. Added necessary information for the Green Bay Laboratory	19Mar2008
S-GB-ALL-O-002-Rev.01	1. Removed Section 7 Responsibilities and distribution. 2. Added in section 11.4.1.3.1 Low Level Soils to determine corrective action for samples received with greater than 10 g of soil. 3. Renumbered document. 4. Up-dated section references in document. 5. Table 8.1 – updated serial numbers. 6. Tables 9.6, 9.7 and 10.1 – VSTD300 Standard added for the Water Curve.	12Dec2008

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STANDARD OPERATING PROCEDURE

SEPARATORY FUNNEL EXTRACTION

REFERENCE METHODS: EPA Method 3510C

LOCAL SOP NUMBER:	S-ALL-GB-O-003-Rev.00
EFFECTIVE DATE:	Date of Final Signature
SUPERSEDES:	ALL-O-003-rev.1, S-ALL-GB-O-003-rev.3
SOP TEMPLATE NUMBER:	SOT-ALL-O-003-Rev.00

LOCAL APPROVAL

Nils Melberg, Laboratory General Manager — Date: 6/16/08

Kate Grams, Laboratory Quality Manager — Date: 6/16/08

Glen Coder, Department Manager — Date: 6/13/08

ANNUAL REVIEW

SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE APPROVAL. SOP IS VALID FOR ONE YEAR FROM DATE OF LAST SIGNATURE.

Signature	Title	Date

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1. Purpose

The purpose of this SOP is to provide a laboratory specific procedure for extracting non-volatile and semi-volatile organic compounds from aqueous samples in a separatory funnel while meeting the requirements specified in EPA method 3510C.

2. Summary of Method

2.1. A measured volume of sample, usually about 1 liter, is serially extracted with solvent in a separatory funnel. Some extractions also require the monitoring and adjusting of the pH of the sample. The extract is separated from the sample and is concentrated, followed by cleanup or analysis.

3. Scope and Application

3.1. This procedure is for extracting water insoluble or slightly water soluble organic compounds from aqueous samples using methylene chloride as the extraction solvent.

3.2. This procedure is applicable for the extraction of semi-volatile compounds (BNAs), polynuclear aromatic hydrocarbons (PAHs), pesticides, and PCBs.

3.3. This procedure is restricted to use by, or under the supervision of, analysts experienced in the use of separatory funnel equipment and reagents. Each analyst must demonstrate the capability to generate acceptable results with this method to be considered qualified to report sample results.

3.4. Analytical SOPs using this extraction procedure include:

S-ALL-GB-O-001	Determination of Semivolatile Organics by GC/MS
S-ALL-GB-O-008	Determination of Semivolatile Organics by GC/MS (Selective Ion Monitoring)
S-GB-O-026	Analysis of Polychlorinated Biphenyls (PCBs) by Gas Chromatography
S-GB-O-027	Analysis of Organochlorine Pesticides by Gas Chromatography

4. Interferences

4.1. Solvents, reagents and glassware can all contribute to compound artifacts or raised baselines; both conditions that can affect chromatography. Analyzing method blanks is therefore crucial in determining the presence of contaminants.

4.2. Phthalate esters are common contaminant products in many products in the lab. All plastic products should be avoided when performing this method.

4.3. Extracts that exhibit interferences can be run through a cleanup procedure (see EPA method 3600). Before using a cleanup method, the analyst should run a series of calibration standards through the procedure to ensure that the elution order of compounds remains the same and that no new interferent has been introduced by the cleanup method. Cleanup SOPs that can be used for this extraction procedure include:

GB-O-032-Rev.0		Gel Permeation Chromatography
S-GB-O-034-REV.1		Sulfuric Acid Cleanup
S-GB-O-035-REV.1		Mercury Cleanup for the Removal of Sulfur from PCB Samples
S-GB-O-036-REV.1		Florisil Cleanup for PCBs
S-GB-O-037-REV.1		Florisil Cartridge Cleanup
S-GB-O-038-Rev.1		Silica Gel Cleanup for Organic Analysis
S-GB-O-039-REV.1		Copper Cleanup for the Removal of Sulfur from PCB Samples

5. Safety

5.1. Standards and Reagents

The toxicity and carcinogenicity of standards and reagents used in this method have not been fully defined. Each chemical compound should be treated as a potential health hazard. Reduce exposure by the use of gloves, lab coats and safety glasses. Material Safety Data Sheets (MSDSs) are on file in the laboratory and available to all personnel. Standard solutions should be prepared in a hood whenever possible.

Methylene chloride creates excessive pressure very rapidly when shaken in an enclosed apparatus, as directed in this method. The shaker funnels used in conjunction with the extraction vessel are designed to automatically vent excess pressure created by methylene chloride. As a result, the extraction mixer should be operated in a hood to avoid exposure of the technician to solvent vapors.

5.2. Samples

Take precautions when handling samples. Samples should always be treated as potentially hazardous "unknowns". The use of personal protective equipment (gloves**,** lab coats and safety glasses) is required when handling samples. In the event a sample container must be opened, it is recommended to perform this in a hood whenever possible. All distillations should be conducted under a fume hood.

6. Definitions

Refer to Glossary section of the Pace Quality Assurance Manual (QAM) for a comprehensive list of terms and definitions. In addition to those listed in the QAM, the following are additional terms found in this SOP.

7. Sample Collection, Preservation, and Handling

Table 7.1 – Sample Collection, Preservation, Storage and Hold time.

Sample type	Collection per sample	Preservation	Storage	Hold time
Aqueous	Amber Glass container with Teflon-lined lid (preferably 1L widemouth).	None	4 ± 2°C	Samples must be extracted within 7 days of collection and must be analyzed within 40 days of extraction.

Samples should be stored separately from all standards, reagents, and highly contaminated samples. To avoid contamination, no food or drink products can be located near samples.

8. Equipment and Supplies

8.1. Instrumentation

Equipment	Vendor	Model / Version	Description / Comments
Lab-Line Automated Separatory Funnel Extractor	Barnsteadt	Model #1600	
Concentrator Water Bath	Fisher	S-EVAP	
Turbo Vaps II	Zymark	Zw 8002	

8.2. General Supplies

Item	Vendor	Model / ID	Catalog #	Description
Self-venting Separatory Funnels	Fisher		NC9802352	Glass, able to hold 2L; with PTFE stopcocks and Teflon lids
Analytical Balance	Ohaus	Model # AR 5120		Capable of reading to 0.01g
Glass beakers	Fisher			
Glass Autosampler Vials	MG Scientific	V300-3 / V300-20N		2.0 mL with Teflon-lined crimp
Micro-syringes	Hamiliton			10-µL, 25-µL, 50-µL, 100-µL, 250-µL, 500-µL, and 1,000-µL,
Glass funnels	Fisher			
Whatman #41 Filters	Fisher	1441-185		185 mm
Glass Stirring Rods	Fisher			
Kuderna-Danish flasks	HGF Scientific	192006-03		500mL with ground glass joints
Kuderna Danish concentrator tubes	HGF Scientific	192010-12		10mL, graduated, with ground glass fitting
Snyder columns	HGF Scientific	192002-DP1/ 192002-M2B		2-ball and 3-ball varieties
Keck clips to hold KD glassware together	HGF Scientific	192002-DP4		Keck Clip #19
Boiling Chips	Fisher	09-191-20		450 g
PH test strips	Fisher			Wide Range
Dispensing Pipettes	Fisher			Adjustable over range of 50 .0 to 100.0 mL, one for each solvent
Wash bottles, PTFE	Fisher			One for each solvent
Powder funnels	Fisher			
Glass wool	Fisher			
Disposable Pasteur pipettes	Fisher			

9. Reagents and Standards

9.1. Reagents

Reagent	Concentration/ Description	Requirements/ Vendor/ Item #
Reagent water	De-ionized water	ASTM Type II water
Sodium Sulfate	Anhydrous, granular, baked at 400°C for 4 hours before use.	MG Scientific / catalog # 8024-24
Methylene Chloride	Extraction solvent	MG Scientific / catalog # 9266-8P
Acetone	Extraction solvent	MG Scientific / catalog # 010-4
Hexane	Exchange solvent (pesticides and PCBs)	MG Scientific / catalog # 9262-8P
Sulfuric Acid, Conc.	Concentrated	Fisher / catalog # 9681-33
Sulfuric Acid Solution 1:1	Add 400 mL conc. Sulfuric Acid to 40 mL Reagent Water	
Sodium Hydroxide pellets		Fisher / catalog # 5318-3
Sodium Hydroxide Solution (10N)	Dissolve 400g sodium hydroxide pellets into 1L of reagent water	

9.2. Analytical Standards

9.2.1. Definitions

Standards are required for initial calibration, calibration verification standards, second source verification, and for preparing LCS, MS, and MSD samples.

Table 9.2 Standard Definitions and vendors

Standard	Description	Comments
Surrogate standard	Surrogates are added to each sample and QC sample to monitor extraction efficiency.	
Spiking Standard	This solution contains all target analytes.	Same solution can be used for the LCS and MS/MSD

9.2.2. Storage Conditions

Table 9.3 – Analytical Standard Storage Conditions

Table 9.2 Surrogate Standards

Standard	Concentration	Manufacturer	Catalog #	Storage
Restek B/N Surrogate Mix for PAHs	5000 ug/mL	Restek	31082	Refrigerator 4 +/- 2°C
Restek B/N Surrogate Mix for BNAs	5000 ug/mL	Restek	31082	Refrigerator 4 +/- 2°C
Restek Acid Surrogate Mix for BNAs	7500 ug/mL	Restek	31083	Refrigerator 4 +/- 2°C
Equity Pesticide Surrogate Spike Mix	200µg/mL each TMX and DCB in Acetone	Supelco or equivalent	5-05935	Refrigerator 4 +/- 2°C

Table 9.3 LCS and MS Standards

Standard	Concentration	Manufacturer	Catalog #	Storage
PAH Standard	500 ug/mL	Accustandard	M-160-FL-R-5X	Refrigerator 4 +/- 2°C
BNA Standard - 70 Component Custom LCS Mix	200 ug/mL	Supelco	861389-U	Refrigerator 4 +/- 2°C
BNA Standard - n-nitrosodiphenylamine	5000 ug/mL	Supelco	46702-U	Refrigerator 4 +/- 2°C
Pesticide Standard Mix A	5 – 50µg/mL in Hexane:Toluene (98:2)	Supelco or equivalent	4-8796	Refrigerator 4 +/- 2°C
Pesticide Standard Mix B	5 – 50µg/mL in Hexane:Toluene (99:1)	Supelco or equivalent	4-8196	Refrigerator 4 +/- 2°C
Aroclor 1260	1000µg/mL in isooctane	Supelco or equivalent	4-4809	Refrigerator 4 +/- 2°C
Aroclor 1016*	1000µg/mL in isooctane	Supelco or equivalent	4-8097	Refrigerator 4 +/- 2°C
Toxaphene Standard	1000µg/mL in Hexane	Restek Corporation or equivalent	32005	Refrigerator 4 +/- 2°C

*South Carolina State Requirement – Both 1016 and 1260 must be spiked in all LCS, MS and MSD

9.2.3. Preparation Procedures

PAHs by SW-846 8270C-SIM

- **Working Spiking Standard Preparation**

Table 9.4 Preparation of PAH LCS and MS Standard Solutions

Spike	Standard or Stock Solution Used	Volume of Standard or Stock Used	Final Volume & Solvent Used	Final Concentration	Amount Spiked into a Sample Aliquot
PAH Working Spike Solution	PAH Standard	10µL	25mL of methylene chloride	0.2µg/mL	1000µL

- **Working Surrogate Standard Preparation**

Table 9.5 Preparation of PAH Surrogate Standard Solutions

Spike	Standard or Stock Solution Used	Volume of Standard or Stock Used	Final Volume & Solvent Used	Final Concentration	Amount Spiked into a Sample Aliquot
Intermediate PAH Surrogate Stock Solution	Restek B/N Mix, Cat. # 31082	300µL	10.0mL of methylene chloride	150µg/mL	
Working PAH Surrogate Solution	Intermediate PAH Surrogate Stock Solution	66.66µL	50.0mL of methylene chloride	0.2µg/mL	1000µL

BNAs by SW-846 8270C

- **Working Spiking Standard Preparation**

Table 9.6 Preparation of BNA LCS and MS Standard Solutions

Spike	Standard or Stock Solution Used	Volume of Standard or Stock Used	Final Volume & Solvent Used	Final Concentration	Amount Spiked into a Sample Aliquot
BNA Working Spike Solution	BNA Standard - 70 Component Custom LCS Mix	250µL	250µL	50µg/mL	250µL
	BNA Standard - n-nitrosodiphenylamine	10µL	10µL	50µg/mL	10µL

- **Working Surrogate Standard Preparation**

Table 9.7 Preparation of BNA Surrogate Standard Solutions

Spike	Standard or Stock Solution Used	Volume of Standard or Stock Used	Final Volume & Solvent Used	Final Concentration	Amount Spiked into a Sample Aliquot
BNA Surrogate Spike Solution	Restek Acid Surrogate Mix for BNAs	5000µL	500mL of Methylene chloride	75µg/mL Acids	1.0 mL
	Restek B/N Surrogate Mix for BNAs	5000µL		50µg/mL Base/Neutrals	

Pesticide by SW-846 8081

- **Working Spiking Standard Preparation**

Table 9.8 Preparation of Pesticide LCS and MS Standard Solutions

Spike	Standard or Stock Solution Used	Volume of Standard or Stock Used	Final Volume & Solvent Used	Final Concentration	Amount Spiked into a Sample Aliquot
Pesticide Matrix Spike Solution	Pesticide Standard Mix A and Mix B	4000µL of each	50mL of Acetone	0.4 – 4.0µg/mL	1000µL
Toxaphene Matrix Spike Solution	Toxaphene Standard	5000µL	100mL of Acetone	50µg/mL	800µL

- **Working Surrogate Standard Preparation**

Table 9.9 Preparation of Pesticide Surrogate Standard Solutions

Spike	Standard or Stock Solution Used	Volume of Standard or Stock Used	Final Volume & Solvent Used	Final Concentration	Amount Spiked into a Sample Aliquot
Pesticide/PCB Surrogate Solution	Equity Pesticide Surrogate Spike Mix	5000µL	500mL of Acetone	2.0µg/mL	500µL

PCB by SW-846 8082

- **Working Spiking Standard Preparation**

Table 9.10 Preparation of PCB LCS and MS Standard Solutions

Spike	Standard or Stock Solution Used	Volume of Standard or Stock Used	Final Volume & Solvent Used	Final Concentration	Amount Spiked into a Sample Aliquot
PCB Matrix Spike Solution	Aroclor 1260	1000µL	200mL of Acetone	5.0µg/mL	1000µL
PCB Matrix Spike Solution	Aroclor 1016*	1000µL	200mL of Acetone	5.0µg/mL	1000µL

*South Carolina State Requirement – Both 1016 and 1260 must be spiked in all LCS, MS and MSD samples.

- **Working Surrogate Standard Preparation**

Table 9.11 Preparation of Surrogate Standard Solutions

Spike	Standard or Stock Solution Used	Volume of Standard or Stock Used	Final Volume & Solvent Used	Final Concentration	Amount Spiked into a Sample Aliquot
Pesticide/PCB Surrogate Solution	Equity Pesticide Surrogate Spike Mix	5000µL	500mL of Acetone	2.0µg/mL	500µL

10. Calibration

10.1. Not applicable to this SOP.

11. Procedures

11.1. See the latest revision of Pace SOP S-GB-O-015, *Cleaning of Glassware Used in the Analysis of Semivolatile Range Organics* for the specifics on glassware cleaning.

11.2. Inspect all required glassware to ensure it is clean and dry. Set up each extraction mixer with as many as four, 2L shaker funnels, including caps and stopcocks; assemble 500mL KD apparatus; prepare water funnels with glass wool and sodium sulfate; and pre-rinse all glassware with methylene chloride.

11.3. Check the pH of any sample aliquots that will be analyzed for Methods 8270, 8081, or 8082 by removing a few drops with a disposable pipette for application to pH strips. Record result.

11.4. Mark the sample level on the container and pour the entire contents into separatory funnel. Rinse the container with 60 mL of methylene chloride and pour into separatory funnel. Narrow-mouth bottles contain 1060 mL of sample. Wide-mouth bottles contain 1000 mL of sample. Containers that were not received full have the sample level meniscus marked as stated above, and after pouring of the sample into the separatory funnel and rinsing with methylene chloride, the container is filled to the mark with water. This water is then poured into a 1000 mL graduated cylinder and the sample volume recorded in the extraction log. If the sample container contains sediment on the bottom of the container, care is taken not to disturb and pour this material into the separatory funnel.

11.4.1. If high concentrations are anticipated, a smaller sample aliquot may be diluted to 1.0 L prior to extraction.

11.5. For each batch of 20 samples, or less, prepare two additional sample aliquots. One will serve as a MS and the second as a MSD. As an alternative if no sample in the batch has sufficient volume available for both a MS and MSD, prepare a second aliquot of a different sample for a Duplicate instead of the MSD. Also prepare 2 aliquots of reagent water to serve as the Method Blank and LCS.

11.6. Add Working Spike and Working Surrogate Solutions as follows:

11.6.1. PAH Analysis – Add 1.0 mL of 0.2 ug/mL Working Spike Solution (9.4) to the LCS, LCSD, MS, and MSD. Add 1.0 mL of the 0.2 ug/mL Working Surrogate Solution (9.5) to each sample aliquot, LCS, LCSD, MB, MS, and MSD.

11.6.2. BNA Analysis – Add 250 uL of Supelco 70 Component Custom LCS Spike Mix, 200 ug/mL (9.6) and 10 uL of Supelco n-Nitrosodiphenylamine, 5000 ug/mL (9.6) to the LCS, LCSD, MS, and MSD. Add 1.0 mL of the Working Surrogate Solution, 75 ug/mL Acids, 50 ug/mL Base/Neutral (9.7) to each sample aliquot, LCS, LCSD, MB, MS, and MSD.

11.6.3. Pesticide Analysis – Add 1.0 mL of 0.4-4.0 ug/mL Working Spike Solution (9.8) to the LCS, LCSD, MS, and MSD. Add 500 uL of the 2.0 ug/mL Working Surrogate Solution (9.9) to each sample aliquot, LCS, LCSD, MB, MS, and MSD.

11.6.4. PCB Analysis – Add 1.0 mL of 5.0 ug/mL Working Spike Solution (9.10) to the LCS, LCSD, MS, and MSD. Add 500 uL of the 2.0 ug/mL Working Surrogate Solution (9.11) to each sample aliquot, LCS, LCSD, MB, MS, and MSD.

11.6.5. Toxaphene Analysis – Add 800 uL of 50 ug/mL Working Spike Solution (9.8) to the LCS, LCSD, MS, and MSD. Add 500 uL of the 2.0 ug/mL Working Surrogate Solution (9.9) to each sample aliquot, LCS, LCSD, MB, MS, and MSD.

11.7. Adjust sample aliquots that will be analyzed for Method 8270 to pH <2 with 1:1 sulfuric acid solution. Adjust sample aliquots that will be analyzed for Methods 8081A or 8082 to pH 5-9 with 1:1 sulfuric acid solution or 10N sodium hydroxide solution.

11.8. Add 60 mL of dichloromethane to each sample aliquot. If the entire content of a sample bottle is extracted, rinse the container with the dichloromethane before adding to the separatory funnel. Then pour tap water into the container to the mark, and measure the tap water volume with the graduated cylinder.

11.9. Seal the separatory funnel and set the Lab-Line extraction mixer to shake for 3.0 minutes at a speed of 30 cycles per minutes. After shaking allow the sample and extract to settle for at least 10 minutes.

11.10. If an emulsion is observed at the water-solvent interface with a volume more than 1/3 of the solvent layer, mechanical techniques should be used to complete separation. Mechanical techniques include stirring, filtration through s plug of glass wool, or centrifuging. If 80% of the solvent cannot be recovered, an alternative extraction method may be required.

11.11. Drain and dry the extract through powder funnels containing glass wool and anhydrous sodium sulfate. As the extract filters through the funnel, collect the extracts for BNA, PCB, and Pesticide analysis in a KD apparatus; and collect the extracts for PAH analysis in a Turbovap tube. Rinse the sodium sulfate with additional methylene chloride.

11.12. Add an additional aliquot of dichloromethane to the separatory funnel and repeat the operations in Sections 11.9 to 11.11 twice, for a total of three extractions.

11.13. For samples to be analyzed by Method 8270C and the target analyte list includes basic compounds, adjust the aliquot to pH $\geq$ 11 with 10 N sodium hydroxide solution and repeat the operations in Sections 11.9 to 11.12, combining all extracts in the same concentrator tube.

11.14. Concentration

11.14.1. Kuderna-Danish Method

11.14.1.1. Add 1-3 boiling chips to each flask and attach a Synder column

11.14.1.2. Place the apparatus on the water bath with the receiver tube partially immersed in the water. The temperature of the water bathe is 70-75°C. The balls in the Synder column should actively chatter, but not flood with solvent through the concentration process.

11.14.1.3. Remove the K-D from the water bath when the extract volume is 3-5 mL. After the unit has cooled, remove the Synder column. Rinse the flask with dichloromethane before removing the Receiver tube.

11.14.2. Turbo Vap® Method (Dry-Vap)

11.14.2.1. Place the concentrator receiver into the evaporator unit. Cover with a piece of aluminum foil held on with a rubber band to avoid cross contamination. A disposable pipette is used to create a hole in the aluminum foil to allow the solvent to escape.

11.14.2.2. Operate the unit according to the manufacturer's instructions until the extract volume is 1-5 mL. Remove the receiver and allow to cool. Rinse down the sides of the flask.

11.15. Solvent – Exchange – Extracts to be analyzed by Methods 8081A and 8082 must be exchanged to hexane.

11.16. Finalizing

11.16.1. Further concentrate extracts and the concentrator rinses to approximately ½ of the target final volume by a gentle stream of dry nitrogen using a blow down manifold or N-EVAP. Extracts concentrated by the Turbo Vap® method are bought to final volume in the Turbo Vap tube. Extracts can also be concentrated by adding a fresh boiling chip, fitting the K-D receiver tube with a micro Synder column, and returning the tubes to the heated water bath.

11.16.2. Quantitatively transfer the target final extract volume of 1.0 mL to a 2.0-mL vial for PAH and BNA analyses. Quantitatively transfer the target final extract volume of 10 mL to a 10-mL vial for Pesticides, PCB, and Toxaphen analyses. Final extract volumes may be adjusted to meet client requirements.

11.16.3. Dilute the final extract to volume with the final solvent.

11.16.4. If the final extract will not be analyzed immediately, it must be stored at less than -10°C or at 4°C, as required by the SOP for the determinative procedure.

11.16.5. If the extract cannot be concentrated to the volumes specified above, it should be diluted or subjected to an approved extract cleanup procedure.

12. Quality Control

12.1. Batch Quality Control

Table 12.1 – Batch Quality Control Criteria

QA Sample	Components	Frequency	Acceptance Criteria	Corrective Action
Method Blank (MB)	Reagent water	One per 20 samples or 12-hour window (whichever is most frequent)	Target analytes must be less than reporting limits	Re-extract and re-analyze associated samples if blank result is greater than RL
Laboratory Control Sample (LCS)	All target analytes	One per batch of up to 20 samples	See analytical SOPs	Re-extract and re-analyze a new LCS if original LCS is outside acceptance limits. **Exceptions:** 1) If LCS recovery is > QC limits and target analytes are non-detect in the associated samples, the sample data may be reported with appropriate data qualifiers.
Matrix Spike (MS)/Matrix Spike Duplicate	All target analytes	One set per batch of up to 20 samples	See analytical SOPs	No corrective actions necessary. If LCS recovery is in range, the system is considered valid and the out-of-control MS/MSDs are footnoted appropriately by the analyst.
Surrogates	All applicable surrogate compounds	Added to each sample, blank and QC sample	See analytical SOPs	Surrogates above limits but no hits- report samples with footnote. Surrogate limits above limits but with hits- re-extract if possible or report as biased high. Surrogates below limits: re-extract if possible or report as biased low.

12.2. LCS equation

$$R = (C/S) * 100$$

Where R = percent recovery
C = spiked LCS concentration
S = concentration of analyte added to the clean matrix

12.3. MS/MSD equation

$$R = \frac{(Cs - C)}{S} * 100$$

Where R = percent recovery
Cs = spiked sample concentration
C = sample concentration
S = concentration of analyte added to the sample

RPD calculations:

$$RPD = \frac{|D_1 - D_2|}{[(D_1 + D_2)/2]} * 100$$

Where RPD = relative percent difference
D_1 = first sample result
D_2 = second sample result

13. Method Performance

13.1. **Method Detection Limit (MDL) Study**: An MDL study must be conducted every 12 months per S-ALL-Q-004, *Method Detection Limit Studies* for each matrix per instrument.

13.2. **Demonstration of Capability (DOC)**: Every analyst who performs this method must first document acceptable accuracy and precision by passing a demonstration of capability study (DOC) per S-ALL-Q-020, *Orientation and Training Procedures*.

14. Pollution Prevention and Waste Management

14.1. Procedures for handling waste generated during this analysis are addressed in ALL-S-002, Waste Handling.

14.2. In order to minimize the amount of waste generated during this procedure, analyst should prepare reagents in an amount which may be used in a reasonable amount of time (i.e. before a reagent expires)

14.3. The company wide Chemical Hygiene and Safety Manual contains additional information on pollution prevention.

15. References

15.1. "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods"; EPA SW-846, latest revision. Method 3510C "Separatory Funnel Extraction".

15.2. Pace Analytical Quality Manual; latest revision.

15.3. NELAC Standard; Quality Systems section; latest revision.

15.4. S-ALL-GB-O-001 *Determination of Semi-Volatile Organics by GC/MS*

15.5. S-ALL-GB-O-008 *Determination of Semi-Volatile Organics by GC/MS (Selective Ion Monitoring)*

15.6. S-GB-O-026 *Analysis of Polychlorinated Biphenyls (PCBs) by Gas Chromatography*

15.7. S-GB-O-027 *Analysis of Organochlorine Pesticides by Gas Chromatography*

15.8. S-GB-O-028 *Preparation of Anhydrous Sodium Sulfate and Sand for Extraction Purposes*

15.9. S-GB-O-032 *Gel Permeation Chromatography*

15.10. S-GB-O-034 *Sulfuric Acid Cleanup*

15.11. S-GB-O-015 *Cleaning of Glassware Used in the Analysis of Semivolatile Range Organics*

16. Tables, Diagrams, Flowcharts, Attachments, Appendices, etc.

16.1. Not applicable to this SOP.

17. Revisions

Document Number	Reason for Change	Date
SOT-ALL-O-003-rev.00	1. Restructured document format to new corporate template. 2. Updated formatting and Responsibilities and Distribution section	16Nov2006
S-ALL-GB-O-003-Rev.00	First issue as Corporate Template	10Jun2008

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STANDARD OPERATING PROCEDURE

DETERMINATION OF SEMI-VOLATILE ORGANICS BY GC/MS (SELECTIVE ION MONITORING)

REFERENCE METHODS: EPA Method SW-846 Method 8270C-SIM

LOCAL SOP NUMBER:	S-ALL-GB-O-008-REV.00
EFFECTIVE DATE:	Date of Final Signature
SUPERSEDES:	GB-O-003-rev.1, GB-O-020-rev.1
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LOCAL APPROVAL

Nils K Melberg — 6/3/08
Nils Melberg, Laboratory General Manager — Date

Kate E. Grams — 6/3/08
Kate Grams, Laboratory Quality Manager — Date

Glen A. Coder — 5/15/08
Glen Coder, Department Manager — Date

ANNUAL REVIEW

SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE APPROVAL. SOP IS VALID FOR ONE YEAR FROM DATE OF LAST SIGNATURE.

Signature	Title	Date

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1. PURPOSE

This Standard Operating Procedure (SOP) is used to determine the concentration of semi-volatile organic compounds in water and solid samples based on SW-846 Method 8270C while using Selective Ion Monitoring (SIM). Samples for analysis are prepared by SW846 Method 3510C and SW846 Method 3546 following Pace SOPs S-ALL-GB-O-003 *Separatory Funnel Extraction of Water Samples for Semivolatile Analysis*, and S-GB-O-045 *Microwave Extraction for the Determination of Polynuclear Aromatic Hydrocarbons and Base/Neutral/Acids in Solid Matrices*.

2. SUMMARY OF METHOD

2.1 Sample extracts are prepared for analysis by an appropriate sample preparation method. The semi-volatile organic compounds are introduced into the gas chromatograph (GC) by injecting an aliquot of the sample extract. The GC conditions are programmed to separate the analytes. The GC effluent is directly introduced to a mass spectrometer (MS) for both identification and quantification of analytes. Analytes are identified by comparison of their mass spectra with spectra of authentic standards. Analytes are quantified by comparing the response of a selected major (quantitation) ion relative to an internal standard using a multi-point calibration curve.

3. SCOPE AND APPLICATION

3.1 This procedure is principally used to determine concentrations of polynuclear aromatic hydrocarbons (PAHs) but can also be used to determine concentrations of other neutral, acidic, and basic semi-volatile organic compounds in extracts prepared from many types of water samples, soil samples and wastes. Analytes must be soluble in dichloromethane and amenable to capillary gas chromatography. A list of applicable compounds is shown herein. Pace Reporting Levels (PRLs) are also shown for water and soil samples. PRLs are subject to change based on current analytical system performance and actual sample matrices.

3.2 This method is applicable to most water and solid samples, regardless of moisture content. Common matrices are ground and surface water, wastewater, aqueous sludge, sediment, soils, and other solid samples. Procedures may need to be adapted to address limits in the method or equipment that might hinder or interference with sample analysis. All adaptations made to address matrix related modifications must be documented within the analytical data

3.3 This procedure is restricted to use by, or under the supervision of, analysts experienced in the use of semi-volatile configured GC/MS systems and interpretation of GC/MS data. Each analyst must demonstrate the capability to generate acceptable results with this method to be considered qualified to report sample results.

3.4 This method cannot be substituted for other similar published methods where permit or regulatory compliance is required.

4. INTERFERENCES

4.1 Interferences may be introduced into sample extracts by contaminants in solvents, reagents, glassware, and any other material that comes in contact with the sample or extract during extract preparation. These interferences must be closely monitored by analyzing Method Blank samples and taking corrective action as required.

4.2 Matrix interferences may result from materials co-extracted from some samples.

4.3 Significant phthalate contamination may result at any time if consistent quality control is not practiced. Plastics, in particular, must be avoided because phthalates are commonly used as plasticizers and are easily extracted from plastic materials.

4.4 Contamination by carryover can occur when high concentration extracts are analyzed prior to low concentration extracts. The contamination may also cause degradation of labile analytes. Whenever carryover is suspected, the effected extracts should be re-analyzed. If significant degradation of the GC/MS systems is suspected, system performances samples should be analyzed and corrective action taken as needed.

5. SAFETY

5.1 Standards and Reagents

The toxicity and carcinogenicity of standards and reagents used in this method have not been fully defined. Each chemical compound should be treated as a potential health hazard. Reduce exposure by the use of gloves, lab coats and safety glasses. Material Safety Data Sheets (MSDSs) are on file in the laboratory and available to all personnel. Standard solutions should be prepared in a hood.

5.2 Samples

Take precautions when handling samples. Samples should always be treated as potentially hazardous "unknowns". The use of personal protective equipment (gloves, lab coats and safety glasses) is required when handling samples. In the event a sample container must be opened, it is recommended to perform this in a hood whenever possible.

5.3 Equipment

5.3.1 Portions of the analytical instrumentation operate at high temperatures and under positive pressure. Care must be taken to minimize accidents and injuries when working on or with this equipment. Instruments should be turned off or the heated zone temperatures lowered to reduce the risk of thermal burns. Allow adequate time for the equipment to cool prior to working on these specific zones.

5.3.2 The GC pneumatic system uses gas under high pressure. These high pressures introduce the risk of injury due to flying objects should a vessel or line rupture. Safety glasses are highly recommended at all times when working in, on or around these pieces of equipment. Even instrumentation that is not operating may contain portions of the system under pressure.

6. DEFINITIONS

Refer to Glossary section of the Pace Quality Assurance Manual (QAM) for a comprehensive list of terms and definitions. In addition to those listed in the QAM, the following are additional terms found in this SOP.

6.1 Run Sequence Log – A logbook that lists all injections and analyses performed on a particular piece of equipment regardless of the use of the data collected from each analysis.

6.2 Tune Period – The period after the DFTPP instrument tune check within which analyses may be performed.

7. SAMPLE COLLECTION, PRESERVATION, AND HANDLING

Table 7.1 – Sample Collection, Preservation, Storage and Hold time.

Sample type	Collection per sample	Preservation	Storage	Hold time
Aqueous	One (1) 1-Liter Amber Glass	None	4 ± 2°C	7 days
Soil/Solid (non-aqueous)	One (1) 8-oz Glass Jar	None	4 ± 2°C	14 days
Extracts	2-5mL Glass vials, same as used for standard storage	None	=-10°C	40 days

8. EQUIPMENT AND SUPPLIES

8.1 Instrumentation

Analytical Instrument/Peripherals	EPIC Pro Name	Serial Number
HP 6890 GC	40MSS2	US00024411
HP 5973 Mass Selective Detector	40MSS2	US81221570
HP 7683 Auto-injector	40MSS2	US95110867
HP 7683 Tray	40MSS2	US11111030
Edwards E2M2 Rough Pump	40MSS2	54939
HP Chem Station Data System	40MSS2	_
HP 6890 GC	40MSS3	US00032758
HP 5973 Mass Selective Detector	40MSS3	US90460025
HP 7683 Auto-injector	40MSS3	US95110858
HP 7683 Tray	40MSS3	US94706602
Edwards HP# G1099-80023 Rough Pump	40MSS3	996318298
HP Chem Station Data System	40MSS3	
HP 6890 GC	40MSS4	US00024414
HP 5973 Mass Selective Detector	40MSS4	US81221586
HP 7683 Auto-injector	40MSS4	US81000351
HP G2614A Tray	40MSS4	CN24822508
Gerstel MACH Unit	40MSS4	1077
Edwards HP# G1099-80023 Rough Pump	40MSS4	
HP Chem Station Data System	40MSS4	

8.2 Chromatography Supplies

Item	Vendor	Model / ID	Catalog #	Description
Analytical Column	Restek	XTI-5 w/ Integraguard	12223-124	30 m, 0.25 mm ID, 0.25 df
Gerstel MACH Column	J&W	DB-5MS	100-2000	30 m, 0.25 mm ID, 0.50 df
Fluorocarbon O-rings	Restek		20377	
Vespel/Graphite Ferrules	Restek		20229	1/16” x 0.4 mm ID
Gooseneck Splitless Liner	Restek		20800	4 mm x 6.5 x 78.5 for Aligent GCs
Guard Column	Restek		20231	0.5 MID
Ferrules	Fisher Scientific		5-5	

8.3 Glassware

Glassware	Description	Vendor / Item # / Description
Volumetric Flasks	10mL, 25mL, 50mL	Class A
Glass Storage Vials	5mL, 10mL, 12mL, with Teflon-lined screw caps	MG Scientific / T102-3-INV, T102-1-INV V138-19, B510-1
Glass Autosampler Vials	2.0 mL with Teflon-lined crimp caps	MG Scientific / V300-3 / V300-20N

8.4 General Supplies

Glassware	Description	Vendor/ Item # / Description
Gas tight syringes	10-µL, 25-µL, 50-µL, 100-µL, 250-µL, 500-µL, and 1,000-µL, as needed, Hamilton or equivalent.	Fisher Scientific / Various
Pipettes	Borosilicate Glass 9" Pipette	MG Scientific / D200-9

9. REAGENTS AND STANDARDS

9.1 Reagents

Reagent	Concentration/ Description	Requirements/ Vendor/ Item #
Dichloromethane		Pesticide Grade or equivalent

9.2 Analytical Standards

9.2.1 Definitions

Standards are required for mass spectrometer tuning, initial calibration, calibration verification standards, second source verification, internal standards, surrogates, and for preparing LCS, MS, and MSD samples. Table 9.1 describes the standards used.

Table 9.1 Standard Definitions and vendors

Standard	Description	Comments
Tune Standard	Decafluorotriphenylphosphine (DFTPP), 4,4'-DDT, pentachlorophenol, and benzidine solution in dichloromethane used to verify ion response ratios and system inertness prior to analysis. [For PAH only analysis, breakdown and tailing factors do not need to be evaluated or controlled]	Must inject no more than 50ng on column. The DFTPP must meet ion ratio criteria as per Section 12.2.1.
Initial Calibration Standards	Standards prepared at varying levels to determine response and retention characteristics of instrument	Method requires a minimum of 5 levels
Continuing Calibration Verification Standard	A calibration standard prepared at mid-level concentration for all target compounds. This standard is used to verify that the instrument response has not changed significantly since the initial calibration was performed.	
Second Source Verification Standard	A standard prepared from a source other than that used for the initial calibration. This mid-level standard verifies the accuracy of the calibration curve.	
Internal Standard	A solution added to all standards, samples, spikes, control samples, and method blanks prior to analysis. This standard is used to adjust response ratios to account for instrument drift.	Naphthalene-d_8 Acenaphthene-d_{10} Phenanthrene-d_{10} Chrysene-d_{12} Perylene-d_{12}
Surrogate Standard	A solution added to all samples, spikes, control samples, and method blanks prior to extraction.	2-Fluorobiphenyl Terphenyl-d_{14} Nitrobenzene-d_5
Spiking Standard	This solution contains all target analytes and is prepared from the same standards as the calibration standards.	

9.2.2 Storage Conditions

Table 9.2 – Analytical Standard Storage Conditions

Standard Type	Description	Expiration	Storage
Stock Solutions	▪ Concentrated reference solution purchased directly from approved vendor	▪ Manufacturer's recommended expiration date for unopened ampulated standards. ▪ All other stock standards must be replaced 1 year after ampule is opened or on expiration date, whichever is sooner.	▪ Manufacturer's recommended storage conditions ▪ When standard is opened, record all information in the standard logbook.
Intermediate and Working Standard Solutions	▪ Reference solutions prepared by dilutions of the stock solution	▪ 1 year from preparation or the expiration date listed for the stock source, whichever is sooner. ▪ Working solutions must be checked frequently and replaced if degradation or evaporation is suspected.	▪ Store in amber vials with Teflon lined screw caps ▪ Manufacturer's recommended storage conditions for stock source solution. ▪ If stock source conditions conflict, store according to method requirements.

9.2.3 Standard Sources

Standards are prepared from commercially available multi-compound stock solutions and neat materials by multiple dilutions. The sources of the stock solutions and neat materials are present in Table 9.3. Recipes for preparing dilutions and working standards, and concentrations for all compounds are presented in Table 10.4. All intermediate standards are prepared using Fisher Optima grade (or better) dichloromethane and stored frozen in glass vials with Teflon lined screw caps or Mininert valves or as recommended by the standard manufacturer.

9.2.4 Stock Standards

Table 9.3 Stock Standards

Standard	Conc.	Purity	Manufacturer	Vendor	Catalog #
DFTPP Tuning Standard	1000 ug/mL	99%	Supelco	Supelco	47548-4
Internal Standard	4000 ug/mL	99%	Restek	Restek	31006
Surrogate Standard	5000 ug/mL	99%	Restek	Restek	31082
Calibration Standard	500 ug/mL	99%	Accustandard	Accustandard	M-610-FL-R-5X
Initial Calibration Verification Standard	2000 ug/mL	99%	Supelco	Supelco	47543-U

9.2.5 Preparation Procedures

9.2.5.1. Intermediate / Working Standard Preparation

Intermediate or working standards are prepared in dichloromethane. Standards made for direct analysis on the GC/MS are made in dichloromethane. Standards made for addition into samples as part of the preparation are made into dichloromethane. Depending on the volume of each solution needed, the standards are brought to volume in volumetric flasks or prepared in smaller, glass vials and brought to volume by additions of solvent with micro syringes.

Volumetric Flask Standard Preparation – Fill appropriate volumetric flask 2/3 full with dichloromethane. Introduce appropriate amount of standard into dichloromethane in flask with a micro-syringe. Dilute to volume with dichloromethane.

9.2.5.2. Calibration Standard Preparation

Calibration standards are made into dichloromethane for the purpose of direct analysis by the analytical instrumentation. The standards must be made in a volumetric fashion. Several alternatives exist but the method employed by Pace – Green Bay utilizes volumetric flasks according to the following procedure. The individual standards can be made according to the details provided Section 10.2.5.3.

9.2.5.3. Preparation of Analytical Standard Solutions

Standards are prepared from commercially available multi-compound stock solutions. The sources of materials, recipes for preparing dilutions and working standards, and concentrations for all compounds are presented below. All standards are prepared using dichloromethane and stored in clear vials with PTFE lined caps.

Storage and Stability of Analytical Standards - All standards must be stored in the dark at less than –10 °C or at a temperature recommended by the manufacturer. They must be replaced every 12 months, or sooner if the standards show signs of degradation. As each standard, from the vendor is opened, record all pertinent information in the stock standard logbook. Record all standard preparations in the working standard logbook.

9.2.5.3.1 DFTPP tuning standard

A Dichloromethane solution containing 50ng/uL of decafluorotriphenylphosphine(DFTPP) is prepared. A stock solution; Supelco cat.# 47548-4; containing DFTPP at 1000ug/mL, is diluted taking 0.500mL and diluting to 10mL of dichloromethane.

9.2.5.3.2 Internal Standard solutions

Stock Solution - Obtained from Restek cat.#31006 containing 1,4-Dichlorobenzene-d4, Naphthalene-d8, Acenaphthene-d10, Phenanthrene-d10, Chrysene-d12 and Perylene-d12 all at 4000ug/mL in dichloromethane.

Water Intermediate Standard - This intermediate standard is prepared by diluting 50uL upto 10mLs of dichloromethane, producing a solution that is 20ug/mL for each component. 10uL of this standard is added to 1mL of every standard, sample, spike and blank analyzed by this method. Producing a on column concentration of 200ug/L.

Soil Intermediate Standard - This intermediate standard is prepared by diluting 500uL upto 1.0mL of dichloromethane, producing a solution that is 2000 ppm for each component. 10uL of this standard is added to 1mL of every standard, sample, spike and blank analyzed by this method. Producing a on column concentration of 20 ppm.

9.2.5.3.3 Surrogate Standard solution

Stock Solution obtained from Restek, cat. #31082 containing 1,2-Dichlorobenzene-d4, Nitrobenzene-d5, 2-Fluorobiphenyl and p-Terphenyl-d14 all at 5000ug/mL in dichloromethane. An intermediate standard is prepared by diluting 300uL up to 10mLs of dichloromethane, producing a standard that is 150ug/mL of each component.

Water Samples

This intermediate is further diluted to produce the daily working standard by diluting 66.7uL of the 150ug/mL intermediate to 50mLs of Dichloromethane. 1.0mL of this daily working standard is spiked into all QC and Samples, producing an on column value of 200ug/L.

Soil Samples

100 uL of the 150 ug/mL intermediate is spiked into all QC and samples, producing an on column value of 15 ug/mL.

9.2.5.3.4 **Initial Calibration Intermediate Standard**

Water Samples

Stock solution is obtained from Accustandard, product # M-610-FL-R-5X, containing the 18 PAH compounds, all at 500ug/mL. The intermediate is prepared by diluting 10uL of the 500ug/L PAH stock, along with 33.5uL of the 150ug/L surrogate intermediate (10.2.5.3.3) upto 10.0mLs dichloromethane, producing a intermediate calibration standard that is 500ug/L of all components.

Soil Samples

Stock solution is obtained from Accustandard, product # M-610-FL-R-5X, containing the 18 PAH compounds, all at 500ug/mL. The intermediate is prepared by diluting 500 uL of the 500 ug/mL PAH Stock Standard along with 50 uL of the 5000 ug/mL B/N Surrogate Stock Solution to 10.0 mL with methylene chloride producing the the high standard of 25 ug/mL. This standard is then further diluted to obtain the concentrations used for calibration.

9.2.5.3.5 **Initial Calibration Working Standards**

9.2.5.3.5.1 Water Samples

The following working calibration standards are prepared by using the intermediate mix listed above (9.2.5.3.4.1):

Standard Concentration (ng on-column)	Amount of Intermediate Standard added	Amount of Intermediate Internal Standard added	**Final Volume**
25	50uL	10uL	1010uL
50	100uL	10uL	1010uL
100	200uL	10uL	1010uL
200	400uL	10ul	1010uL
300	600uL	10uL	1010uL
500	1000uL	10uL	1010uL
CCV – 200	400uL	10uL	1010uL

9.2.5.3.5.2 Soil Samples

The following working calibration standards are prepared by using the intermediate mix listed above (9.2.5.3.4.2):

Standard Concentration (ng on-column)	Amount of Intermediate Standard added	Amount of Intermediate Internal Standard added	Final Volume
0.25	10uL	10uL	1010uL
0.50	20uL	10uL	1010uL
1.0	40uL	10uL	1010uL
4.0	160uL	10ul	1010uL
10.0	400uL	10uL	1010uL
20.0	800uL	10uL	1010uL
25.0	1000uL	10uL	1010uL
CCV – 10.0	400uL	10uL	1010uL

9.2.5.3.6 **Initial Calibration Verification Standard**

9.2.5.3.6.1 Water Samples

Stock Solution is obtained from Supelco, cat# 47543-U, containing the 18 PAH compounds all at 2000ug/mL. A working solution is prepared by diluting 5uL of the 2000ug/mL PAH stock, along with 67uL of the 150ug/mL B/N surrogate intermediate(9.2.5.3.3) up to 50mLs with dichloromethane. This produces an ICV with a concentration of 200ug/L.

9.2.5.3.6.2 Soil Samples

Stock solution is obtained from Supelco, cat # 47543-U, containing the 18 PAH compounds, all at 2000 ug/mL. An intermediate is prepared by diluting 100 uL of the 2000 ug/mL PAH Stock along with 40 uL of 5000 ug/mL B/N Surrogate Stock Solution to 2.0 mL with dichloromethane. To produce the working ICV solution, the above intermediate ICV solution is further diluted by taking 100 uL of the intermediate ICV and diluting to 1.0 mL with dichloromethane to produce a 10 ug/mL working ICV standard .

9.2.5.3.7 **LCS/MS Spiking Standard**

9.2.5.3.7.1 Water Samples

Stock solution is obtained from Accustandard, product # M-610-FL-R-5X, containing the 18 PAH compounds, all at 500ug/mL. Intermediate standard is prepared by diluting 10uL of the 500ug/mL upto 25.0mLs with Dichloromethane. 1.0 mL of this

standard is spiked into all Lab Control and Matrix Spikes, producing a on-column concentration of 200ug/L.

9.2.5.3.7.2 Soil Samples

Stock solution is obtained from Accustandard, product # M-610-FL-R-5X, containing the 18 PAH compounds, all at 500ug/mL. 20 uL of this solution is spiked into all LCS and MS samples, producing an on-column concentration of 10 ug/mL.

10. CALIBRATION

10.1 Tune Verification

The mass spectrometer tune status must be verified prior to initial calibration and at the beginning of each analytical sequence. For analysis by Selective Ion Monitoring, the response ratio criteria for DFTPP may be immaterial unless a custom spectral library were established under SIM conditions. Therefore, unless a program specific requirement mandates ion ratio criteria be followed, the laboratory must analyze a DFTPP standard but only for the purpose of verifying the alignment of the mass spectral axis. If the quality program requires otherwise and the ion ratios do not meet the criteria for the method (see section 12.2.1), follow the equipment manufacturers' instructions for re-tuning the mass spectrometer. The tune status must be verified after the tuning procedures.

Refer to section **12.2 Procedures** for details on the analysis and evaluation of this standard.

10.2 Initial Calibration (ICAL)

10.2.1 Analysis of Standards

An initial calibration curve using a minimum of five points is analyzed prior to analyzing client samples. The lowest concentration must be at or below the equivalence of the standard reporting limit. The lowest calibration point reflects the practical quantitation limit for that compound, a level below which all reported results must be qualified as estimated values. Refer to Tables 11.1 and 11.2 for compound concentrations.

Table 10.1 – Calibration Standard Compound Concentrations for Water Analysis

Analyte	PQL water (ug/L)	Std 1 ug/L	Std 2 ug/L	Std 3 ug/L	Std 4 ug/L	Std 5 ug/L	Std 6 ug/L
Acenaphthene	0.050	0.025	0.050	0.10	0.20	0.30	0.50
Acenaphthylene	0.050	0.025	0.050	0.10	0.20	0.30	0.50
Anthracene	0.050	0.025	0.050	0.10	0.20	0.30	0.50
Benz(a)anthracene	0.050	0.025	0.050	0.10	0.20	0.30	0.50
Benzo(a)pyrene	0.050	0.025	0.050	0.10	0.20	0.30	0.50
Benzo(b)fluoranthene	0.050	0.025	0.050	0.10	0.20	0.30	0.50
Benzo(g,h,i)perylene	0.050	0.025	0.050	0.10	0.20	0.30	0.50
Benzo(k)fluoranthene	0.050	0.025	0.050	0.10	0.20	0.30	0.50
Chrysene	0.050	0.025	0.050	0.10	0.20	0.30	0.50
Dibenz(a,h)anthracene	0.050	0.025	0.050	0.10	0.20	0.30	0.50
Fluoranthene	0.050	0.025	0.050	0.10	0.20	0.30	0.50
Fluorene	0.050	0.025	0.050	0.10	0.20	0.30	0.50
Indeno(1,2,3-cd)pyrene	0.050	0.025	0.050	0.10	0.20	0.30	0.50
2-Methylnaphthalene	0.050	0.025	0.050	0.10	0.20	0.30	0.50
Naphthalene	0.050	0.025	0.050	0.10	0.20	0.30	0.50
Phenanthrene	0.050	0.025	0.050	0.10	0.20	0.30	0.50
Pyrene	0.050	0.025	0.050	0.10	0.20	0.30	0.50
1-Methylnaphthalene	0.050	0.025	0.050	0.10	0.20	0.30	0.50

Table 10.2 – Calibration Standard Compound Concentrations for Soil Analysis

Analyte	PQL soil (ug/kg)	Std 1 (ug/kg)	Std 2 (ug/kg)	Std 3 (ug/kg)	Std 4 (ug/kg)	Std 5 (ug/kg)	Std 6 (ug/kg)	Std 7 (ug/kg)
Acenaphthene	16.7	8.3	16.7	33.3	133.3	333.3	666.7	833.3
Acenaphthylene	16.7	8.3	16.7	33.3	133.3	333.3	666.7	833.3
Anthracene	16.7	8.3	16.7	33.3	133.3	333.3	666.7	833.3
Benz(a)anthracene	16.7	8.3	16.7	33.3	133.3	333.3	666.7	833.3
Benzo(a)pyrene	16.7	8.3	16.7	33.3	133.3	333.3	666.7	833.3
Benzo(b)fluoranthene	16.7	8.3	16.7	33.3	133.3	333.3	666.7	833.3
Benzo(g,h,i)perylene	16.7	8.3	16.7	33.3	133.3	333.3	666.7	833.3
Benzo(k)fluoranthene	16.7	8.3	16.7	33.3	133.3	333.3	666.7	833.3
Chrysene	16.7	8.3	16.7	33.3	133.3	333.3	666.7	833.3
Dibenz(a,h)anthracene	16.7	8.3	16.7	33.3	133.3	333.3	666.7	833.3
Fluoranthene	16.7	8.3	16.7	33.3	133.3	333.3	666.7	833.3
Fluorene	16.7	8.3	16.7	33.3	133.3	333.3	666.7	833.3
Indeno(1,2,3-cd)pyrene	16.7	8.3	16.7	33.3	133.3	333.3	666.7	833.3
2-Methylnaphthalene	16.7	8.3	16.7	33.3	133.3	333.3	666.7	833.3
Naphthalene	16.7	8.3	16.7	33.3	133.3	333.3	666.7	833.3
Phenanthrene	16.7	8.3	16.7	33.3	133.3	333.3	666.7	833.3
Pyrene	16.7	8.3	16.7	33.3	133.3	333.3	666.7	833.3
1-Methylnaphthalene	16.7	8.3	16.7	33.3	133.3	333.3	666.7	833.3

10.2.2 Calibration Response Factors

Response factors (RF) establish the relationship of the instruments response in comparison with the concentration of any given analyte. The RF includes the concentration and response of the internal standard as well. By relating the IS concentration and response in an inverse manner, the target analyte concentration is adjusted to account for drift in the instrument on a per injection basis. As instrument response increases as indicated by the response of the internal standard, the concentration of the target is mathematically decreased, and vice versa.

To calculate the RF for any given calibration standard (or calibration verification standard), tabulate the area response of the characteristic ions against concentration for each compound and each internal standard. Calculate response factors (RF) for each compound relative to one of the internal standards. The internal standard selected for the calculation of the RF for a compound should be the internal standard that has a retention time closest to the compound being measured. Response factors are calculated using the following equation.

$$RF = \frac{A_x C_{is}}{A_{is} C_x}$$

Where:
A_x = Area of the characteristic ion for the compound being measured.
A_{is} = Area of the characteristic ion for the specific internal standard.
C_{is} = Concentration of the specific internal standard (µg/L).
C_x = Concentration of the compound being measured (µg/L).

Most, if not all modern chromatography data systems are capable of calculating this factor and using it to quantify analyte concentrations. The 8270C method has minimum requirements that these response factors must meet in order to be considered valid. The method uses a subset of the target analyte list to evaluate the performance of the system. These compounds are referred to as the System Performance Check Compounds or the SPCCs. The SPCCs serve as an indicator of instrument sensitivity and, by meeting a minimum value, ensure that the laboratory has adequate sensitivity to analyze and reliably report data for environmental samples. For the SIM method, all target compounds are considered to be SPCC compounds and the average RF for each SPCC compound must be as follows:

Naphthalene	≥0.700
2-Methylnaphthalene	≥0.400
Acenaphthylene	≥0.900
Acenaphthene	≥0.900
Fluorene	≥0.900
Phenanthrene	≥0.700
Anthracene	≥0.700
Fluoranthene	≥0.600
Pyrene	≥0.600
Benzo(a)anthracene	≥0.800
Chrysene	≥0.700
Benzo(b)fluoranthene	≥0.700
Benzo(k)fluoranthene	≥0.700
Benzo(a)pyrene	≥0.700
Indeno(1,2,3-cd)pyrene	≥0.500
Dibenzo(a,h)anthracene	≥0.400
Benzo(g,h,i)perylene	≥0.500

Two of the PAH's response factors are allowed to not meet these requirements.

10.2.3 Calibration Curve Fit

The calibration curve is a representation of the relationship of the instrument response and analyte concentration. The curve is used to quantitate the concentration of an unknown based on its response and this known relationship. The curve is produced in several ways depending on the nature of the "goodness of fit".

Average Response Factor (ARF): The average response factor is determined by averaging the response factors calculated for each calibration level for each target analyte. The average RF can be used to calculate the concentration of target analytes in samples provided the criteria are met for consistency in the RFs for any given analyte. An average response factor is the default curve fitting option for calibrations. It is in the most basic sense, a linear regression that is forced through zero at the origin. Because of its simplicity and the interception of the y axis at the origin, this is the preferred technique for curve fitting. A calculation of the percent relative standard deviation (%RSD) is used to determine the acceptability of the use of the ARF (see Table 11.3).

The % RSD is calculated as follows: %RSD = SD*100 / ARF

Where: SD = Standard deviation of the averaged RFs for a given compound

The average response factor is also used to diagnose the integrity of the chromatography system as it relates to calibration linearity. The ***Calibration Check Compounds (CCCs)*** are a subset of the target analyte list that must meet specific criteria (see Table 11.3) for the calibration to be acceptable. For the CCCs, the %RSD for each is compared to the method criteria (≤30% for CCCs). If that of any CCC exceeds the criteria, the system needs to be inspected for potential sources of errors and recalibrated. **For the SIM method, all target compounds are considered CCC compounds.**

Linear Regression: The linear regression calibration curve is derived from a least

squares regression analysis of the calibration points. A calibration curve based on this technique will have the format of y=ax+b where "a" is the slope of the line and "b" is the y intercept. In order to use this curve fit technique, a minimum of 5 calibration points must be available and the origin cannot be included as one of the points. This technique works well for calibrations where the response of the instrument is linear in nature but does not necessarily intercept the y axis at the origin. However, because the linear regression is not forced through the origin, very low levels of contaminants below the response of the lowest calibration point may generate erroneous reportable results. A calculation of the correlation coefficient "r" is used to determine the acceptability of a linear regressed curve. A linear curve maybe used if the RSD is >15%, but <30% (see Table 11.3).

Non-linear Regression: The non-linear regression calibration curve is derived from a least squares regression analysis of the calibration points. A calibration curve based on this technique will have the format of $y= ax^2+bx+c$. In order to use this curve fit technique, a minimum of 6 calibration points must be available and the origin cannot be included as one of the points. This technique works well for calibrations where the response of the instrument gradually decreases with increasing concentrations. Using this technique, an analyst may be able to generate calibration curves with correlation coefficients very close or equivalent to 1.000. However, because the non-linear regression is not forced through the origin, very low levels of contaminants below the response of the lowest calibration point may generate erroneous reportable results. Likewise, high levels of contamination may not be able to be calculated due to regression equations with multiple intercepts of either axis on the calibration plot.

A calculation of the coefficient of determination (COD) is used to determine the acceptability of a non-linear regressed curve (see Table 11.3). Either the low or high calibration points may be dropped to meet linearity criteria provided the laboratory meets the minimum 5 calibration point requirements. Points within the center of the curve may not be dropped unless an obvious problem is discovered and documented. The point must be dropped in its entirety or reanalyzed. Re-analysis should be within the same 12 hour time window and must occur within 8 hours of the original analysis. If not possible, the entire calibration curve must be re-analyzed. Within a new 12 hour window.

10.3 Calibration Verification

10.3.1 Second Source Verification (SCV)

In addition to meeting the linearity criteria, any new calibration curve must be assessed for accuracy in the values generated. Accuracy is a function of both the "fit" of the curve to the points used and the accuracy of the standards used to generate the calibration points. By meeting the fit criteria, the accuracy relative to the goodness of fit is addressed. However, because all calibration points are from the same source, it is possible that the calibration points may meet linearity criteria but not be accurately made in terms of their true value.

Therefore, to assess the accuracy relative to the purity of the standards, a single standard from a secondary source must be analyzed and the results obtained must be assessed relative to the known true value. This step is referred to as ***Secondary Source Verification*** or, alternatively as ***Initial Calibration Verification***. This secondary source must be from an alternative vendor or, in the event an alternative vendor is not available, from a different lot from the same vendor. The accuracy of the standard is assessed as a percent difference from the true value according to the following equation:

$$\% \text{ Difference} = [\text{Result}_{SCV} - \text{TrueValue}_{SCV}] / \text{TrueValue}_{SCV} * 100$$

See Section 10.2.5.3.6 for details on the preparation of this standard. See Table 11.3 for control criteria

10.3.2 Continuing Calibration Verification (CCV)

As part of the analytical process, the instrumentation must be checked periodically to determine if the response has changed significantly since the initial calibration was established. This verification process is known as ***Continuing Calibration Verification***. The validity of the initial calibration is checked at the beginning of every analytical sequence and every 12 hours thereafter for as long as the instrument is analyzing samples and is accomplished by analyzing a midpoint calibration standard (CCV).

The values obtained from the analysis of the CCV are compared to the true values and a percent change calculated. The percent change must meet the method specified criteria for the analysis to proceed for an additional 12 hours.

The actual determination of change in instrument response is based on the type of curve fit used for each analyte. Calibration curves based on an average response factor are assessed based on the percent difference of the RF calculated for the CCV from the average RF established in the initial calibration. Calibration curves based on a linear or non-linear regression are assessed based on the percent drift of the calculated result from the known true value of the standard. The equations for these calculations are as follows:

% Difference: $[RF_{CCV} - AvgRF_{CAL}] / AvgRF_{CALI} \times 100$

% Drift: $[Result_{CCV} - TrueValue_{CCV}] / TrueValue_{CCV} \times 100$

Table 10.3 – Calibration Acceptance and Verification Criteria

Calibration Metric	Parameter / Frequency	Criteria	Comments
Calibration Curve Fit	Average Response Factor Linear Regression Non-linear Regression	%RSD = 15% r = 0.99 COD = 0.99	If not met, try linear regression fit if RSD is >15% and <30%. If not met, try non-linear regression fit If not met, remake standards and recalibrate
System Performance Check Compounds (SPCCs)	All Target compounds	Naphthalene ≥0.700 2-Methylnaphthalene ≥0.400 Acenaphthylene ≥0.900 Acenaphthene ≥0.900 Fluorene ≥0.900 Phenanthrene ≥0.700 Anthracene ≥0.700 Fluoranthene ≥0.600 Pyrene ≥0.600 Benzo(a)anthracene ≥0.800 Chrysene ≥0.700 Benzo(b)fluoranthene ≥0.700 Benzo(k)fluoranthene ≥0.700 Benzo(a)pyrene ≥0.700 Indeno(1,2,3-cd)pyrene ≥0.500 Dibenzo(a,h)anthracene ≥0.400 Benzo(g,h,i)perylene ≥0.500 Two of the PAH's response factors are allowed to not meet these requirements.	Some possible problems are standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, poor purging efficiency, and active sites in the column or chromatographic system.
Calibration Check Compounds (CCCs)	All Target compounds	%RSD < 30%	%RSD for the calibration check compounds (CCC's) must be £**30**% regardless of curve fit used.
Second Source Verification Standard	Immediately after each initial calibration	% Diff ±20%	Acceptance criteria are ±20% for all analytes. See S-ALL-Q-025
Continuing Calibration Verification	Prior to the analysis of any samples and every 12 hours thereafter		If the requirements for continuing calibration are not met, these corrective actions must be taken prior to reanalysis of standards. Only two injections of the same standard are permitted back to back.
	SPCCs	Must meet response criteria listed above	
	Internal Standard RT Internal Standard Response	RT ± 30 sec -50% to + 200%	Use midpoint calibration standard as reference Use midpoint calibration standard as reference
	CCCs	RF ± 20% Diff. Result ± 20% Drift	Use for Avg RF calibration curvesUse for linear and non-linear calibration curves

10.4 Calibration Corrective Actions

10.4.1 Calibration Linearity Problems

10.4.1.1 Check instrumentation/equipment condition.

10.4.1.2 ***Enter maintenance in instrument maintenance logbook.***

10.4.1.3 Perform another initial calibration.

10.4.1.4 No data can be reported.

10.4.1.5 Generate on Non-Conformance Memo.

10.4.2 Secondary Verification Problems

10.4.2.1 Check instrumentation/equipment condition.

10.4.2.2 ***Enter maintenance in instrument maintenance logbook.***

10.4.2.3 Perform another initial calibration.

10.4.2.4 No data can be reported.

10.4.2.5 Generate on Non-Conformance Memo

10.4.3 Continuing Verification Problems

10.4.3.1 Reanalyze the original CCV standard to determine instrument consistency.

10.4.3.2 Prepare and analyze a new CCV standard to determine preparation consistency / standard integrity.

10.4.3.3 Document instrument maintenance

10.4.3.4 Reanalyze CCV standard to determine if maintenance was effective in restoring performance.

10.4.3.5 Complete recalibration of instrument.

10.4.3.6 ***If samples were analyzed in spite of verification failures, note the following exceptions for addressing those results. Deviations from this requirement must be noted on the injection log with a thorough explanation for the deviation from policy.***

Exceptions: If calibration verification is above the upper control limit, samples non-detected for those analytes may be reported without reanalysis.

11. PROCEDURES

11.1 GC/MS System Preparation

11.1.1 Operating Parameters

Configure the GC/MS system to match the following operating parameters based on instrument

configuration. The parameters themselves are saved as a method on the chromatography data system. By loading the last method used, the instrument will auto-configure to match the parameters from the last time the system was operated under that method. Verify that the settings in the software match the appropriate configuration.

Table 11.1 –Instruments and Operating Parameters

Instrument IDs	**Component**	**Settings and Consumables**	
40MSS2	Gas Chromatograph	**Column:** Restek XTI-5 w/ Integraguard 30 m, 0.25 mm ID, 0.25df **Inlet Liner:** Restek 4 mm Single Gooseneck Injection Port Liners **Inlet Seal:** Restek Gold Plated inlet seal **Column Ferrules:** Restek 04.mm Vespel/Graphite	Mass Range: 50-500 AMU Mode: SIM Pressure / Flow: 2.0 mL / min Initial Temperature: 75°C Initial Time: 1.0 min Final Temperature: 20°C / min to 290°C 2 min hold 20°C / min to 340°C 2 min hold Final Time: 18.25 min Injector Temperature: 295°C Transfer Line Temperature: 310°C Source Temperature: 310°C Injector : EPC in Pulsed Splitless Mode, 70 psi until 1.0 min
	Mass Spectrometer	Tune File: Named to date of tune	
	Autosampler	1.0 uL Injection 3 Solvent rinses from each solvent vial	
Instrument IDs	**Component**	**Settings and Consumables**	
40MSS3	Gas Chromatograph	**Column:** Restek XTI-5 w/ Integraguard 30 m, 0.25 mm ID, 0.25df **Inlet Liner:** Restek 4 mm Single Gooseneck Injection Port Liners **Inlet Seal:** Restek Gold Plated inlet seal **Column Ferrules:** Restek 04.mm Vespel/Graphite	Mass Range: 50-500 AMU Mode: SIM Pressure / Flow: 2.0 mL / min Initial Temperature: 75°C Initial Time: 1.0 min Final Temperature: 20°C / min to 290°C 2 min hold 20°C / min to 340°C 2 min hold Final Time: 18.25 min Injector Temperature: 295°C Transfer Line Temperature: 310°C Source Temperature: 310°C Injector : EPC in Pulsed Splitless Mode, 70 psi until 1.0 min
	Mass Spectrometer	Tune File: Named to date of tune	
	Autosampler	1.0 uL Injection 3 Solvent rinses from each solvent vial	
Instrument IDs	**Component**	**Settings and Consumables**	
40MSS4	Gas Chromatograph	**Column:** Gerstel MACH Column DB-5MS 30 m, 0.25 mm ID, 0.50 df **Inlet Liner:** Restek 4 mm Single Gooseneck Injection Port Liners **Inlet Seal:** Restek Gold Plated inlet seal **Column Ferrules:** Restek 04.mm Vespel/Graphite	Mass Range: 50-500 AMU Mode: SIM Pressure / Flow: 2.0 mL / min Initial Temperature: 50°C Initial Time: 30 sec Final Temperature: 50°C / min to 270°C 5°C / min to 280°C 50°C / min to 340°C 129 sec hold Final Time: 10.25 min Injector Temperature: 270°C Transfer Line Temperature: 310°C

			Source Temperature: 310°C Injector : EPC in Pulsed Splitless Mode, 70 psi until 1.0 min
	Mass Spectrometer	Tune File: Named to date of tune	
	Autosampler	1.0 uL Injection 3 Solvent rinses from each solvent vial	

11.2 Tune Verification

At the beginning of each analytical sequence, prior to the analysis of any standards or samples, the mass spectrometer tune conditions must be verified. This is done by analyzing a standard containing DFTPP (refer to table 10.3). The tune verification standard can be combined with the CCV standard provided that the amount of DFTPP introduced into the system meets the criteria in Table 10.1. For semi-volatile analysis, the system must also be verified for inertness **unless PAHs are the only class of analytes to be analyzed**. This is done simultaneously by the inclusion of DDT, benzidine and pentachlorophenol. DDT is used to verify breakdown conditions; benzidine and pentachlorophenol are used to check for tailing due to system activity.

11.2.1 Mass Axis Alignment / Ion Ratio Verification

After the analysis of this standard, the mass spectrum of DFTPP must be evaluated against the following criteria.

Table 11.2

Mass (m/z)	Mass Axis Criteria	Ion Abundance criteria
51	Present	30.0-80.0% of m/z 198
68	-	<2.0% of m/z 69
69	Present	Present
70	-	<2.0% of m/z 69
127	Present	25.0-75.0% of m/z 198
197	-	<1.0% of m/z 198
198	Present	Base peak, 100% relative abundance
199	Present	5.0-9.0% of m/z 198
275	Present	10.0-30.0% of m/z 198
365	-	>0.75% of m/z 198
441	-	Present, but less than m/z 443
442	Present	40.0-110.0% of m/z 198
443	Present	15.0-24.0% of m/z 442

To evaluate the tune spectra, following the operating instructions for the chromatography data system to access the data file and obtain mass spectra for DFTPP. If the software has a program or macro for automatically selecting the spectra and evaluating the response ratios, use this option. Otherwise, the spectra must be obtained in one of the following manners, in the listed order.

1. **Take one scan for DFTPP; or**
2. **Using an average of three scans, centered on the apex of the peak; or,**
3. **Using an average of all scans across the width of the peak, taken at half height; or,**
4. **Using an average of all scans taken across the width of the peak from baseline to baseline.**

A background scan taken immediately before but not including the peak must be subtracted.

Once obtained, evaluate the ion ratios against the criteria listed above. If the ions and ratios meet the criteria, then analysis may proceed for 12 hours. The window for analysis is 12 hours from the injection date / time for the DFTPP tune verification. After that, the tune must be verified again to establish a new analytical window. The same Ion Abundance Criteria used for the DFTPP tune coupled with the initial calibration must be used for all subsequent analyses associated with that initial calibration.

If the tune standard does not meet the criteria, refer to the following corrective actions to address the

problem:

- Retune the mass spectrometer following the equipment manufacturers' instructions. The tune status must be verified after the tuning procedures.
- If this fails, change filament and retune.
- If this fails, take down the mass spectrometer and clean the instrument.

11.3 Calibration Verification

After the instrument tune conditions are verified and the system meets tune criteria, the instrument must undergo calibration verification. If it has already been determined that the instrument needs to be recalibrated, follow the procedures listed in section 11.2.1 (Analysis of Standards). Otherwise, analyze a Continuing Calibration Verification Standard to determine the current calibration status.

If the CCV meets control criteria, the system is deemed to be in control and analysis of samples may commence. If the CCV does not meet control criteria, follow the corrective action procedures listed section 11.4.3 (Continuing Verification Problems). If the tune verification has been combined with the CCV, the 12 hour analysis window begins from the analysis date / time of the CCV.

Note: In situations where the instrument will run unattended (i.e. overnight), the analyst may load sequential (back-to-back) CCVs in anticipation of that the first in the series may fail due to carry over from a previous sample. If so, both CCVs must be evaluated according to the protocol set forth in the Quality Assurance Manual within Section 6 – Equipment and Measurement Traceability.

11.4 Sample Preparation

11.4.1 Samples

11.4.1.1 Water Samples

Aqueous samples are prepared according to EPA Method 3510C. These procedures are contained in a separate standard operating procedure. Refer to S-ALL-GB-O-003 *Separatory Funnel Extraction of Water Samples for Semivolatile Analysis* for details on the preparation of aqueous samples.

Prior to analysis, each sample, MB, LCS, MS, and MSD is spiked with 10uL of the internal standard solution (10.2.5.3.2).

11.4.1.2 Soil Samples

Solid samples are prepared according to EPA Method 3546. These procedures are contained in a separate standard operating procedure. Refer to S-GB-O-045 *Microwave Extraction for the Determination of Polynuclear Aromatic Hydrocarbons and Base/Neutral/Acids in Solid Matrices* for details on the preparation of soil or solid samples.

Prior to analysis, each sample, MB, LCS, MS, and MSD is spiked with 10uL of the internal standard solution (10.2.5.3.2).

11.4.1.3 Dilutions

Dilutions on sample extracts must be prepared in a volumetric fashion. Sample aliquots should be taken in volumetric syringes and brought to volume by the addition of solvent via an appropriate syringe. In the event a dilution is made to bring a target analyte into calibration range, the analyst should make a dilution such that the target analyte is roughly the equivalent of the mid calibration point whenever possible.

If dilutions are made on extracts that already contain internal standards, a proportional aliquot of internal standard solution must be added to the diluted extract based on the

volume of diluent used.

11.5 Sample Analysis

11.5.1 GC/MS System Preparation

11.5.1.1 Operating Parameters – Set up the instrument parameters shown in Table 12.1.

11.5.1.2 System Tuning and GC Performance Checks – Analyze the Tuning Solution and tune the mass spectrometer to meet the criteria shown in Section 12.2.1. Verify acceptable GC system performance as described in Section 12.2.1. Print out a tune report.

11.5.2 Batch Sequence – Generate a sequence to run a batch of samples.

11.5.2.1 Initial Calibration – The typical batch for initial calibration should include:

Tune Standard
Calibration Level 1
Calibration Level 2
Calibration Level 3
Calibration Level 4
Calibration Level 5
Calibration and System Performance Solution

11.5.2.2 Sample Analysis – The typical batch for sample analysis should include the following. Preparation of LCS, MS, MSD, and Duplicate sample extracts is described in the appropriate sample preparation SOP.

Tune Standard
Calibration and System Performance Solution
Instrument Blank
Method Blank
Laboratory Control Sample
Laboratory Control Sample Duplicate
20 samples
Matrix Spike
Matrix Spike Duplicate

11.5.3 Autosampler – Load the autosampler with standards and samples for the batch created above.

11.5.4 Analyze Samples – Analyze all standards, quality control samples, and environmental samples.

11.6 Data Reduction

11.6.1 Qualitative Analysis

Retention Time Comparison: The relative retention time (RRT) of the sample component must be within ±0.06 RRT units of the component in the calibration verification standard. Extracted Ion Current Plots (EICPs) may be used to provide a more reliable assignment of RT in the presence of coeluting components.

Mass Spectrum Comparison: The characteristic ions from the reference mass spectrum are defined as the three ions of greatest relative intensity, or any ions over 30% relative intensity if less than three such ions occur in the reference spectrum. Compounds are identified as present when the following criteria are met.

- The intensities of the characteristic ions of a compound maximize in the same scan or within one scan of each other.
- The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum.
- Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the sum of the two peak heights. When daily check standards meet criteria for resolution, nothing will be done. When daily check standard does not meet the method requirement for resolution, samples running under that check standard will be flagged stating the method requirement for resolution was not met for affected compounds.
- Under SIM conditions, only those ions collected will be present in the spectrum. Therefore, the best benchmark for spectral comparison should be the spectra obtained from the opening CCV. Ion intensity ratios should agree within 30% of those obtained in the standard.
- Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When gas chromatographic peaks obviously represent more than one sample component (i.e., a broadened peak with shoulder(s) or a valley between two or more maxima), appropriate selection of analyte spectra and background spectra is important.

Table 11.3 Ions

Compound	Primary Ion	Secondary Ion
Naphthalene	128	
2-Methylnaphthalene	142	141
1-Methylnaphthalene	142	141
Acenaphthylene	152	
Acenaphthene	154	152
Fluorene	166	165
Phenanthrene	178	
Anthracene	178	
Fluoranthene	202	
Pyrene	202	
Benzo(a)anthracene	228	226
Chrysene	228	226
Benzo(b)fluoranthene	252	
Benzo(k)fluoranthene	252	
Benzo(a)pyrene	252	
Indeno(1,2,3-cd)pyrene	276	
Dibenzo(a,h)anthracene	278	
Benzo(g,h,i)perylene	276	
Nitrobenzene-d(5)-SS	82	
2-Fluorobiphenyl-SS	172	
Terphenyl-d(14)-SS	244	
Naphthalene-d(8)-IS	136	
Acenaphthene-d(10)-IS	164	
Phenanthrene-d(10)-IS	188	
Chrysene-d(12)-IS	240	
Perylene-d(12)-IS	264	

11.6.2 Quantitative Analysis – Quantitation is based on the integrated abundance of the target analyte's quantitation ion using the internal standard technique. See Table 12.4 for Internal Standard Assignments.

Table 11.4 Internal Standard Assignments

Compound	Internal Standard
Naphthalene	Naphthalene-d(8)-IS
2-Methylnaphthalene	Naphthalene-d(8)-IS
1-Methylnaphthalene	Naphthalene-d(8)-IS
Acenaphthylene	Acenaphthene-d(10)-IS
Acenaphthene	Acenaphthene-d(10)-IS
Fluorene	Acenaphthene-d(10)-IS
Phenanthrene	Phenanthrene-d(10)-IS
Anthracene	Phenanthrene-d(10)-IS
Fluoranthene	Phenanthrene-d(10)-IS
Pyrene	Chrysene-d(12)-IS
Benzo(a)anthracene	Chrysene-d(12)-IS
Chrysene	Chrysene-d(12)-IS
Benzo(b)fluoranthene	Perylene-d(12)-IS
Benzo(k)fluoranthene	Perylene-d(12)-IS
Benzo(a)pyrene	Perylene-d(12)-IS
Indeno(1,2,3-cd)pyrene	Perylene-d(12)-IS
Dibenzo(a,h)anthracene	Perylene-d(12)-IS
Benzo(g,h,i)perylene	Perylene-d(12)-IS
Nitrobenzene-d(5)-SS	Naphthalene-d(8)-IS
2-Fluorobiphenyl-SS	Acenaphthene-d(10)-IS
Terphenyl-d(14)-SS	Chrysene-d(12)-IS

Raw Data Results: The GC/MS data system will calculate the concentration of each analyte in the sample extract. If supplied with the preparation parameters, the system may be able to calculate the results back to the original matrix. The calculation for the concentration of the target analyte in the original matrix is listed below and is based on the calibration table in units of ppm (ug/mL).

If the initial analysis of the sample or a dilution of the sample has a concentration that exceeds the calibration range, the sample must be analyzed at a higher dilution. All dilutions should keep the response of the major constituents near the middle of the linear range of the curve.

11.6.2.1 Results Calculation – Aqueous Sample:

$$\text{Concentration } (\mu g/L) = \frac{(A_x)(I_s)}{(A_{is})(RF)(V_o)}$$

Where:

A_x = Area of characteristic ion for compound being measured.
I_s = Amount of internal standard injected (ng).
A_{is} = Area of characteristic ion for the internal standard.
RF = Average Relative Response factor for compound being measured.
V_o = Volume of water purged (ml), taking into consideration any dilutions made.

11.6.2.2 Soil/ Solid calculations:

$$Low \text{ Conc. (ug/kg)} = \frac{(A_x)(I_s)}{(A_{is})(RF)(W_s)}$$

Where:

A_x, I_s, A_{is}, RF = Same as in water and water-miscible waste above.
V_t = Volume of total extract (ml).
V_i = Volume of extract added (ml) for purging.
S_v = Volume of diluted extract.
W_s = Weight of sample extracted or purged (g). The wet weight or dry weight may be used, depending upon the specific applications of the data.

12 QUALITY CONTROL

12.1 Instrument Quality Control: Refer to Table 11.3 for initial and continuing calibration criteria and corrective actions.

12.2 Batch Quality Control

Table 12.1 – Batch Quality Control Criteria

QA Sample	Components	Frequency	Acceptance Criteria	Corrective Action
Method Blank (MB)	Reagent water	One (1) per 20 samples	1) Target analytes must be less than reporting limit. 2) If results are reported to MDL, target analytes in MB should be non-detect	1) Qualify results and / or re-extract associated samples. ***Exceptions:*** 1) If sample ND, report sample without qualification 2) If sample result >20x MB result report sample without any qualifier. 3) If sample result <20x MB detects, report sample with appropriate qualifier to indicate an estimated value. Client must be alerted and authorize this condition.
Laboratory Control Sample (LCS)	Full Target List compounds	One (1) per batch of up to 20 samples. LCSD is performed for water samples where no volume provided for Ms/MSD.	Laboratory derived limits Full Target List: Marginal exceedances allowed according to NELAC 2003 Chap 5 D.1.1.2.1.e	1) If LCS passes,no further action necessary. 2) Check spike solution .or appropriately qualify data. 3) Re-extract samples where possible or appropriately qualify data. ***Exceptions:*** 1) If LCS rec > QC limits and these compounds are non-detect in the associated samples, the sample data may be reported with appropriate data qualifiers.
Matrix Spike (MS)	Full Target List compounds	One (1) per batch of up to 20 samples, must include one TCLP MS for any analyzed in sequence	Laboratory derived limits	1) If LCS and MBs are acceptable, the MS/MSD chromatogram should be reviewed and it may be reported with appropriate footnote indicating matrix interferences. Qualify the parent sample only.
MSD / Duplicate	MS Duplicate *OR (alternative)* Sample Dup	One (1) for every 5% of all environmental samples	Laboratory Derived Limits	1) Report results with an appropriate footnote.

12.3 Sample Quality Control

Table 12.2 – Sample Quality Control criteria

QA Sample	Components	Frequency	Acceptance Criteria	Corrective Action
Internal Standard	Naphthalene-d_8 Acenaphthene-d_{10} Phenanthrene-d_{10} Chrysene-d_{12} Perylene-d_{12}	Added to all standards, samples, spikes, control samples, and method blanks prior to analysis	**Retention Time:** RT must be ± 30 seconds from last calibration check on all samples	**Retention Time Failure:** 1) If matrix interference is NOT probable, the analytical system must be checked for source of retention time shifting. 2) Affected samples should be reanalyzed in the absence of an obvious instrument or matrix related interference.
Surrogate Standards	2-Fluorobiphenyl Terphenyl-d_{14} Nitrobenzene-d_5	Added to all samples, spikes, control samples and method blanks prior to extraction.	Laboratory derived limits	Assess impact of sample matrix In the absence of obvious matrix interference (high background, extremely dark extract), re-extract sample. ***Exceptions:*** Surr rec above criteria and target compounds < RL, result may be reported with appropriate footnote. Surr rec out of control due to obvious sample matrix interference (i.e. co-elution), report results with appropriate footnote. One surrogate compound is allowed to be out of control. If two or more surrogate compounds are out of control, the samples must be re-extracted and reanalyzed. If there is insufficient sample available for re-extraction, the data must be appropriately qualified.

13 METHOD PERFORMANCE

13.1 Method Detection Limit (MDL) Study: An MDL study must be conducted annually per S-ALL-Q-004, Method Detection Limit Studies for each matrix per instrument.

13.2 Demonstration of Capability (DOC): Every analyst who performs this method must first document acceptable accuracy and precision by passing a demonstration of capability study (DOC) per S-ALL-Q-020, Orientation and Training Procedures.

13.3 Method Modifications

13.4 Method modifications for EPA method 8270C are as follows:

13.5 Modifications should be targeted to improve quality, efficiency or the cost effectiveness of the procedure.

13.6 All major modifications to the procedure that may directly affect data quality must be thoroughly documented. A new demonstration of capability and equivalency must be performed and kept on record.

13.7 Procedures identified as "Best Practices" by the PACE 3P Program will be incorporated into this document as minimum requirements for Pace laboratories.

14 POLLUTION PREVENTION AND WASTE MANAGEMENT

14.1 Procedures for handling waste generated during this analysis are addressed in ALL-S-002, Waste Handling.

14.2 In order to minimize the amount of waste generated during this procedure, analyst should prepare reagents in an amount which may be used in a reasonable amount of time (i.e. before a reagent expires)

14.3 The company wide Chemical Hygiene and Safety Manual contains additional information on pollution prevention.

15 REFERENCES

15.1 USEPA, SW-846, Method 8270C, "Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS), December 1996.

15.2 USEPA, SW-846, Method 8000B, "Determinative Chromatographic Separations", December 1996.

16 TABLES, DIAGRAMS, FLOWCHARTS, ATTACHMENTS, APPENDICES, ETC.

Not applicable to this SOP.

17 REVISIONS

Document Number	Reason for Change	Date
SOT-ALL-O-008-rev.00	Restructured document format. Added tables and other content to create an "SOP Template" in which local edits are allowed. Modified signature page to include department manager and SOP template number. Updated SOP template number. Made the tuning criteria red so edits can be made to reflect local tuning criteria used. Updated calibration sections with new calibration policies described in the PASI Quality Manual revision 10.0.	28Nov2006
S-ALL-O-008-Rev.00	First issue in Template format.	15May2008

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STANDARD OPERATING PROCEDURE

Total Cyanide using Micro-Distillation and Lachat 8000 Flow Injection

Reference Method: SW846 9012A and EPA 335.4

SOP NUMBER:	S-GB-I-043-REV.01
EFFECTIVE DATE:	Date of Final Signature
SUPERSEDES:	S-GB-I-043-REV.00

APPROVAL

Nils Melberg, Laboratory General Manager — Date: 11/06/08

Kate Grams, Laboratory Quality Manager — Date: 12/29/08

Chad Rusch, Department Manager — Date: 11/5/08

ANNUAL REVIEW

SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE APPROVAL. SOP IS VALID FOR ONE YEAR FROM DATE OF LAST SIGNATURE.

Signature	Title	Date

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1. Purpose

This Standard Operating Procedure (SOP) describes the analyses of Total Cyanide using Micro-Distillation and Analyzed by Lachat 8000 Flow Injection using methods SW846 9012A and EPA Method 335.4.

2. Scope and Application

2.1 This SOP is applicable the analysis of Cyanide in drinking, ground, surface, and saline waters, domestic and industrial wastes, soils, and TCLP, SPLP, ASTM extracts. The applicable range is MDL to the top standard in the curve. The current Pace Reporting Limit is 20 ug/L. The current MDL can be found in EpicPro.

2.2 This SOP utilizes the Lachat 8000 analyzer.

3. Summary of Method

3.1 By means of a passive miniature distillation device, MICRO DIST, cyanide in the sample is released by digesting and acidifying cyanide complexes, and converting them to hydrocyanic acid (HCN). The cyanide ion is trapped in a 1.0 M sodium hydroxide absorbing solution, which is diluted to 0.25M solution during distillation. By means of flow injection analysis, the 0.25M Noah distillate is converted to cyanogens chloride by reaction with chloramines-T, pyridine and barbituric acid to give a red-colored complex. The absorbance of this complex is measured at 570 nm by measuring the peak area resulting from the sample. The peak area is proportional to the concentration of the cyanide in the sample.

3.2 All samples must be distilled before analysis.

4. Interferences

4.1 Most non-volatile interferences are eliminated or minimized by the distillation procedure. Some of the known interferences are aldehyde, nitrate-nitrite, and oxidizing agents, such as chlorine, thiosulfate, and sulfide.

4.2 Oxidizing agents such as chlorine decompose most cyanide. Test a drop of the sample with potassium iodine-starch paper (KI-starch paper) at time of collection; a blue color indicates need for treatment. Add ascorbic acid, a few crystals at a time, until a drop of sample produces no color changes; then add an additional 0.06 g ascorbic acid per liter of sample.

4.3 False positive results may be obtained by samples that contain Nitrate/or nitrite. Sulfamic acid is added to all samples prior to distillation to eliminate this interference.

4.4 Sulfides adversely affect the procedure by producing hydrogen sulfide during distillation. If a drop of sample on lead acetate paper indicated the presence of sulfide, treat the stabilized sample (pH >12) with bismuth nitrate. Repeat until a drop on the lead acetate paper does not darken. Filter sample to remove precipitate and use filtrate as sample to be distilled.

5. Safety

5.1 All samples, standards, and reagents should be treated as hazardous. Safety glasses, gloves, and lab coats are to be worn. The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined. However, each chemical compound should be treated as a potential health hazard. Exposure to these chemicals must be reduced to the lowest possible level by a safe technique. Special care should be taken when handling the high concentration acids and oxidizing reagents used for sample digestion.

5.2 The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of any chemical. A reference file of Material Safety Data Sheets (MSDS) and a formal safety plan are made available to all personnel involved in chemical analysis and should be consulted prior to handling samples and standards.

5.3 Excess reagents, samples and method process wastes are characterized and disposed of in an acceptable manner. For further information on waste management consult the current version of ALL-S-002, *Waste Handling*.

5.4 The laboratory Chemical Hygiene Plan/Health and Safety Plan contains additional information on pollution prevention

6. Definitions

Definitions can be found in Section 10 of the most recent version of the Pace Analytical Services, Inc. Quality Manual.

7. Sample Collection, Preservation and Handling

Table 1. Sample Collection, Preservation and Handling

Matrix	Prep Method	Container(s)	Preservation Hold Time	Shipment Conditions	Lab Storage Conditions
Aqueous	SW-846 9012A EPA 335.4	250 ml plastic containers	pH >12; NaOH 14 days	On ice 4+/- 2° Celsius	4°C
Solid	SW-846 9012A	glass or plastic containers	None 14 days	On ice 4+/- 2° Celsius	4°C

Reagents and Standards

Table 2. REAGENTS

Reagent	Alias	Concentration	Directions found in:
Potassium Cyanide	Stock Standard	Neat	
Potassium Cyanide	Second Source Stock Standard	Neat	
Potassium Hydroxide		Neat	
Sodium Hydroxide		Neat	
Noah – 0.25 N	Carrier Solution	0.25 N	Table 4
Deionized Water			
Potassium Phosphate, Monobasic, (KH_2PO_4)		Neat	
Phosphate Buffer	Buffer Solution	0.71 M	Table 4
Chloramine-T hydrate		Neat	
Chloramine-T Reagent	Color Reagent		Table 4
Barbituric Acid		Neat	
Pyridine		Neat	
Hydrochloric Acid		12 M	
Pyridine-Barbituric Acid Reagent	Pyridine-Barbituric Acid Reagent		Table 4
p-dimethylaminobenzalrhodanine	Indicating solution		Table 4
Standard Silver Nitrate Solution		0.0192 N	
Magnesium Chloride Hexahydrate		Neat	
Sulfuric Acid		Concentrated	
Sulfuric Acid/Magnesium Chloride Solution	Releasing Agent	7.11 M H_2SO_4 0.79 M MgCl	Table 4
Nitrate Bismuth		Neat	
Lead Acetate Paper		Neat	
Sulfamic Acid		Neat	
Sea Sand (Washed)*		Neat	

***** Washed with 50% sulfuric acid (v/v) solution and then dried.

Table 3. STANDARDS

Standard	Concentration	Direction found in Section:	Alias
Potassium Cyanide	1000 mg/L	Table 5	Stock Standard
Potassium Cyanide Must be different Lot # than Stock	1000 mg/L	Table 5	Second Source Stock Standard
Level 1 Calibration Standard	0.40 mg/L	Table 5	Cal Std. 1
Level 2 Calibration Standard	0.20 mg/L	Table 5	Cal Std. 2
Level 3 Calibration Standard	0.10 mg/L	Table 5	Cal Std. 3
Level 4 Calibration Standard	0.05 mg/L	Table 5	Cal Std. 4
Level 5 Calibration Standard and RLVS Standard	0.02 mg/L	Table 5	Cal Std. 5
Level 6 Calibration Standard	0.00 mg/L	Table 5	Cal Std. 6
Initial Calibration Verification – 1	0.10 mg/L	Table 5	ICV – 1
Initial Calibration Verification – 2	0.05 mg/L	Table 5	ICV – 2
Continuing Calibration Verification	0.20 mg/L	Table 5	CCV
Working Standard (1)	10 mg/L	Table 5	Working Standard (1)
Secondary Working Standard (1)	100 mg/L	Table 5	Secondary Working Standard (1)
Secondary Working Standard (2)	1.2 mg/L	Table 5	Secondary Working Standard (2)
Matrix Spike/Matrix Spike Duplicate – Liquid	0.10 mg/L	Table 5	MS/MSD-Liquid
Matrix Spike/Matrix Spike Duplicate – Solid	0.10 mg/L	Table 5	MS/MSD-Solid
Laboratory Control Spike/Laboratory Control Spike Duplicate - Liquid	0.10 mg/L	Table 5	LCS/LCSD-Liquid
Laboratory Control Spike/Laboratory Control Spike Duplicate - Solid	0.10 mg/L	Table 5	LCS/LCSD-Solid

Table 4. PREPARATION OF REAGENTS

Standard	Alias	Final Concentration	Directions	Final Volume
NaOH – 0.25 N	Carrier Solution	0.25 N	Weigh 10 g of neat NaOH into ~ 500 ml DI water in 1 L plastic container. Dilute to volume. Prepare fresh monthly.	1000 ml
Phosphate Buffer	Buffer Solution	0.71 M	Weigh 97 g of neat KH_2PO_4 into ~ 500 ml DI water in 1 L volumetric flask. Dilute to volume. Shelf life = 1 month.	1000 ml
Chloramine-T Reagent	Color Reagent		Weigh 2 g of neat Chloramine-T hydrate into ~ 250 ml DI water in 500 ml volumetric flask. Dilute to volume. PREPARE DAILY!	500 ml
Pyridine-Barbituric Acid Reagent	Pyridine-Barbituric Acid Reagent		MAKE UNDER HOOD!!!!!!! Weigh 15 g barbituric acid into a 1 L beaker Add 100 ml DI. Add 75 ml pyridine, mix to dissolve Add 15 ml conc. HCL. Transfer to 1 L volumetric flask and dilute to volume. Shelf life = 1 month.	1000 ml
p-dimethylaminobenzalrhodanine	Indicator Solution		Weigh 20 mg of neat p-dimethylaminobenzalrhodanine into a 100 ml volumetric flask. Dilute into 100 ml acetone. Shelf life = 1 year.	100 ml
Sulfuric Acid/Magnesium Chloride Solution	Releasing Agent	7.11 M H_2SO_4 0.79 M MgCl	Weigh 110.8 g DI water in beaker. Add 32.2 g Magnesium Chloride Hexahydrate ($MgCl_2.6H_2O$). Slowly add 139 g concentrated H_2SO_4. Transfer to automatic pipette container. Cool. Shelf life = 1 year.	200 g

Table 5. PREPARATION OF STANDARDS

Standard	Alias	Final Concentration	Directions	Final Volume
Potassium Cyanide	Stock Standard.	1000 mg/L	POISON!!!!! Weigh 2.51 g of neat KCN and 2 g of neat KOH into ~900 ml DI water in 1 L volumetric flask. Dilute to volume. Shelf life = 3 month. Standardize against AgNO3. If concentration of stock standard is between 995 – 1005 mg/L then use 1ml of stock solution.	1000 ml
Potassium Cyanide	Second Source Stock Standard	1000 mg/L	POISON!!!!! Weigh 2.51 g of neat second source KCN and 2 g of neat KOH into ~900 ml DI water in 1 L volumetric flask. Dilute to volume. Shelf life = 3 month. Standardize against AgNO3. If concentration of stock standard is between 995 – 1005 mg/L then use 1ml of stock solution.	1000 ml
Working Standard (1)	Working Standard (1)	10 mg/L	Pipette 1.0 ml stock standard into 100 ml volumetric flask. Dilute to volume with 0.25N NaoH. PREPARE DAILY!	100 ml
Working Standard (2)	Working Standard (2)	1.2 mg/L	Pipette 1.2 ml working standard (1) into 100 ml volumetric flask. Dilute to volume with DI. PREPARE DAILY!	100 ml
Secondary Working Standard (1)	Secondary Working Standard (1)	100 mg/L	Pipette 10 mL second source stock standard into 100 ml volumetric flask. Dilute to volume with DI. PREPARE DAILY!	100 ml
Secondary Working Standard (2)	Secondary Working Standard (2)	1.2 mg/L	Pipette 1.2 ml secondary working standard (1) into 100 ml volumetric flask. Dilute to volume with DI. PREPARE DAILY!	100 ml
Level 1 Calibration standard	Cal. Std. 1	0.40 mg/L	Pipette 4.0 mls of working standard (1) into 100 ml volumetric flask. Dilute to volume with 0.25N NaOH. Prepare monthly.	100 ml
Level 2 Calibration Standard	Cal. Std. 2	0.20 mg/L	Pipette 2.0 mls of working standard (1) into 100 ml volumetric flask. Dilute to volume with 0.25N NaOH. Prepare monthly.	100ml
Level 3 Calibration Standard	Cal. Std. 3	0.10 mg/L	Pipette 1.0 mls of working standard (1) into 100 ml volumetric flask. Dilute to volume with 0.25N NaOH. Prepare monthly.	100 ml
Level 4 Calibration Standard	Cal. Std. 3	0.050 mg/L	Pipette 0.50 mls of working standard (1) into 100 ml volumetric flask. Dilute to volume with 0.25N NaoH. Prepare monthly.	100 ml
Level 5 Calibration Standard and RLVS Standard	Cal. Std. 5	0.020 mg/L	Pipette 0.20 mls of working standard (1) into 100 ml volumetric flask. Dilute to volume with 0.25N NaoH. Prepare monthly.	100 ml
Level 6 Calibration Standard	Cal. Std. 6	0.000 mg/L	Use 0.25N NaOH only.	100 ml
Continuing Calibration Verification	CCV – 1	0.20 mg/L	Pipette 2.0 mls of working standard (1) solution into 100 ml volumetric flask. Dilute to volume with 0.25N NaOH. Prepare monthly.	100 ml
Initial Calibration Verification –1	ICV – 1	0.10 mg/L	Pipette 0.50 mls of secondary working standard (2) solution into sample tube. Dilute to volume with DI. Prepare daily.	6 ml
Initial Calibration Verification –2	ICV – 2	0.050 mg/L	Pipette 0.25 mls of secondary working standard (2) solution into sample tube. Dilute to volume with DI. Prepare daily.	6 ml
Matrix Spike/Matrix Spike Duplicate – Liquid	MS/MSD - Liquid	0.10 mg/L	Pipette 0.50 mls of working standard (2) into sample tubes. Dilute to volume with sample. Prepare daily.	6 ml
Matrix Spike/Matrix Spike Duplicate – Solid	MS/MSD-Solid	0.10 mg/L	Pipette 0.50 mls of working standard (2) into sample tubes. Add solid sample. Dilute to volume with DI. Prepare daily.	6 ml
Laboratory Control Spike/Laboratory Control Spike Duplicate – Liquid	LCS/LCSD-Liquid	0.10 mg/L	Pipette 0.50 mls of working standard (2) into sample tubes. Dilute to volume with DI. Prepare daily.	6 ml
Laboratory Control Spike/Laboratory Control Spike Duplicate – Solid	LCS/LCSD-Solid	0.10 mg/L	Pipette 0.50 mls of working standard (2) into sample tubes. Dilute to volume with DI. Prepare daily.	6 ml

8. Equipment and Supplies

Table 6. EQUIPMENT

Equipment	Manufacturer	Model(s)/Catalog number •
Lachat 8000	Lachat	Lachat
Micro-Distillation	Lachat	Micro Distillation
Top loading Analytical Balance	Mettler	BA310P
1000 µL Pipette	Eppendorf	05-402-76 (Fisher Cat#)
500 µL Pipette	Eppendorf	05-402-72 (Fisher Cat#)
250 µL Pipette	Eppendorf	05-402-69 (Fisher Cat#)
Repipetors (0.5 - 5.0mL)	Barnstead/Thermolyne	13-687-33 (Fisher Cat#)
Vented Hood	Hamilton	
Spoonula (Lab Spoon)	FisherBrand or equivalent	14-375-10 (Fisher Cat#)
Gloves – Heat Resistant		
Cyanide Manifold	Lachat	10204-00-1-A
Interference filter – 570 nm	Lachat	

- Or equivalent

Table 7. Supplies

Supplies	Manufacturer	Catalog number •
Distillation tubes	Lachat	A17001
Culture Tubes 13X100	Fisher	71500 13100
Volumetric Flasks	Fisher	Various
Parafilm	Fisher	
Sea Sand	Fisher	S25-3
• Or equivalent		

9. Calibration and Standardization

9.1 Instrument Settings

Sample throughput:	80 samples/h, 45s/sample
Pump and Speed:	35
Cycle Period:	45
Peak Base Width:	39 S
% Width Tolerance:	100
Threshold:	25000
Inject to start of peak:	24 s
Chemistry:	Direct

9.2 Follow steps 11.2 –11.2.30 to run calibration curve.

9.3 Calibration Criteria

Calibration Rep Handling:	Replace
Calibration Fit Type:	1st Order Polynomial
Weighting Method:	None
Force through zero:	No

9.3.1 The instrument must be calibrated every time it is set up.

9.3.2 The correlation coefficient must be at least 0.995.

9.3.3 The calibration curve must be a minimum of 5 standards plus a blank.

9.3.4 Place working standards in decreasing concentration.

9.4 Stock Standard verification

9.4.1 The stock standard must be standardized monthly to verify the concentration. **This standardization must be documented in the logbook.**

9.4.2 Standardize the stock standard against 0.01920 N Silver Nitrate ($AgNO_3$) at the time of preparation and on a monthly basis. Using a buret, titrate a 1.0 mL aliquot of the cyanide stock diluted to 100 ml standard with 0.25 N NaOH and 0.5 mL indicator solution, with $AgNO_3$ solution to a salmon colored endpoint. **Record the volume of titrant used in the logbook**.

9.4.3 Perform the titration along with a blank of 100 mL 0.25 N NaOH with 0.5 mL indicator solution. Subtract the volume of titrant used on the blank from the amount used to titrate the sample and calculate the concentration of the Stock Standard. **Record the concentration of the stock cyanide solution in the logbook**. **1 mL $AgNO_3$ = 1 mg CN. If after performing the titration, 1 mL $AgNO_3$ does not equal 1 mg CN, the CN stock standard needs to be discarded and reprepared.**

10. Procedure

10.1 Distillation Procedure

NOTE: Document all sample volumes, standards and reagents used in the distillation on the prep log.

This section of the SOP details the steps in distilling the samples before analysis. Samples must be checked for sulfides before distilling. If sulfides are present and the samples treated with bismuth nitrate, the entire calibration curve must be similarly treated and distilled. Refer to section 4.4 for procedure. In the following procedure, **D** and **M** refer to the marks on the collector tube. **D** means "distillation" end, and **M** means "measuring" end.

10.1.1 Set the controller to 120°C, allow the heater to warm up. The operating temperature of the distillation block needs to be verified annually.

10.1.2 Label tubes with the **M** end up, place as many properly labeled collector tubes as you have samples into the collector tube rack.

10.1.3 For liquid samples, place a drop of sample on lead acetate paper. If the paper darkens this indicate the presence of sulfide. Treat the stabilized sample (pH >12) with bismuth Nitrate. Repeat until a drop on the lead acetate paper does not darken. Filter sample to remove precipitate and use filtrate as sample to be distilled. Place 6 ml of sample into each properly labeled sample tube using a calibrated automatic pipette. Add ~ 0.1 g sulfamic acid.

NOTE: If samples contain and are treated for sulfide, the entire calibration curve must also be similarly treated and distilled along with the samples.

10.1.4 For soil samples, weigh out 0.20 g of soil or sludge to the nearest 100th on a calibrated balance and dilute to 6 ml with deionized water tube with a calibrated automatic pipette into each properly labeled sample tube. Add ~ 0.1 g sulfamic acid.

10.1.5 For liquid samples, prepare one method blank by adding 6 mls of DI water to properly labeled sample tube using a calibrated automatic pipette. Add ~ 0.1 g sulfamic acid.

10.1.6 For soil samples, prepare one method blank by weighing out 0.20 g of washed sea sand to the nearest 100th on a calibrated balance and dilute to 6 ml with deionized water tube with a calibrated automatic pipette into a properly labeled sample tube. Add ~ 0.1 g sulfamic acid.

10.1.7 For liquid samples, prepare one LCS (and one LCSD if needed/requested) by pipetting 6.0 ml of deionized water, ~ 0.1 g sulfamic acid, and 0.50 ml of 1.2 mg/L CN standard into two properly labeled sample tubes using a calibrated automatic pipette. See Table 5.

10.1.8 For soil samples, prepare one LCS (and one LCSD if needed/requested) by weighing out 0.20 g of washed sea sand to the nearest 100th on a calibrated balance. Bring to 6 ml volume with deionized water. Add ~ 0.1 g sulfamic acid and 0.50 ml of 1.2 mg/L CN standard using a calibrated automatic pipette into each properly labeled sample tube. See Table 5.

10.1.9 For liquid samples, select one parent sample and prepare one MS/MSD pair per 10 samples by adding 6.0 ml of sample, ~ 0.1 g sulfamic acid, and 0.50 ml of 1.2 mg/L CN standard into two properly labeled sample tubes using a calibrated automatic pipette. See Table 5.

10.1.10 For soil samples, select one parent sample and prepare one MS/MSD pair by weighing out 0.20 g of sample to the nearest 100th on a calibrated balance. Bring to 6 ml volume with deionized water. Add ~ 0.1 g sulfamic acid and 0.50 ml of 1.2 mg/L CN standard using a calibrated automatic pipette into each properly labeled sample tube. See Table 5.

10.1.11 Using a calibrated pipette, add 0.75 ml of 7.111 M sulfuric acid / 0.79 M magnesium chloride solution to the sample tube using the supplied automatic pipette.

10.1.12 Immediately push the **D** end of a Cyanide-1 collector tube over the open end of each sample tube to start the seal.

10.1.13 Place the assembly in the press, putting the sample tube through the hole in the white base. Before pressing, the user should grip the collector tube firmly at the breakaway point to keep the tube from shifting during the pressing procedure.

10.1.14 The pressing motion should be a smooth constant pressure, which is just enough to slide the sample tube inside the collector tube. A jerky, forced motion may cause added strain to the tube and could potentially crack it. Press down on the handle until the stop ring on the sample tube hits the **D** end of the collector tube.

10.1.15 Put on heat-resistant gloves. Push the sample tube and **D** end of each tube all the way into the preheated block so that the collector tube stop ring touches the block. Placing 21 tubes should take less than one minute.

10.1.16 Set the timer for 30 minutes.

10.1.17 When 30 minutes is up, remove the first tube, use heat-resistant gloves, from the block and immediately pull its sample tube using a downward twisting motion as opposed to a sideways motion. You must remove the sample tube within 4 seconds of removing it for the block or suck-back of the sample will occur. Dispose of the sample tube and the hot solution.

10.1.18 Invert each collector tube and place it into the collector tube rack, now with the **D** end up. It should take less than two minutes to pull and separate all 21 tubes.

10.1.19 Hold collector tube horizontally and rinse its walls with the distillate in order to homogenize it. Roll tube in order to collect all droplets from the walls of the tube. Return the tube to an upright position so the **D** end is up.

10.1.20 With the **D** end up, break the collector tube in half by pulling the **D** end hard toward yourself to break it, the twisting and tearing off the **D** end. Discard the **D** end.

10.1.21 In the **M** end of the tube dilute to the 6.0 ml mark with DI water. This results in the original sample volume, but now in 0.25 M NaOH. Pour in culture tube.

10.1.22 Parafilm if sample determination is not done immediately.

10.2 Basic System Operation – Analytical

This portion of the SOP is designed to allow the user to set up and run a method, print a sample report, then shut down using the more basic software functions. For a more detailed explanation of the many other options, the user should refer to the Lachat Software Reference Manual. It is assumed that a method program has already been created for the chemistries you wish to run.

10.2.1 Turn on computer with ON/OFF button. Turn on printer. The power to the monitor, autosampler and reaction module is controlled with a multi-outlet noise filter and surge suppresser located behind the reaction module. Turn the red switch to “ON”.

10.2.2 Allow the autosampler to perform its startup routine and wait until the autosampler stops with the probe above the wash bath.

10.2.3 Log into the Network with your Login name and password. Windows program will be activated. Program Manager screen will appear. Click twice on Lachat Instruments. Click twice on the Omnion FIA icon on the Lachat Instruments window. The startup box will come up, and then click on **‘OK’**. The autosampler probe will go into the wash bath and dilutor activity may be heard. The injection valves may turn to the Inject state if they were not already there.

10.2.4 To encourage GALP (Good Automated Laboratory Practice), Omnion requires that the operator “Log-in” every time with name and password. Enter your assigned name and password in the correct case in the spaces indicated and then click on the **‘OK’** button.

10.2.5 After you have logged in, the Omnion FIA Main Menu will appear on the screen. The header should contain the serial number of the software key. No messages should be seen about the SS420 boards, or any serial port failures. Click on the Instrument button labeled ‘FIA Instrument 1’.

10.2.6 Each valve allocated to this instrument will be cycled from Load to Inject and Load to Inject again. This is a test of the valves and if no messages are received about failing valves, then they are OK.

10.2.7 If a valve fails, a box will tell you which channel's valve failed. You can press OK and continue. You should arrange for service for the failing valve by calling Lachat Instruments.

10.2.8 After the injection valves are tested, an instrument window for FIA Instrument 1 will appear. Omnion will automatically open the last Method, Tray, DQM Plan and Data File used. Arrow up to 'File" and click. When window appears click on '**Open Method'**.

10.2.9 Under Open Method File Directories, click on **c:\omnion\methods** and then click on the method you will be running. A list of methods will appear. Highlight the appropriate one in the **File Name** box and click on **'OK'**.

10.2.10 The Method will open and the **Analyte Table** will appear. It will show the Analyte Name and which Channel it is run on. The concentration Units and concentration of the calibration standards will be listed. To the far right will be the timing periods, which the instrument uses to detect the peaks.

10.2.11 Click on **'File'** again and then **'Open Tray'**. The **'Open Tray File'** window will come up. Directories will be **c:\omnion\trays\method**. Click on the method you will be running. A list of previous trays for that particular method will appear. Click on a recent **tray file name and** the on **'OK'** to call it up. Edit this tray below the Calibration Standards with the sample numbers you will be running. Also edit any dilutions that will be required.

10.2.12 Click on **Save Tray As** and edit name of tray to reflect today's' date and letter to reflect which run: YYMMDDL. L is the sequence of the tray that day i.e., a=first tray, b=second tray and so on. Example: 960730a.

10.2.13 Click on **File** again and then on **Open DQM**. The Open DQM File window will come up. Directories will be **c:\omnion\DQM\method**. Click on the method you will be running and then on the method **DQM File Name**. Click on **OK** and the DQM (Data Quality Management) Plan will appear.

10.2.14 This DQM Plan supplements the tray table itself and acts as a standard operating procedure to be used when running this tray. Check the DQM to make sure it will apply to this tray, or edit it if necessary. If any changes were necessary then the DQM should be saved, and then replace the DQM in the tray, to make the changes permanent. If no changes were necessary, then minimize this window.

10.2.15 Click on the **Run Tray** button. The Tray Run Window will appear. Leave the **Method** and **Tray** spaces blank to run the currently loaded Method and tray. You must fill in the **Data File** space so that Omnion knows where to put the data it will generate. Click on **Catalog** after the **Data File** space to see a list of previous data files. Click on an old file name and then edit it to match today's tray name. Click on **OK**.

10.2.16 Follow Section 17.3 of Lachat QuikChem Method 10-204-00-1-A for proper setup of manifold. Insert the proper manifold for the desired analysis to the proper channel specified in the Analyte Table. The load/inject valve for each channel has six connections with the following designations:

Port #	Function
1	Sample Loop Inlet
2	Carrier Stream Inlet (From Pump)

(Short section of plastic tubing remains port #2 at all times)

3	Outlet to reaction manifold
4	Sample loop outlet
5	Sample loop waste line
6	Sample source line (from sampler, pump)

10.2.17 Each reaction manifold has a line with pump tubing attached labeled "carrier". Disconnect the pump tubing from this line and reconnect it to the section of line that comes from port #2. Connect the section of tubing coming from the reaction manifold to port #3.

10.2.18 Connect the outlet line from the manifold, located top right, to the bottom inlet of the flow cell.

10.2.19 Insert 0.55 mm i.d. x 200 cm backpressure loop between top outlet of flow cell and the waste line.

10.2.20 Place waste line into proper cyanide waste collection container.

10.2.21 Install proper 570 interference filter.

10.2.22 Allow 15 minutes for heating unit to warm up to 60ºC.

10.2.23 Install micro-sample loop in ports #1 and # 4.

10.2.24 Install the pump tubing onto pump cartridges. Check for wear on the pump tubing by rolling between thumb and fingers when stretched across a pump cartridge. Replace tubing if "flat" spots are felt.

10.2.25 Move tension levers to left to provide proper tension.

10.2.26 Check all connections for leakage and proper flow. Make sure waste lines are routed to proper container.

10.2.27 Fill standard, check standard and blank vials with proper solutions. Fill sample tubes with proper samples.

10.2.28 When ready, click on **RUN** on the Tray Run Window and the analysis will start. The symbol for the tray on the toolbar will turn to a **STOP** sign until analysis is complete.

10.2.29 If necessary to stop the run anytime, click on the **STOP** sign. A window will come down with the options to RESUME or ABORT TRAY.

10.2.30 After instrument has calibrated, click on the **Review Calibration** button on the toolbar. The graph of the calibration will be displayed along with the area of each standard. If the r-value of the calibration is 0.995 or better, print the calibration graph and allow the analysis to continue.

10.2.31 After analysis is completed the **STOP** sign in the Toolbar will be replaced with **Run Tray.** Click on File and the window will come down. Click on Export Data. Export data window will appear. Highlight whatever Data Items and Channel Dependent Data Items you want exported to EXCEL Save Export Data As window will appear. Directories should be R:\Wetchem\data\lachat\test\year\month.

10.2.32 Highlight the text file you have just run in the File Name box. Click on **OK** and data will be exported to EXCEL. Then go back and click on File again. When window comes down, click on Open Runtime Rpt. Open Runtime Report File window will appear. It should have current data, method and file name of analysis just completed, or if going back at a later date, then highlight the one that you want. Click on **OK** and the Runtime Report will appear on the screen. Click on File and then on Print/Export Runtime Rpt. Runtime Report window will appear.

10.2.33 Click on **OK** to print. On Print window choose the Print Range you want. **ALL** is normally highlighted. Click on **OK**.

10.2.34 Samples that have results greater than the highest standard in the calibration curve need to be diluted appropriately so the result falls within the calibration curve, and reanalyzed. Document all dilutions on prep log.

10.2.35 Document all standards and reagents used in analysis in raw data. Sign and date raw data.

10.2.36 After analysis is complete, place reagent lines in D.I. water and rinse several minutes. Remove lines from water and pump air through the lines until dry.

10.2.37 Turn off pump, release tension levers on pump cartridges and remove pump tubing from cartridges.

10.2.38 Disconnect pump tubing to port #2 at the pump tubing connector, disconnect line to port #3 at port #3 connector and connect pump tubing from #2 to line from manifold.

10.2.39 Disconnect manifold outlet line from flow cell inlet connector.

10.2.40 Wrap pump tubing lightly around manifold panel and store in appropriate box, with sample loop and interference filter.

10.2.41 Any daily or periodic maintenance must be recorded in the instrument daily logbook.

10.3 SHUTDOWN:

10.3.1 Click on **EXIT** icon

10.3.2 Omnion FIA Data System Window appears. Click on **Logoff**.

10.3.3 Window listing **User** Name and question: **Logoff Current Session?** Click on **YES**.

10.3.4 Window for User Name and Password comes up. Click on **EXIT**.

10.3.5 Window comes up with: **Terminate Data System?** Click on **YES.**

10.3.6 Turn off computer, printer and switch on surge suppresser.

10.4 Calculations:

10.4.1 The instrument provides calculated sample results in ug/L. Calculations are only necessary if a dilution was used.

Liquid Calculation

Raw Data Value (ug/L) x Dilution Factor / 1000 = Cyanide (mg/L)

Soil Calculation

$$\frac{\text{Raw Data Value (ug/L) X 0.006 L X Dilution Factor}}{\text{(0.00020 Kg x \% solids in decimal form x 1000)}} = \text{Cyanide(mg/Kg)}$$

11. Quality Control

11.1 Refer to the most current version of SOP GB-Q-009 *Common Laboratory Calculations and Statistical Evaluation of Data* for equations and calculation details.

11.2 **Initial Calibration Verification (ICV)**

11.2.1 The ICV must be analyzed before samples.

11.2.2 The ICV is distilled with the batch.

11.2.3 Concentration must be within ± 10% of the true value. When measurements are outside the control limits, the analysis must be terminated, the problem corrected, and the calibration re-verified.

11.2.4 If the ICV is greater than the control limit and the samples are non-detects, the sample may be reported without a flag.

11.2.5 The lot number of the Potassium Cyanide Standard used to make the ICV must be different from that of the calibration curve standards.

11.3 **Continuing Calibration Verification (CCV)**

11.3.1 The CCV is analyzed after every 10 samples.

11.3.2 The CCV is not distilled with the batch.

11.3.3 Concentration must be within ± 10% of the true value. When measurements are outside the control limits, the analysis must be terminated, the problem corrected, and the calibration re-verified. If the reset CCV fails, recalibrate and reanalyze all samples back to the last acceptable CCV.

13.3.3.1 If the CCV is greater than the control limit and the samples are non-detects, the sample may be reported without a flag.

11.3.4 The lot number of the Potassium Cyanide Standard used to make the CCV must be different from that of the ICV.

11.4 **Initial Calibration Blank (ICB) and Continuing Calibration Blank (CCB)**

11.4.1 The ICB must be analyzed after the ICV and before samples. The CCB must be analyzed after the CCV and before samples.

11.4.2 The ICB and CCB are not distilled with the batch.

11.4.3 The absolute value must be < PRL. When measurements are above the PRL, terminate analysis, correct the problem, and the calibration re-verified. If the reset of the I/CCB fails, recalibrate and reanalyze all analytical samples analyzed since the last compliant calibration blank.

13.4.3.1 If the sample concentration is greater than ten times the concentration in the ICB or CCB, the samples do not need to be reanalyzed.

11.5 **Reporting Limit Verification Standard (RLVS)** – A standard prepared at the concentration of the Pace Reporting Limit. It is analyzed after the calibration, recovery 60-140% of true value. If outside the limits, reanalyze once. If still outside the limits, recalibrate.

11.6 **Method Blank (MB)**

11.6.1 A MB is carried through all prep procedures and analyzed with a frequency of 5% or one per batch of up to 20 environmental samples. Must be distilled with batch.

11.6.2 The absolute value must be < PRL.

13.6.2.1 When measurements are above the PRL, terminate analysis, correct the problem, verify the calibration, and reanalyze all analytical samples analyzed since the last compliant calibration blank.

13.6.2.2 If the analyte is detected in the method blank, method blank criteria is evaluated and flagged with an appropriate (B) qualifier to the MDL when MDL reporting is required: qualify with an appropriate "B" qualifier sample results less than 20 times the absolute value detected in the blank. Additionally, method blank acceptance may be based on project specific criteria or determined from analyte concentrations in the sample and are evaluated on a sample-by-sample basis. Other criteria may apply, such as regulatory limit and the analyte concentration in the samples.

11.7 **Laboratory Control Sample (LCS)**

11.7.1 The LCS is carried through all preparation procedures with frequency of 5% or one per batch of up to 20 environmental samples. A Laboratory Control Spike Duplicate (LCSD) must be analyzed if there is insufficient sample volume to perform a matrix spike/matrix spike duplicate or if the client requests one. Must be distilled with batch.

11.7.2 Concentration must be within $\pm$ 10% of the true value for waters. For soils, the concentration must be within calculated in –house limits or default limits of $\pm$ 20%.

11.7.2.1 When measurements are outside the control limits, check for errors in calculations, standards preparation and spiking. If an error or problem is found and can be corrected by amending the calculations and the results falls within the limits, accept the data and report without a qualifier flag.

11.7.2.2 If no errors are found and sufficient sample is available, re-prepare the LCS (and/or LCSD) and all associated samples. If the recovery is within the limits in the analysis, accept the second set of data. If the recovery is still out side the limits after re-analysis, contact the PM to determine the resolution. If the client does not require additional work, report the data, applying an appropriate flag to the samples associated with the non-compliant LCS.

11.7.2.3 If sufficient sample volume is not available, report the sample data with an appropriate (L) qualifier flag on each of the samples associated with the non-compliant LCS (and/or LCSD). Contact the project manager regarding the occurrence.

11.7.3 When an LCSD is performed, the precision between the LCS and LCSD must a be =/< 20% RPD.

11.7.3.1 When measurements are outside the control limits, check for errors in calculations, standards preparation and spiking. If an error or problem is found and can be corrected by amending the calculations and the results falls within the limits, accept the data and report without a qualifier flag.

11.7.3.2 If no calculation errors are found when measurements are outside the control limits, flag the parent sample with an appropriate “R” data qualifier.

11.8 Matrix Spike (MS) and Matrix Spike Duplicate (MSD)

11.8.1 One pair per up to 10 environmental samples or 10% frequency whichever is more frequent. Must be distilled with batch.

11.8.2 Both QC samples must be calculated for accuracy and precision.

11.8.3 Concentration must be within $\pm$ 10% of the true value for waters. For soils, the concentration must be within calculated in –house limits or default limits of $\pm$ 20%.

11.8.3.1 If the four times the concentration of the spike is less than the level of the parent, accuracy need not be calculated.

11.8.3.2 When measurements are outside the control limits, check for errors in calculations, standards preparation and spiking. If an error or problem is found and can be corrected by amending the calculations and the results falls within the limits, accept the data and report without a qualifier flag.

11.8.3.3 If no calculation errors are found when measurements are outside the control limits, flag the parent sample with an appropriate “M” data qualifier.

11.8.4 The precision between the MS and MSD must a be =/< 20% RPD.

11.8.4.1 When measurements are outside the control limits, check for errors in calculations, standards preparation and spiking. If an error or problem is found and can be corrected by amending the calculations and the results falls within the limits, accept the data and report without a qualifier flag.

11.8.4.2 If no calculation errors are found when measurements are outside the control limits, flag the parent sample with an appropriate "R" data qualifier.

11.8.5 The parent sample used for MS/MSD pair is either determined by the client or selected at random from client samples as sample volume allows. No field, filter, trip or equipment blanks can be used for MS/MSD.

11.8.6 The lot number of the Potassium Cyanide used to make the CCV is different for the MS/MSD.

11.9 The appropriate leach blank must be distilled and analyzed along with the appropriate samples as leached on the same leach date. The absolute value must be < PRL. When measurements are above the PRL, terminate analysis, investigate and correct the problem, verify the calibration, and reanalyze all analytical samples analyzed.

11.10 When preparation of a sample exceeds 14 days past the time of collection, notify the project manager before proceeding. If a sample is run past 14 days after collection, flag the result with an appropriate "H" data qualifier.

11.11 If a sample was diluted due to matrix effects and the result is a non-detect, the result must be qualified with an appropriate "D" data qualifier.

11.12 See attachments Table A and Table B for a summary of QC.

12. Method Performance

12.1 There are several requirements that must be met to insure that this procedure generates accurate and reliable data. A general outline of requirements has been summarized below. Further specifications may be found in the Laboratory Quality Manual and specific Standard Operating Procedures.

12.1.1 The analyst must read and understand this procedure with written documentation maintained in his/her training file.

12.1.2 An initial demonstration of capability (IDC) must be performed per S-ALL-Q-020, *Orientation and Training Procedure*s. A record of the IDC will be maintained in his/her QA file with written authorization from the Laboratory Manager and Quality Manager.

12.1.3 An annual method detection limit (MDL) study will be completed per S-ALL-Q-004, *Method Detection Limit Studies*, for this method and whenever there is a major change in personnel or equipment. The results of these studies are retained in the quality assurance office.

12.1.4 Periodic performance evaluation (PE) samples are analyzed per S-ALL-Q-010, *PE/PT Program*, to demonstrate continuing competence. All results are stored in the QA office.

13. Pollution Prevention and Waste Management

13.1 Pollution prevention encompasses any technique or procedure that reduces or eliminates the quantity or toxicity of waste at the point of generation.

13.2 The quantity of chemicals purchased is based on expected usage during its shelf life and disposal cost of unused material. Actual reagent preparation volumes reflect anticipated usage and reagent stability.

13.3 Excess reagents, samples and method process wastes are characterized and disposed of in an acceptable manner. For further information on waste management consult the current version of ALL-S-002, *Waste Handling*.

13.4 The laboratory Chemical Hygiene Plan/Health and Safety Plan contains additional information on pollution prevention.

14. References

14.1 QuikChem Method 10-204-00-1-A, Lachat Instruments, August 28, 2000

14.2 Micro Dist Method Cyanide-1, Lachat Instruments, October 12, 2000

14.3 SW846 9012A, Revision 1.0, December 1996

14.4 EPA 600 R-93-100, Revised August 1993, Method 335.4

14.5 Standard Methods for the Examination of Water and Wastewater, 18th Edition, p. 4-18, Methods 4500-CN^- A, B, C, and D (1992)

15. Tables, Diagrams, Flowcharts, Appendices, Addenda etc.

15.1 Table A: **QUALITY CONTOL**

15.2 Table B: **ANALYST/TECHNICIAN DATA ASSESSMENT**

15.3 CN bench sheet example

15.4 CN prep sheet example

15.5 Flowchart

16. Revisions

Revision Number	Reason for Change	Date
S-GB-I-043.Rev.0	Updated to current Pace format First Issue.	15Feb2007
S-GB-I-043.Rev.01	Updated signature page. Deleted Section 7. Renumbered document. Section 12 - Updated data qualifiers Section 13 – Updated SOP references. Section 14 – Updated SOP reference Table B – Updated qualifiers	30Jul2008

Table A. QUALITY CONTROL

Preparation Method ⇨ Quality Control Measure ⇩	**EPA 335.4 SW846 9012A**
Method Blank	One per batch of samples, up to 20 environmental samples, whichever is more frequent. Must be distilled with batch.
Laboratory Control Spike and Duplicate	One per batch of samples, up to 20 environmental samples, whichever is more frequent. A LCSD is required if MS/MSD is not performed. Must be distilled with batch.
Matrix Spike / Matrix Spike Duplicate	One pair per batch of samples, up to 10 environmental samples, whichever is more frequent. Must be distilled with batch.
Initial Calibration	Minimum of 5 standards plus blank. Must be performed every time before samples are analyzed.
RLVS Standard	After the calibration
Calibration Verification (ICV/CCV)	ICV – analyzed after calibration but before samples. **The ICV is distilled with batch.** CCV – analyzed after every 10 samples. **The CCV is not distilled with batch.**
Calibration Blank (ICB/CCB)	ICB – analyzed after ICV. **The ICB is not distilled with batch.** CCB – analyzed after every CCV pair. **The CCB is not distilled with batch.**
Leach Blank	The appropriate leach blank must be distilled and analyzed along with the appropriate samples as leached on the same leach date.

Table B. ANALYST/TECHNICIAN DATA ASSESSMENT

Analytical Method Acceptance Criteria⇨ Data Assessment Measure ⇩	**If these conditions are not achieved ⇒**
Method Blank and Leach Blanks	• 1
Accuracy & Precision Matrix Spike Samples	• 2
Accuracy & Precision Laboratory Control Spikes	• 3
Initial Calibration	• 4
RLVS standard	• 5
Initial / Continuing Calibration Verification	• 6
Initial / Continuing Calibration Blank	• 7

1. In the absence of project specific requirements, sample detects less than 20 times the method blank contamination level is reported with the appropriate "B" data qualifier. Sample detects greater than 20 times the method blank contamination are reported without qualification.

2. In the absence of project specific or method requirements, in-house generated limits will be used. If the concentration of the spike is less than 25% of the concentration of the parent, dilute parent to a level that the subsequent spike concentration will be greater than 25% the parent and so the parent concentration is above the EQL. Rerun the parent, MS, and MSD at this new dilution. If the MS and/or MSD fails at the diluted concentration, use appropriate "M" qualifier to flag the parent sample. If the parent, MS, or MSD is greater than the top standard in the curve, dilute and reanalyze the parent, MS, and MSD following the above guidance. If the concentration of the spike is greater than 25% of the concentration of the parent, use appropriate "M" qualifier to flag the parent sample if either the MS and/or MSD fails. If the MS and MSD fails precision control limits flag the parent with the appropriate "R" (precision) data qualifier.

3. If sample volume does not allow re-analysis the entire prep/analytical batch of samples shall be flagged with the appropriate "L" (accuracy) and appropriate "R" (precision) qualifier to reflect the deficiencies.

4. If correlation coefficient is less than 0.995 perform maintenance and recalibrate.

5. It is analyzed after the calibration, recovery 60-140% of true value. If outside the limits, reanalyze once. If still outside the limits, recalibrate.

6. If ICV/CCV is outside the control limits reanalyze the ICV/CCV to verify the instrument is out of control. If the 2nd analysis is outside control limits, perform maintenance and recalibrate. Samples that bracket the out of control standards must be reanalyzed. If the ICV/CCV recovers greater than the control limit and the samples bracketing the out of control ICV/CCV are non-detects, the results may be reported without a flag.

7. If ICB/CCB is outside the control limits reanalyze the ICB/CCB to verify the instrument is out of control. If the 2nd analysis is outside control limits, perform maintenance and recalibrate. Samples that bracket the out of control standards must be reanalyzed. Samples that are > 10X the concentration in the CCB the samples do not have to be reanalyzed.

CN Bench Sheet Example

Pace Analytical Services, Inc.

Analytical Review Report Date Printed: 02/16/07 Approved By:
Analysis Date: 1/25/2007 Analyst: DAW Approved Date:
Method: EPA 335.4 Data File: 012507.TXT Worksheet#: 99738
Workbook Name: CN012507

Lab Number	P/F	Dil	Raw Amt	TV	Matrix	%Rec	LCL	UCL	RPD	Max RPD	Units	Parameter
ICV 100	Pass	1	0.0928	0.100	W	92.8	90	110.0			mg/L	Cyanide, Total
ICV 50	Pass	1	0.05076	0.050	W	101.5	90	110.0			mg/L	Cyanide, Total
ICB	Pass	1	0.00083		W		0	0.0			mg/L	Cyanide, Total
WCG2101-077MB	Pass	1	-0.0034		W			+/-0.02			mg/L	Cyanide, Total
WCG2101-077MBLCS	Pass	1	0.09607	0.100	W	96.1	90	110.0			mg/L	Cyanide, Total
880226-015		1	0.01847		W						mg/L	Cyanide, Total
880226-015MS	Pass	1	0.11191	0.100	W	93.4	90	110.0			mg/L	Cyanide, Total
880226-015MSD	Pass	1	0.11494	0.100	W	96.5	90	110.0	2.7	20	mg/L	Cyanide, Total
880237-002		1	0.1669		W						mg/L	Cyanide, Total
880237-004		1	0.34831		W						mg/L	Cyanide, Total
CCV 200	Pass	1	0.20375	0.200	W	101.9	90	110.0			mg/L	Cyanide, Total
CCB	Pass	1	-0.005		W		0	0.0			mg/L	Cyanide, Total
880253-002		1	-0.0017		W						mg/L	Cyanide, Total
880321-004		1	0.03305		W						mg/L	Cyanide, Total
880321-006		1	-0.0033		W						mg/L	Cyanide, Total
880321-011		1	-0.0047		W						mg/L	Cyanide, Total
880353-001		1	-0.0055		W						mg/L	Cyanide, Total
880353-002		1	-0.0006		W						mg/L	Cyanide, Total
880353-003		1	-0.004		W						mg/L	Cyanide, Total
880353-004		1	-0.004		W						mg/L	Cyanide, Total
880353-005		1	-0.0055		W						mg/L	Cyanide, Total
880353-006		1	-0.0036		W						mg/L	Cyanide, Total
CCV 200	Pass	1	0.20142	0.200	W	100.7	90	110.0			mg/L	Cyanide, Total
CCB	Pass	1	-0.0055		W		0	0.0			mg/L	Cyanide, Total
880373-002		1	-0.0043		W						mg/L	Cyanide, Total
880373-005		1	-0.0047		W						mg/L	Cyanide, Total
880373-006		1	0.00484		W						mg/L	Cyanide, Total
880373-007		1	-0.0044		W						mg/L	Cyanide, Total
880397-001		1	-0.0017		W						mg/L	Cyanide, Total
880397-001MS	**Fail**	1	0.06266	0.100	W	62.7	90	110.0			mg/L	Cyanide, Total
880397-001MSD	**Fail**	1	0.0368	0.100	W	36.8	90	110.0	52.0	20	mg/L	Cyanide, Total
880326-001		1	-0.0028		D						mg/L	Cyanide, Total
880326-002		1	-0.0032		D						mg/L	Cyanide, Total
880326-002MS	Pass	1	0.10242	0.100	D	102.4	90	110.0			mg/L	Cyanide, Total
CCV 200	Pass	1	0.19927	0.200	W	99.6	90	110.0			mg/L	Cyanide, Total
CCB	Pass	1	-0.0062		W		0	0.0			mg/L	Cyanide, Total
880326-002MSD	Pass	1	0.10181	0.100	D	101.8	90	110.0	0.6	20	mg/L	Cyanide, Total
CCV 200	Pass	1	0.19698	0.200	W	98.5	90	110.0			mg/L	Cyanide, Total
CCB	Pass	1	-0.0059		W		0	0.0			mg/L	Cyanide, Total

CN Prep Sheet Example

Pace Analytical Services, Inc. Distillation Log

Prep WS#: 17852
Prep Date: 1/25/07
Run Date: 1/25/07
Analyst: DAW

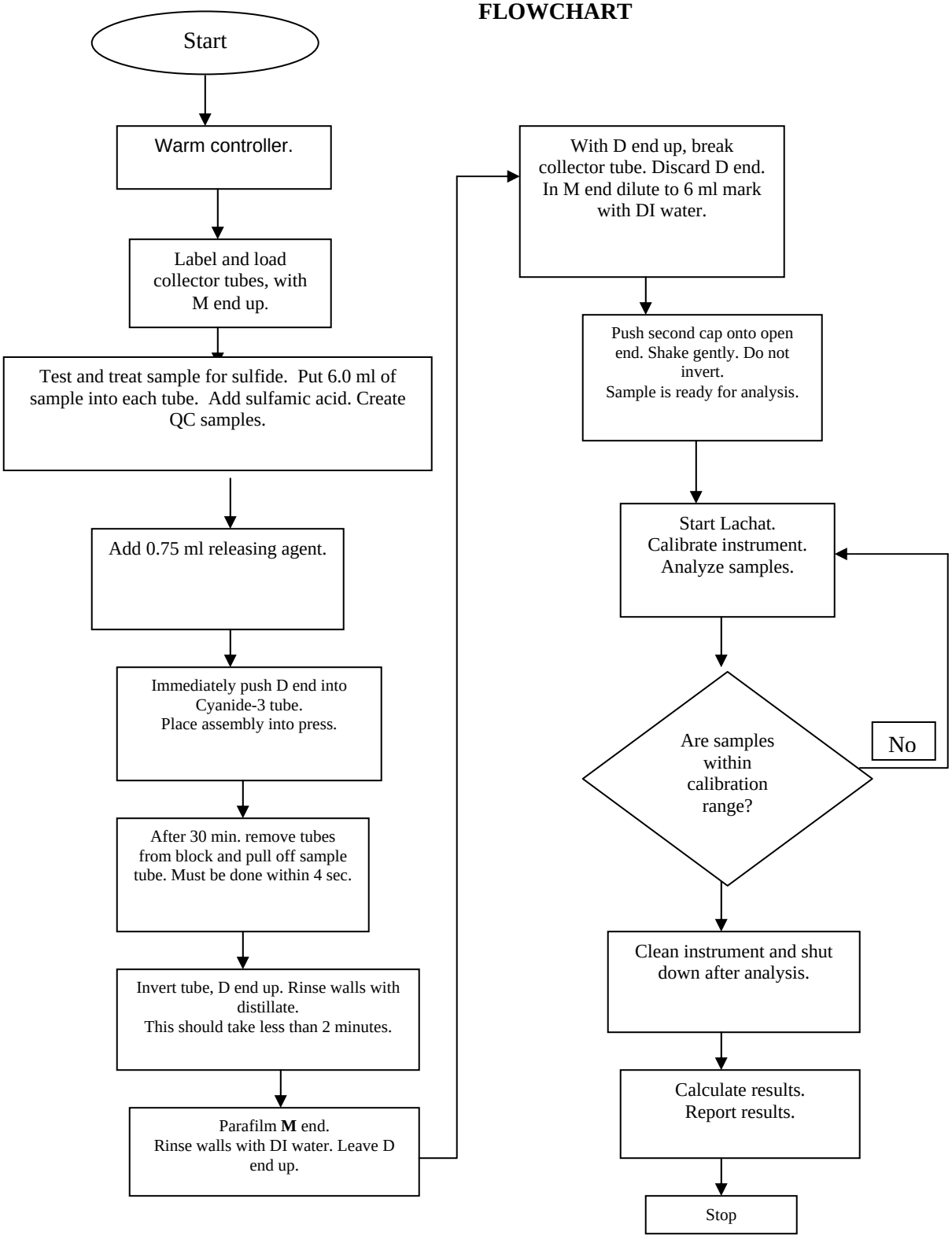
Total Cyanide
EPA 335.4

	Matrix	Sample #	Pre-Dilution	Initial Vol/ Final Vol	Spike Log Number		Matrix	Sample #	Pre-Dilution	Initial Vol/ Final Vol	Spike Log Number
1	W	ICV 100		6ml/6ml		31	D	880326-002MSD		6ml/6ml	
2	W	ICV 50		6ml/6ml		32					
3	W	ICB		6ml/6ml		33					
4	W	WCG2101-077MB		6ml/6ml		34					
5	W	WCG2101-077MBLCS		6ml/6ml		35					
6	W	880226-015		6ml/6ml		36					
7	W	880226-015MS		6ml/6ml		37					
8	W	880226-015MSD		6ml/6ml		38					
9	W	880237-002		6ml/6ml		39					
10	W	880237-004		6ml/6ml		40					
11	W	880253-002		6ml/6ml		41					
12	W	880321-004		6ml/6ml		42					
13	W	880321-006		6ml/6ml		43					
14	W	880321-011		6ml/6ml		44					
15	W	880353-001		6ml/6ml		45					
16	W	880353-002		6ml/6ml		46					
17	W	880353-003		6ml/6ml		47					
18	W	880353-004		6ml/6ml		48					
19	W	880353-005		6ml/6ml		49					
20	W	880353-006		6ml/6ml		50					
21	W	880373-002		6ml/6ml		51					
22	W	880373-005		6ml/6ml		52					
23	W	880373-006		6ml/6ml		53					
24	W	880373-007		6ml/6ml		54					
25	W	880397-001		6ml/6ml		55					
26	W	880397-001MS		6ml/6ml		56					
27	W	880397-001MSD		6ml/6ml		57					
28	D	880326-001		6ml/6ml		58					
29	D	880326-002		6ml/6ml		59					
30	D	880326-002MS		6ml/6ml		60					

There could be three kinds of dilutions in this run: pre, prep, analytical. Pre-dilutions are done before the sample is prepped. Prep-dilutions are done during the prep step. Analytical-dilutions are done at the instrument. The Pre-dilutions are noted on the prep log. The Prep-dilutions are noted in the Initial/Final Volumes on the Prep Log. On the raw data, the dilution noted is the Pre-dilution X the Analytical-dilution. The raw data dilution does not include the Prep-dilution.

Comments: _____

FLOWCHART


Start
Warm controller.
Label and load collector tubes, with M end up.
Test and treat sample for sulfide. Put 6.0 ml of sample into each tube. Add sulfamic acid. Create QC samples.
Add 0.75 ml releasing agent.
Immediately push D end into Cyanide-3 tube.
Place assembly into press.
After 30 min. remove tubes from block and pull off sample tube. Must be done within 4 sec.
Invert tube, D end up. Rinse walls with distillate.
This should take less than 2 minutes.
Parafilm **M** end.
Rinse walls with DI water. Leave D end up.
With D end up, break collector tube. Discard D end. In M end dilute to 6 ml mark with DI water.
Push second cap onto open end. Shake gently. Do not invert.
Sample is ready for analysis.
Start Lachat.
Calibrate instrument.
Analyze samples.
Are samples within calibration range?
No
Clean instrument and shut down after analysis.
Calculate results.
Report results.
Stop

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STANDARD OPERATING PROCEDURE

The Determination of Mercury by Cold Vapor Atomic Absorption Spectroscopy

Reference Methods: EPA SW-846 Methods 7470A and 7471B

SOP NUMBER:	S-GB-M-004-REV.00
EFFECTIVE DATE:	Date of Final Signature
SUPERSEDES:	First Issue

APPROVAL

Nils Melberg, Laboratory General Manager — Date: 09/19/08

Kate Grams, Laboratory Quality Manager — Date: 09/19/08

Chad Rusch, Department Manager — Date: 09/19/2008

ANNUAL REVIEW

SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE APPROVAL. SOP IS VALID FOR ONE YEAR FROM DATE OF LAST SIGNATURE.

Signature	Title	Date

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1. PURPOSE

1.1 The purpose of this Standard Operating Procedure (SOP) is to describe the determination of mercury in water, soil/solid samples, and biological tissue.

2. SCOPE AND APPLICATION

2.1 This method is applicable to water samples (including drinking water, surface water, and domestic and industrial wastewaters), solid samples (including soils, sediments, sludges, and, solid wastes), wipes, TCLP leachates, and biological tissue samples.

2.2 This procedure is restricted to use by, or under the supervision of, analysts experienced in the digestion of samples for metals analysis and analysis of digestates by atomic absorption spectrometry. Each analyst must demonstrate the capability to generate acceptable results with this method to be considered qualified to report sample results.

3. SUMMARY OF METHODS

3.1 Cold vapor atomic absorption utilizes the volatile property of elemental mercury at the 253.7 nm wavelength. To release mercury from organic complexes, the sample is digested with oxidizing reagents and acids in a hot block digester. After digestion, the oxidizing reagents are neutralized. Stannous chloride is added to reduce ionic mercury to the ground state. The Flow Injection Analysis System sweeps the volatile elemental mercury out of the sample and into the cell of an atomic absorption spectrophotometer. The absorbance signal is proportional to the amount of mercury in the sample.

4. INTERFERENCES

4.1 Biota samples can contain diverse matrix types, each of which may present analytical challenges. Spiked samples and Laboratory Control Samples are important for determining digestion efficiency.

4.2 Potassium permanganate is added to eliminate possible interference from sulfide. Concentrations as high as 20 mg/L of sulfide, as NaS, do not interfere with recovery of added inorganic Mercury from D.I. water.

4.3 Copper has also been reported to interfere; however, copper concentrations as high as 10mg/L had no effect on recovery of Mercury from spiked samples.

4.4 Samples high in chlorides require up to 7.5 mL of additional potassium permanganate. During the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation at 253.7 nm. Care must therefore be taken to ensure that free chlorine is absent before the Mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine hydrochloride reagent. Samples may be diluted to decrease the chlorides. Alternatively, the sample may be allowed to stand for at least an hour under a hood (without active purging) to remove the chlorine.

4.5 Certain volatile organic materials that absorb at this wavelength may also interfere. A preliminary run without reagents would determine if this type of interference is present.

5. SAFETY

5.1 Standards and Reagents - The toxicity and carcinogenicity of standards and reagents used in this method have not been fully defined. Each chemical compound should be treated as a potential health hazard. Reduce exposure by the use of gloves, lab coats and safety glasses.

5.2 Material Safety Data Sheets (MSDSs) – A reference file of MSDS are on file in the laboratory and available to all personnel. A formal safety plan has been prepared and distributed to all personnel with documented training.

5.3 Special care should be taken when handling the high concentration acids and oxidizing reagents used for sample digestion. All digestions must be conducted in a properly functioning fume hood.

5.4 Samples - Take precautions when handling samples. Samples should always be treated as potentially hazardous "unknowns". The use of personal protective equipment (gloves, lab coats and safety glasses) is required when handling samples.

5.4.1 Extreme caution must be used when preparing rodents for digestion. The samples must undergo a special procedure to destroy any Hantavirus, which may be present. Refer to the most recent version of SOP S-GB-L-002 *Small Rodent Handling and Homogenization* for details.

5.5 Analysts should take necessary safety precautions when handling chemicals and samples. Proper personal protective equipment may include safety gloves, lab coats, and safety glasses or goggles. Analysts should be familiar with the MSDS sheets for all chemicals and reagents they use for this procedure and the location of the MSDS sheets within the laboratory. Any questions or concerns should be taken to the laboratory Chemical Hygiene/Safety Officer.

6. DEFINITIONS

6.1 Definitions of terms found in this SOP can also be found in the Pace Quality Manual. When definitions are not consistent with NELAC defined terms, an explanation will be provided in this SOP or the Pace Analytical Services' Quality Manual Glossary, Section 10.0.

6.2 Biota Control Blank (Matrix Blank) - A sample of a matrix that is used for the control spike. The biota control blank will either be catfish, tilapia, chicken, or other tissue which ever is available at the time of analysis. The biota control blank should be "farm-raised" to minimize background mercury levels. The concentration in the biota control blank will be subtracted from the concentration of the laboratory control spike. This is done because the biota control blank is known to have some contamination. This SOP will reference biota control blank for ease. Note: For plant material analysis, alfalfa can be used as the biota control blank matrix.

6.3 Reagent Grade – Analytical reagent (AR) grade, ACS reagent grade, and reagent grade are synonymous terms for reagents, which conform to the current specifications of the Committee on Analytical Reagents of the American Chemical Society.

6.4 Standardized Reference Material (SRM) – A certified reference material produce by the U.S. National Institute of Standards and Technology or other equivalent organization and characterized for absolute content, independent of analytical method. A SRM is analyzed with each analytical batch of biota samples.

6.5 Pace Reporting Limit (PRL) – The level at which method, permit, regulatory and client specific objectives are met. The reporting limit may never be lower than the Limit of Detection (i.e. statistically determined MDL). Reporting limits are corrected for sample amo unts, including the dry weight of solids, unless otherwise specified.

7. SAMPLE COLLECTION, PRESERVATION, AND HANDLING

7.1 BIOTA SAMPLES

7.1.1 Biota samples can be collected in clean plastic or glass containers or plastic baggies.

7.1.2 Biota samples are kept frozen until time of preparation to preserve integrity. Hold time is 28 days from removal from freezer.

7.2 SOIL SAMPLES

7.2.1 Soil and waste samples should be collected in clean wide-mouth glass containers to facilitate obtaining representative aliquots for measurement.

7.2.2 Samples should be stored at 4±2°C and analyzed as soon as possible to minimize microbiological decomposition of organic solids. Samples must be analyzed within 28 days of collection.

7.3 WIPE SAMPLES

7.3.1 Wipe should be collected in clean wide-mouth glass containers.

7.3.2 Samples should be stored at 4±2°C and analyzed as soon as possible to minimize microbiological decomposition of organic solids. Samples must be analyzed within 28 days of collection.

7.4 WATER SAMPLES

7.4.1 Water samples may be collected in plastic or glass containers and must be preserved with HNO_3 to pH <2 and stored at room temp, acid not to exceed 5% of the container capacity.

7.5 NOTE: Aqueous samples that react violently to the addition of acid may be collected without chemical preservation with proper variances approved by the regulatory authority. The responsibility of requesting this variance lies with the sample collector.

7.6 NOTE: Samples may be preserved in the lab. The samples may not be processed until 24 hours after preservation with a pH test of <2.

7.6.1 Samples must be analyzed within 28 days of collection.

8. EQUIPMENT AND SUPPLIES

8.1 Heating Block – Operated at 95 ± 5°C. Heating block should be Environmental Express "Hot Block", or equivalent.

8.2 Digestion Vials – Pre-cleaned 68- mL screw cap vials, Environmental Express (SC475), or equivalent.

8.3 Analytical Balance – Capable of weighing to 0.01g.

8.4 Volumetric Flasks – Assorted, Class A

8.5 Graduated Cylinder – 50-mL

8.6 Mechanical Pipettes – Assorted adjustable air-displacement pipettes with disposable tips (Eppendorf or equivalent).

8.7 pH Strips

8.8 CVAA-FIMS with autosampler

8.9 Inert Sparging and Carrier Gas – Argon

8.10 Autosampler vials

8.11 Autosampler Pump Tubing

8.12 Specimen Cups

8.13 DOLT-3

8.14 Analytical Balance – Capable of weighing to 0.0001g.

9. REAGENTS AND STANDARDS

9.1 Trace Metals Water

9.2 Nitric Acid (HNO_3) – Trace metals grade

9.3 Hydrochloric Acid (HCl) – Trace metals grade

9.4 Sulfuric Acid (H_2SO_4) – Trace metals grade

9.5 Sodium Chloride (NaCl)

9.6 Potassium Permanganate ($KMnO_4$) solution (5%) – Dissolve 50.0 g of $KMnO_4$ into ~800 mL of trace metals water. Dilute to 1000 mL. Prepare fresh each month.

9.7 Potassium Persulfate Solution ($K_2S_2O_8$) solution (5%) – Dissolve 50.0 g of $K_2S_2O_8$ into ~800 mL of trace metals water. Dilute to 1000 mL. Warm to dissolve. Prepare fresh each month.

9.8 Hydroxylamine Hydrochloride ($NH_2OH \bullet HCl$) Solution (12%) – Dissolve 120 g NaCl and 120g $NH_2OH \bullet HCL$ in ~800 mL of trace metals water. Dilute to 1000 mL. Prepare fresh each month.

9.9 Stannous Chloride Solution ($SnCl_2$) - Dissolve 11.0 g of SnCl in ~ 800 mL of trace metals water. Add 30 mL of HCL. Dilute to 1000 mL. Prepare fresh every other day.

9.10 Analytical Standards – Standard solutions are required calibration, calibration checks, and sample spiking solutions. The following describes the contents of each type of solution. The commercial sources for stock solutions, recipes for preparing dilutions and working standards, and concentrations in standard solutions are presented in Table 1, Table 2, and Table 3.

Table 1
Stock Standards

Standard	Concentration	Vendor	Catalog #
Hg Calibration Stock	1000µg/mL	Inorganic Ventures, Inc.	CGHG1-1
ICV Calibration Stock	1000µg/mL	High-Purity Standards	100033-1

Standards are used until they expire based on the manufacturer's expiration date.

Table 2
Intermediate and Calibration Standards
Waters

Standard	Stock Standard	Conc.	Amount Used	Amount of conc. HNO_3 used	Final Volume (with trace metals water)	Final Conc.
Hg ICV Stock	-	1000µg/mL	-	-	-	1000 µg/mL
Hg Calibration Intermediate	Hg Calibration Stock	1000µg/mL	20 µL	6.0 mL	200 mL	100 ppb
Hg ICV Intermediate	Hg ICV Stock	1000 µg/ml	20 µL	6.0 mL	200 mL	100 ppb
Hg Cal. 1	-	-	-	-	20 mL	0.0 ppb
Hg Cal. 2	Hg Cal. Intermediate	100 ppb	40 µL	-	20 mL	0.2 ppb
Hg Cal. 3	Hg Cal. Intermediate	100 ppb	200 µL	-	20 mL	1.0 ppb
Hg Cal. 4	Hg Cal. Intermediate	100 ppb	500 µL	-	20 mL	2.5 ppb
Hg Cal. 5	Hg Cal. Intermediate	100 ppb	1000 µL	-	20 mL	5.0 ppb
Hg Cal. 6	Hg Cal. Intermediate	100 ppb	2000 µL	-	20 mL	10.0 ppb
Hg ICV	Hg ICV Intermediate	100 ppb	800 µL	-	20 mL	4.0 ppb
Hg CCV	Hg ICV Intermediate	100 ppb	1000 µL	-	20 mL	5.0 ppb
Hg ICB/CCB	-	-	-	-	20 mL	0.0 ppb

All intermediate dilution solutions must be prepared as needed, or at least every 7 days. Working solutions must be prepared fresh daily. Solutions may be stored at room temperature.

Table 3
Intermediate and Calibration Standards
Soils/Biota

Standard	Stock Standard	Conc.	Amount Used	Amount of conc. HNO_3 used	Final Volume (with trace metals water)	Final Conc.
Hg ICV Stock	-	1000µg/mL	-	-	-	1000 µg/mL
Hg Calibration Intermediate	Hg Calibration Stock	1000µg/mL	20 µL	6.0 mL	200 mL	100 ppb
Hg ICV Intermediate	Hg ICV Stock	1000 µg/ml	20 µL	6.0 mL	200 mL	100 ppb
Hg Cal. 1	-	-	-	-	30 mL	0.0 ppb
Hg Cal. 2 and PRLS	Hg Cal. Intermediate	100 ppb	60 µL	-	30 mL	0.2 ppb
Hg Cal. 3	Hg Cal. Intermediate	100 ppb	300 µL	-	30 mL	1.0 ppb
Hg Cal. 4	Hg Cal. Intermediate	100 ppb	750 µL	-	30 mL	2.5 ppb
Hg Cal. 5	Hg Cal. Intermediate	100 ppb	1500 µL	-	30 mL	5.0 ppb
Hg Cal. 6	Hg Cal. Intermediate	100 ppb	3000 µL	-	30 mL	10.0 ppb
Hg ICV	Hg ICV Intermediate	100 ppb	1200 µL	-	30 mL	4.0 ppb
Hg CCV	Hg ICV Intermediate	100 ppb	1500 µL	-	30 mL	5.0 ppb
Hg ICB/CCB	-	-	-	-	30 mL	0.0 ppb

All intermediate dilution solutions must be prepared as needed, or at least every 7 days. Working solutions must be prepared fresh daily. Solutions may be stored at room temperature.

10. CALIBRATION

10.1 A digested calibration curve is made up every time there are samples prepared. The curve is associated to the sample batch it is prepped with. Calibration requires analysis of a

calibration blank and at least five levels of calibration solutions. The lowest calibration concentration is the Pace Reporting Limit.

10.2 The resultant correlation coefficient must be greater than 0.995. If this does not occur, then the instrument must be recalibrated and or the calibration curve and the associated samples must be re-prepped.

10.3 The calibration curve must pass an Initial Calibration Verification (ICV) that is analyzed after the calibration standards and before any samples. The ICV concentration is near the midpoint of the calibration curve and is made from a source other than the one used to make the calibration standards.

10.4 Pace Reporting Limit Standard (PRL Std) – A standard prepared at the concentration of the Pace Reporting Limit. It is analyzed after the calibration, recovery 60-140% of true value. If outside the limits, reanalyze once. If still outside the limits, recalibrate.

10.5 Every ten samples or less must be bracketed by Continuing Calibration Verifications (CCV). The CCV concentration is near the midpoint of the calibration curve.

10.6 The ICV and CCV limits are +/- 10% of their expected values. If one fails, then the instrument must be re-calibrated and any samples after the failure or not bracketed by an acceptable CCV, must be reanalyzed.

10.7 An acceptable Initial Calibration Blank (ICB), must be analyzed after the ICV.

10.8 Continuing Calibration Blanks (CCB) are analyzed after the CCVs.

10.9 The control limit for the ICB and CCB is less than the Pace Reporting Limit. If one fails, then the instrument must be re-calibrated and any samples, after the failure or not bracketed by an acceptable CCB, must be reanalyzed.

11. PROCEDURE

11.1 Sample Preparation

11.1.1 Water samples

11.1.1.1 Verify preservation in the samples by checking their pH with a test strip (done in Sample Receiving).

11.1.1.2 Prior to analysis the samples and the calibration curve must be digested.

11.1.1.3 Turn on the heating block and set the temperature to maintain a sample temperature of 95±5°C. Before placing samples in the block to digest, verify that the sample well temperature is correct and adjust as required. Record the temperature in the sample logbook. Verify that the hood is functioning.

11.1.1.4 Add 20 mL of trace metals water and the appropriate amounts (as shown in Table 2) of Hg Calibration Intermediate and Hg ICV Intermediate to digestion vials for the curve, ICV, CCV, ICB, and CCB.

11.1.1.5 Add 20 mL of trace metals water to a digestion vial for the Method Blank.

11.1.1.6 Add 20 mL of trace metals water and 1.0 mL of Hg ICV Intermediate to two digestion vials for the Laboratory Control Spike

and Laboratory Control Spike Duplicate. Only prep LCSD if requested by client or there is not enough sample to run an MS/MSD.

11.1.1.7 Add 20 mL of each well-mixed sample to digestion vials.

11.1.1.8 To prepare a Matrix Spike and Matrix Spike Duplicate, a sample with sufficient volume is chosen at random or assigned by the client. An additional 20 mL of this sample along with 1.0 mL of Hg ICV Intermediate is added to two digestion vials.

11.1.1.9 To each digestion vial add 0.5 mL of concentrated nitric acid. Swirl the digestion vials gently.

11.1.1.10 To each digestion vial add 1.0 mL of concentrated sulfuric acid. Swirl the digestion vials gently.

11.1.1.11 Add 3 mL of 5% $KMnO_4$, place lid or cap on tube so as to allow pressure to vent but minimizing evaporation, swirl the digestion vials gently, and let stand for 15 minutes. If a sample does not maintain a purple or brown color, an additional 3 mL of $KMnO_4$ solution is added to all samples, QC, and standards. **Note: If the sample still does not maintain color, discard applicable samples and dilute the samples prior to digestion.**

11.1.1.12 Add 1.6 mL of 5% Persulfate solution. Swirl the digestion vials gently.

11.1.1.13 Digest samples for 2 hours at 95±5°C.

11.1.1.14 Remove samples and let cool to room temperature.

11.1.1.15 Add 1 mL of 12% sodium chloride/hydroxide solution. Swirl the digestion vials gently.

11.1.1.16 Samples are now ready for analysis.

11.1.2 Soil/Solid/Biota/Wipe Samples

11.1.2.1 Prior to analysis the samples and calibration curve must be digested.

11.1.2.2 Turn on the heating block and set the temperature to maintain a sample temperature of 95±5°C. Before placing samples in the block to digest, verify that the sample well temperature is correct and adjust as required. Record the temperature in the sample logbook. Verify that the hood is functioning.

11.1.2.3 Add 30 mL of 3% HNO_3 and the appropriate amounts (as shown in Table 2) of Hg Calibration Intermediate and Hg ICV Intermediate to digestion vials for the curve, ICV, CCV, ICB, and CCB.

11.1.2.4 Prepare one Method Blank by leaving one digestion vial blank. For biota analysis, a Biota Control Blank is also prepared by weighing 0.6 g of homogenized biota control blank tissue into a digestion vial.

11.1.2.5 Prepare the Laboratory Control Spike (LCS) for soils, wipes, and wastes by adding 1.5 mL of Hg ICV Intermediate to the digestion vial. Prepare the LCS for biota samples by weighing 0.6 g of homogenized biota control blank into the digestion vial. Add 1.5 mL of Hg ICV Intermediate the vial. Only prep a Laboratory Control Spike Duplicate (LCSD) if requested by client or there is not enough sample to run an MS/MSD. Prepare the LCSD in the same fashion as the LCS.

11.1.2.6 For biota samples weigh approximately 0.05 g of Standard Reference Material on an analytical balance (must read to at least 4 places past the decimal) into a labeled digestion vial.

11.1.2.7 Weigh 0.6 g of homogenized sample into a labeled digestion vial. Record the weight to the nearest 0.01 g in the digestion logbook. For samples with high liquid content, a larger sample size may be used, as long as the digestion is complete. For wipes, put the WHOLE wipe in the digestion vial.

11.1.2.8 To prepare a Matrix Spike and Matrix Spike Duplicate, a sample with sufficient volume is chosen at random. Weigh 2 additional 0.6 g aliquots into digestion vials. Add 1.5 mL of Hg ICV Intermediate to each vial.

11.1.2.9 Add 30 mL of 3% HNO_3 solution to all QC and samples. Swirl digestion vials to gently mix.

11.1.2.10 To each digestion vial add 0.5 mL of concentrated nitric acid. Swirl digestion vials to gently mix.

11.1.2.11 To each digestion vial add 2.0 mL of concentrated hydrochloric acid. Swirl digestion vials to gently mix.

11.1.2.12 Add 3 mL of 5% $KMnO_4$, place lid or cap on tube so as to allow pressure to vent but minimizing evaporation, swirl the digestion vials gently, and let stand for 15 minutes. If a sample does not maintain a purple or brown color, an additional 3 mL of $KMnO_4$ solution is added to all samples, QC, and standards. **Note: If the sample still does not maintain color, discard set and dilute the sample prior to digestion.** For Biota samples, add 6ml of KMnO4 to start with.

11.1.2.13 Digest samples for 30 minutes at 95$\pm$5°C.

11.1.2.14 Remove samples and let cool to room temperature.

11.1.2.15 Add 3 mL of 12% hydroxylamine hydrochloride solution. Swirl digestion vials to gently mix.

11.1.2.16 Samples are now ready for analysis.

11.2 BASIC SYSTEM OPERATION – ANALYTICAL

11.2.1 This portion of the SOP is designed to allow the user to set up and run a method, print a sample report, then shut down using the more basic software functions. For a more detailed explanation of the many other options, the user should refer to the Reference Manual.

11.2.1.1 Verify the carrier argon gas supply is on.

11.2.1.2 Switch on the FIMS 100.

11.2.1.3 Verify the computer is on. If not switch on the computer and enter network password and click on Start.

11.2.1.4 Go to programs, FIMS, and click on the AA WinLab Analyst and choose a custom workspace.

11.2.1.5 Click on GBWRK.FMS and then OK.

11.2.1.6 Go to "Sample Information Editor", File, Open Sample info File.

11.2.1.7 Choose the most recent applicable file and click OK.

11.2.1.8 Make changes to the calibration curve IDs in locations 1-9 and enter sample information starting with Autosampler Location #10. Enter the LIMS ID numbers under sample ID columns.

11.2.1.9 Go to File, Save As and change the Sample Info File identification to match the data file name and click OK.

11.2.1.10 In the menu click on Print and sample information to get a copy of the sample information you just entered to check for errors.

11.2.1.11 Close the window by clicking on the X in the upper right-hand corner.

NOTE: Only sample information should be entered in this file. Information on blanks, standards and QC samples is entered in the QC page of Method Editor.

11.2.1.12 Under the QC page you set up the QC sample ID, i.e. ICVs and CCVs and the autosampler location. Set the QC concentration and the control limits.

11.2.1.13 On the Schedule Timing page set up when the QC will be analyzed, i.e. after calibration, after 10 samples, and at the end. IF re-calibration occurs the QC must be analyzed at the same frequency.

11.2.1.14 Under the Actions Calib. And Periodic page, specify what to do if calibration QC fails, for example recalibrate, recalibrate and rerun, or stop.

11.2.1.15 On the Actions: End and Retry page, specify what QC to run at the end of a run and corrective action if QC fails.

11.2.1.16 Under the Options page, set how you want data printed (usually default). It is also possible to specify saving the peaks and add comments about the run.

11.2.1.17 In the Automated Analysis Window there are 2 pages: Set UP, and Analyze.

11.2.1.18 Under "Use Autosampler Locations listed Below", type in the numbers or range of numbers to be analyzed.

11.2.1.19 Select the name of the Results Data Set to save the results. Naming example: HG092800A, denotes the element, month, day and year. A letter is used for describing each run within a day's output.

11.2.1.20 The Save Data box and Print Log box should already be selected.

11.2.1.21 Off After Analysis. Pumps should be checked.

11.2.2 Starting the Analysis

11.2.2.1 Prepare the required reagents: Carrier solution and reducing agent.

11.2.2.2 Clamp down the tubes by swinging the pressure levers until they lock. Place inlets of each solution in proper container: Yellow/blue in the carrier and red/red in the reductant. Click on the FIAS icon to turn on the pump to draw solutions through the tubing. Check on the flow.

11.2.2.3 Click on the Analyze All button. The system will run the blank and standards specified in the Element Parameter file, then the entire sample specified in the Sample Info. File. Check the calibration curve by clicking on Calibration icon on the tool bar.

11.2.2.4 To run the blank and standards only: In order to check the calibration curve before running any samples:

11.2.2.5 Click on Calibration, the system will run the blank and standards specified in the Element File and complete the calibration curve. To check the calibration curve, click on the Calibration icon on the toolbar.

11.2.2.6 To continue the run, click on the Auto control window then click on Analyze sample. The system will run the samples specified in the Sample Info. file.

11.2.2.7 To change or stop the element file that has already started: Click on Analyze. A dialogue box will appear with these options:

Stop immediately

Stop after current replicate

Stop after completing all replicates for current sample

11.2.2.8 To restart the analysis from the beginning: In the Automated Analysis Control window, click on RESET. Start the analysis as usual.

11.2.2.9 To continue the analysis where it was interrupted or continue with a specific sample: In the Automated analysis Control window, click on Analyze All or Analyze Samples. A dialog box appear, elect one of the options. Click on OK.

11.2.2.10 Performing a recalibration: You define the type and frequency of automatic recalibration on the Checks page of the Method.

Stop the analysis.

In the Automated Analysis Control window, click on Reset.

In the Automated Analysis Control window, click on Calibrate.

11.2.2.11 Analyzing One or More Selected Samples: IN the Automated Analysis Control window, click on Select Location – a dialog box appears. Select the Analyze Samples In Locations option. Enter the autosampler locations of the solutions to analyze in the test box: Enter individual locations or a range of locations. Use comas to separate the locations and ranges, e.g. 10-15,18,20,25-30. Click OK.

11.2.2.12 Resetting the Autosampler: In the Automated Analysis Control window, click on Reset. Analyze the sample; the system will begin with the first sample in the sample list on the Set Up page of the Automated Analysis Control window.

11.2.2.13 Raising or Lower Sample Probe: In the Automated Analysis Control window, click on Probe Up/Down. The sample probe moves up or down but remains at the sample autosampler locations.

11.2.2.14 Rinsing the Sampling Probe and Sampling Tube: In the Automated Analysis Control window, select Location – a dialog box appears. Select “Go to Wash.” Click on OK. The sampling probe moves to the wash location. In the FIAS Control window: Make sure the FIAS-valve is in the correct position to rinse the sample channel. Click on the Pump.

11.2.2.15 The sample pump feeds the rinse fluid from the wash container through the sample channel. Click on Pump again to stop it. Click on

Move Probe Up/Down to raise the probe out of the wash container in the automated analysis Control window.

11.2.3 System Shutdown

11.2.3.1 Place inlets of the carrier and reagent lines in a container of DI water. Rinse the sample, carrier, and reagent tubing with DI water. In the FIAS Control window, click on Valve Fill/Inject a number of times while the pump is running. This ensures that the sample channel and the inside of the FIAS-valve are rinsed effectively.

11.2.3.2 After adequate time, remove, all the tubes from the rinse containers. Click on Move Probe Up/Down to raise the sampling probe.

11.2.3.3 Allow the pump to run until all the tubes and the gas/liquid separator are empty. Then click on the Pump button to stop the pump.

11.2.3.4 Make sure that the FIAS-valve is in the Fill position.

11.2.3.5 Swing all the pressure levers away from the pump tube magazines.

11.2.3.6 Exit the AA WinLab application.

11.2.3.7 Switch off the FIMS spectrometer.

11.3 CALCULATIONS

11.3.1 **Water Samples** – Since initial sample aliquot and final digestate volumes are the same, the mercury analyzer data system will calculate the concentration directly. No further calculations are necessary unless the sample was diluted.

11.3.2 **Soil/Solid/Biota Samples** -

Final Result (mg/kg dry weight corrected) =

$$\frac{\text{Raw data result (ug/L)} * \text{Final Volume (L)} * \text{Dilution Factor}}{\text{Sample weight (g)} * \text{Dry weight for soil/solid (decimal form)}}$$

Biota results are reported on an as is/wet weight basis. The dry weight correction in the formula is not applicable.

11.3.3 Wipes

Final Result (ug/wipe) =

$$\frac{\text{Raw data result (ug/L)} * \text{Final Volume (L)} * \text{Dilution Factor}}{\text{1 wipe}}$$

11.3.4 **Accuracy**-

$$\text{Spike Percent Recovery} = \frac{\text{Spike Sample Result} - \text{Sample Result}}{\text{Spike Added}} \times 100$$

11.3.5 **Precision-**

$$\text{Relative Percent Difference} = \frac{\text{Spike Sample Result} - \text{Spike Sample Duplicate Result}}{(\text{Spike Sample Result} + \text{Spike Sample Duplicate Result})/2} \times 100$$

12. QUALITY CONTROL

12.1 Calibration Blanks – Calibration blanks (ICB and CCB) may not contain concentrations in excess of the Pace Reporting Limit. If blank results are not acceptable, analysis of the batch should be halted. Corrective actions could include preparation of fresh calibration standards and blanks.

12.2 Calibration Checks- Calibration checks (ICV and CCV) must agree within 10% of the true value. If the results are unacceptable, re-calibrate the system and then re-analyze the check solution and samples.

12.3 Pace Reporting Limit Standard (PRL Std) – A standard prepared at the concentration of the Pace Reporting Limit. It is analyzed after the calibration, recovery 60-140% of true value. If outside the limits, reanalyze once. If still outside the limits, recalibrate.

12.4 Laboratory Control Spike – A Laboratory Control Spike (LCS) must be prepared and analyzed with every sample batch or every 20 samples, whichever is more frequent. A Laboratory Control Spike Duplicate (LCSD) is performed if there is insufficient sample available for a MS/MSD or if requested by the client. The LCS and LCSD must meet criteria 85-115% recovery or all the samples prepared in the batch must be re-prepped and re-analyzed. The acceptance criteria for precision if 20% RPD. If insufficient sample remains to re-prep and re-analyze, the data qualifiers is given to all associated samples.

12.5 Method Blank – A Method Blank (MB) must be prepared and analyzed with every sample batch or every 20 samples, whichever is more frequent. The MB must not contain mercury at a concentration at or above the Pace Reporting Limit. Any samples digested with an unacceptable method blank must be re-prepped and analyzed unless the sample concentrations are less than the reporting limit or more than 10 times the value found in the method blank. If those cases that MDL reporting is required, the MB must be evaluated to the MDL. For MDL reporting, an appropriate data qualifier is given to samples associated with +/-MB hits between the +/-MDL and +/-PRL where the sample results are less than 10 times the value found in the method blank. Please refer to the attachment section for the flagging charts.

12.6 Matrix Spike/ Matrix Spike Duplicate – A Matrix Spike/Matrix Spike Duplicate (MS/MSD) must be prepared and analyzed for each group of samples that are similar in matrix at a frequency of 5%. The sample used for MS/MSD pair is either determined by the client or selected at random from client samples as sample volume allows. No field, filter, trip or equipment blanks can be used for MS/MSD. If one or both spike recoveries are outside 85-115% recovery acceptance criteria, the parent sample is given an appropriate data qualifier. If the RPD is outside 20% RPD criteria the parent sample is given an appropriate data qualifier. Parent sample is chosen at random or assigned by the client.

12.7 All reported results must be within the range of the calibration curve. Dilute when results are greater than the high standard in the curve.

13. METHOD PERFORMANCE

13.1 There are several requirements that must be met to insure that this procedure generates accurate and reliable data. A general outline of requirements has been

summarized below. Further specifications may be found in the Laboratory Quality Manual.

13.1.1 The analyst must read and understand this procedure with written documentation maintained in his/her training file.

13.1.2 An initial demonstration of capability (IDC) must be performed per S-ALL-Q-020, *Orientation and Training Procedure*s. A record of the IDC will be maintained in his/her QA file with written authorization from the Laboratory Manager and Quality Manager.

13.1.3 An annual method detection limit (MDL) study will be completed per S-ALL-Q-004, *Method Detection Limit Studies*, for this method and whenever there is a major change in personnel or equipment. The results of these studies are retained in the quality assurance office.

13.1.4 Periodic performance evaluation (PE) samples are analyzed per S-ALL-Q-010, *PE/PT Program*, to demonstrate continuing competence. All results are stored in the QA office.

14. POLLUTION PREVENTION AND WASTE MANAGEMENT

14.1 The quantity of chemicals purchased is based on expected usage during its shelf life and disposal cost of unused material. Actual reagent preparation volumes reflect anticipated usage and reagent stability.

14.2 Excess reagents, samples and method process wastes are characterized and disposed of in an acceptable manner. For further information on waste management consult the current version of ALL-S-002, *Waste Handling*.

15. REFERENCES

15.1 SW-846 7470A, Revision 1, September 1994

15.2 SW-846 7471B, Revision 2, February 2007

15.3 PASI Quality Manual, current revision

15.4 National Environmental Laboratory Accreditation Conference (NELAC), July 2003 Standards

16. TABLES, DIAGRAMS, FLOWCHARTS, APPENDICES, ETC.

16.1 Mercury Process Flow Chart

16.2 Flagging chart A: LOD/LOQ Blank Flagging and Reporting

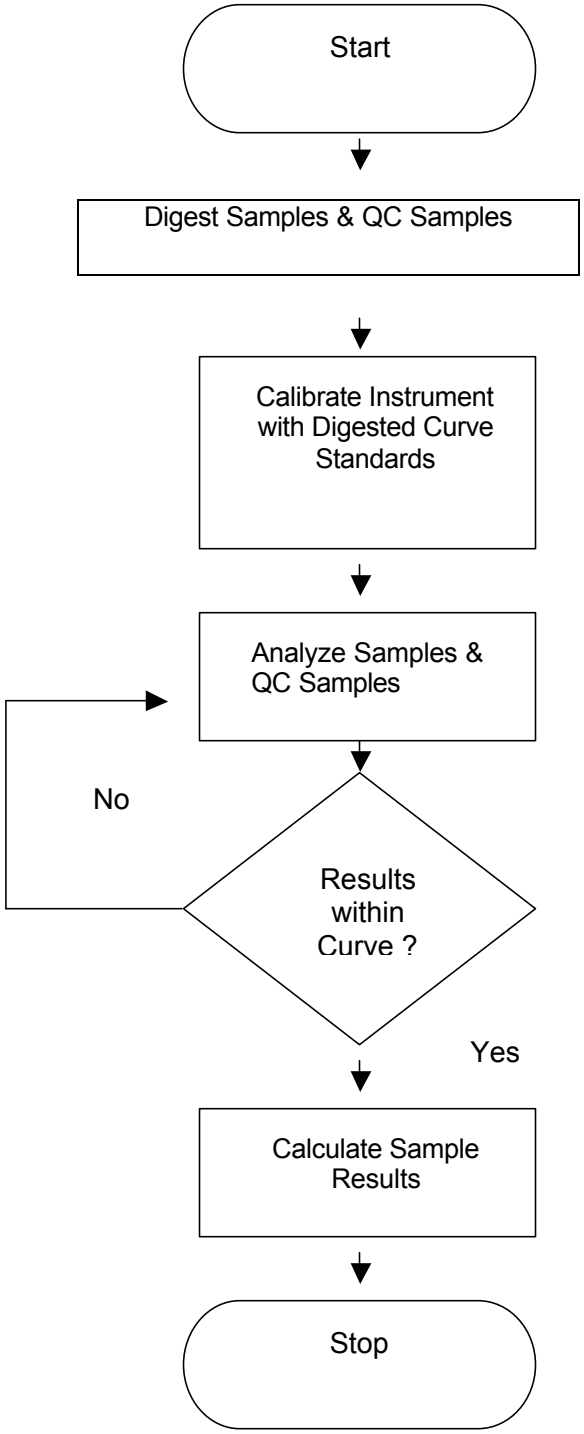
16.3 Flagging chart B: PRL or PSRL Blank Flagging and Reporting

16.4 Flagging chart C: MDL Blank Flagging and Reporting

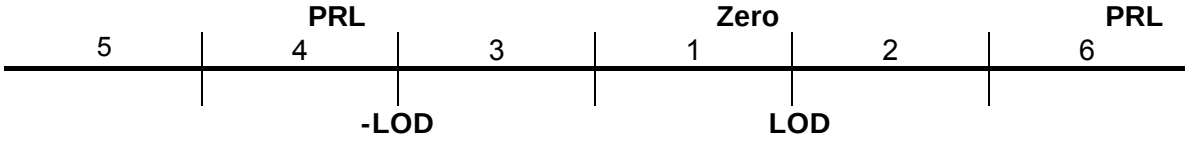
17. REVISIONS

Document Number	Reason for Change	Date
GB-I-036-Rev.0	Combined G2-MET-17 Rev.2 and G2-MET-Rev1 into 1 SOP in new format.	August 28, 2006
GB-I-036-Rev.1	Added Reference to Wipes	December 15, 2006
GB-I-036-Rev.2	Updated Signature Page Updated Section 4.4 - Samples may be diluted to decrease the chlorides Added Section 6.2 Updated Tables 2 and 3. Added Sections 12.1.1.11 and 12.1.1.12 Added Sections 12.1.2.4 and 12.1.2.5 Added Sections 12.2.1, 12.2.3 thru 12.2.10 Updated Section 14	January 2, 2008
S-GB-M-004-REV.00	Updated Method Reference from SW846 7471A to SW846 7471B throughout document. Updated SOP reference to S-GB-M-004-REV.00. Section 4.4 – Added last sentence as alternative Section 5.4.1 – Update SOP reference and name Section 6.2 – Changed biota control blank source from "must" to "should" be farm raised. Section 7 – Deleted Renumbered document Section 10.4 – Added PRLS Table 3 – Added PRLS to HgCal 2 standard Section 12.3 – Added PRLS Section 12.4, 12.5, and 12.6 – Updated flagging language to reflect EpicPro. Section 12.5 – Changed MB contamination from 20 times to 10 times to reflect 7471B requirements. Section 15 – Updated SW-846 7471 reference Flagging Charts A, B, and C – Where ever "A flag" appeared, changed to "appropriately flag". Flagging Charts A, B, and C – Where ever "20 times" appeared, changed to "10 times".	September 12, 2008

Mercury Process Flow Chart



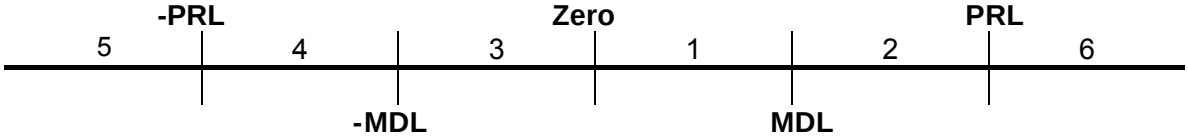
17.1 Flagging Chart A: LOD/LOQ Blank Flagging and Reporting



Blank Position® Sample Position¯	5	4	3	1	2	6
1	R	Appropriately Flag Report < LOD Comment	Report < LOD	Report < LOD	Report < LOD	Report < LOD
2	R	Appropriately Flag Report result w/10X Rule Comment	Report result	Report result	Appropriately Flag Report result w/10X Rule Comment	R
3	R	Appropriately Flag Report <LOD Comment	Report <LOD	Report <LOD	Report <LOD	Report <LOD
4	R	Appropriately Flag Report <LOD Comment	Report <LOD	Report <LOD	Appropriately Flag Report result w/10X Rule Comment	Report <LOD
5	R	R	R	R	R	R
6	R	Appropriately Flag Report result w/10X Rule Comment	Report result	Report result	Appropriately Flag Report result w/10X Rule Comment	Report result w/10X Rule -or- R if result is not 10X MB

R= Analyst discretion to Re-run, Re-calculate, or Re-digest
X= Value in Method Blank (MB).

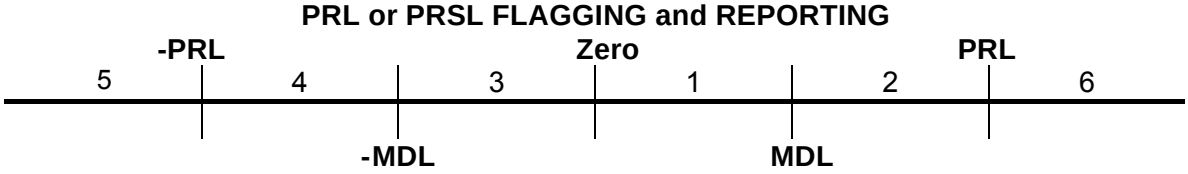
17.2 Flagging Chart B: PRL or PSRL Blank Flagging and Reporting



Blank Position® Sample Position¯	5	4	3	1	2	6
1	R	Report < PRL	Report < PRL	Report < MDL	Report < PRL	Report < PRL
2	R	Report < PRL	Report < PRL	Report result	Report < PRL	Report < PRL
3	R	Report < PRL	Report < PRL	Report <MDL	Report < PRL	Report PRL
4	R	Report < PRL	Report < PRL	Report < PRL	Report < PRL	Report < PRL
5	R	R	R	R	R	R
6	R	Report result	Report result	Report result	Report result	Report result w/10X Rule -or- R if result is not 10X MB

R= Analyst discretion to Re-run, Re-calculate, or Re-digest
X= Value in Method Blank (MB).
PRL= Pace Reporting Limit

17.3 Flagging Chart C: MDL Blank Flagging and Reporting



Blank Position® **Sample Position¯**	5	4	3	1	2	6
1	R	Report < PRL	Report < PRL	Report < PRL	Report < PRL	Report < PRL
2	R	Report Result Appropriately Flag W/ 10X Rule Comment	Report Result	Report Result	Report Result Appropriately Flag W/ 10X Rule Comment	R
3	R	Report < PRL	Report < PRL	Report < PRL	Report < PRL	Report < PRL
4	R	Report < PRL	Report < PRL	Report < PRL	Report < PRL	Report < PRL
5	R	R	R	R	R	R
6	R	Report result Appropriately Flag W/ 10X Rule Comment	Report result	Report result	Report Result Appropriately Flag W/ 10X Rule Comment	Report result Appropriately Flag w/10X Rule -or- R if result is not 10X MB

R= Analyst discretion to Re-run, Re-calculate, or Re-digest
X= Value in Method Blank (MB).
PRL= Reporting Limit

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STANDARD OPERATING PROCEDURE

Determination of Trace Metals in Waters and Wastes By Inductively Coupled Plasma Mass Spectroscopy

Reference Methods: SW-846 6020A WITH 3010A AND 3050B

SOP NUMBER:	S-GB-M-006-REV.00
EFFECTIVE DATE:	Date of Final Signature
SUPERSEDES:	First Issue

APPROVAL

Nils Melberg, Laboratory General Manager — Date: 09/25/08

Kate Grams, Laboratory Quality Manager — Date: 09/25/08

Chad Rusch, Department Manager — Date: 09/25/2008

ANNUAL REVIEW

SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE APPROVAL. SOP IS VALID FOR ONE YEAR FROM DATE OF LAST SIGNATURE.

Signature	Title	Date

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1. Purpose

The purpose of this Standard Operating Procedure (SOP) is to provide a consistent format for acid digestion and analyzing samples using the ICPMS. It applies to the Thermo X Series II ICPMS.

2. Scope and Application

2.1 Inductively coupled plasma-mass spectrometry (ICPMS) is applicable to the determination of sub-ppb (ug/L) concentrations of a large number of elements in biota, aqueous, and solid extracts or digests. When dissolved constituents are required, samples must be filtered and acid-preserved prior to analysis. Dissolved samples are typically acid digested prior to analysis. Acid digestion prior to filtration and analysis is required for aqueous and solid samples for which total (acid-leachable) elements are required.

2.2 This SOP is applicable to the determination of the analytes listed in Table A, at a minimum. On instrument reporting limits are listed in Tables M, N, and O, based on their matrix and prep method. Please see the QA manager for the most current MDLs for each method.

2.3 If Method 6020A is used to determine any analytes not listed in Table A, it is the responsibility of the analyst to demonstrate the accuracy and precision of the method in the matrix to be analyzed. The analyst is always required to monitor potential sources of interferences and take appropriate action to ensure data of known quality.

2.4 Use of this method is restricted to analysts who are knowledgeable in the recognition and in the correction of spectral, chemical, and physical interferences in ICP-MS.

3. Summary of Method

3.1 Prior to analysis samples, which require total ("acid-leachable") values, must be digested using appropriate sample preparation methods. A number of methods are recommended in SW846 for the sample preparation/digestion of various matrices for trace metals analysis by ICPMS. The prep methods utilized are listed below. The analytes they are applicable for are listed in the attachments.

3.1.1	**SW846 3010A**	Wastes, aqueous samples	Found in attachment I
3.1.2	**SW846 3050B**	Soils, Sludges, solid wastes	Found in attachment II
3.1.4	**M3050B**	Biota	Found in attachment IV

3.2 Method 6020A describes the multi-elemental determination of analytes by ICP-MS. The method measures ions produced by a radio frequency inductively coupled argon plasma. Analyte species originating in a liquid are nebulized and the resulting aerosol transported by argon gas into the plasma torch. The ions produced are entrained in the plasma gas and introduced, by means of an interface, into a mass spectrometer. The ions produced in the plasma are sorted according to their mass-to-charge ratios and quantified with a channel electron multiplier. Interferences must be assessed and valid corrections applied or the data flagged to indicate problems. Interference correction must include compensation for background ions contributed by the plasma gas, reagents, and constituents of the sample matrix.

4. Interferences

4.1 Isobaric Elemental Interferences – Isobaric elemental interferences result when isotopes of different elements have the same nominal mass-to-charge ratio and cannot be resolved with the instruments spectrometer. One way to solve this problem is to measure a different isotope for which there is no interference. Alternatively, one can monitor another isotope of the element and subtract an appropriate amount from the element being analyzed, using known isotope ratio information. Corrections for most of the common elemental interferences are programmed into the software.

4.2 Isobaric Polyatomic Interferences – Isobaric polyatomic interferences result when ions containing more than one atom have the same nominal mass-to-charge ratio as an analyte of interest and can not be resolved by the instrument's spectrometer. Examples include ArCl+ (mass 75) which interferes with As. ClO+ (mass 51) which interferes with V, which must be corrected by measuring ClO+ at mass 53. When possible an interference free isotope should be chosen, to be measured.

4.3 Physical interferences are associated with the sample nebulization and transport processes as well as with ion-transmission efficiencies. Nebulization and transport processes can be affected if a matrix component causes a change in surface tension or viscosity. Changes in matrix composition can cause significant signal suppression or enhancement. Dissolved solids can deposit on the nebulizer tip of a pneumatic nebulizer and on the interface skimmers (reducing the orifice size and the instrument performance). Total solid levels below 0.2% (2,000 mg/L) have been currently recommended to minimize solid deposition. An internal standard can be used to correct for physical interferences, if it is carefully matched to the analyte so that the two elements are similarly affected by matrix changes.

4.4 Memory interferences can occur when there are large concentration differences between samples or standards, which are analyzed sequentially. Sample deposition on the sampler and skimmer cones, spray chamber design, and the type of nebulizer affects the extent of the memory interferences, which are observed. The rinse period between samples must be long enough to eliminate significant memory interference.

4.5 It is important to note that matrix matching acid concentrations and compositions between standards, blanks and samples is required and cannot be ignored.

4.6 Chromic acid should never be used to clean any container used in ICP-MS analysis.

4.7 Borosilicate glass in sample containers can lead to interference of Boron concentrations in samples. This is also true of volumetric flasks, thus when dilution in the flask is complete the standards must be removed as soon as possible from the dilution container and placed into a clean plastic container.

5. Safety

5.1 The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable. Cautions are included for known extremely hazardous materials.

5.2 A reference file of Material Safety Data Sheets (MSDS) is made available to all personnel involved in the chemical analysis, and is located at the front desk. A formal safety plan has been prepared and is distributed to all personnel with documented training.

5.3 Analysts should take necessary safety precautions when handling chemicals and samples. Proper personal protective equipment may include safety gloves, lab coats, and safety glasses or goggles. Analysts should be familiar with the MSDS sheets for all chemicals and reagents they use for this procedure and the location of the MSDS sheets within the laboratory. Any questions or concerns should be taken to the laboratory Chemical Hygiene/Safety Officer.

6. Definitions

Refer to the most current version section 10 of the Pace Quality Manual.

7. Sample Collection, Preservation and Handling

7.1 All sample containers must be HDPE, glass, or Teflon. The containers are purchased pre-cleaned and documented to be contaminant free.

7.2 Aqueous Samples

7.2.1 Dissolved samples must be filtered through a 0.45-um pore diameter membrane filter at the time of collection or as soon after as practically possible. The laboratory can perform the filtration if the step was not performed in the field. The filtrate is then preserved to a pH<2 with nitric acid, acid not to exceed 5% of the container capacity.

7.2.2 Total samples are preserved to a pH<2 with nitric acid, acid not to exceed 5% of the container capacity.

NOTE: Aqueous samples that react violently to the addition of acid maybe collected without chemical preservation with proper variances approved by the regulatory authority. The responsibility of requesting this variance lies with the sample collector.

NOTE: Samples may be preserved in the lab. The samples may not be processed until 24 hours after preservation with a pH test of <2, unless otherwise noted on the data.

7.3 Solids samples require no chemical preservation.

7.4 Shipments of samples to the laboratory require thermal preservation in the form of cubed or block ice. At the time of laboratory receipt, proper thermal preservation is checked by measuring the temperature of melt water or when provided the temperature blank. The Pace Analytical acceptable temperature range is 2 to 6^0 C. All QAPjP and regulatory authority requirements become priority over this requirement.

7.5 There are no thermal storage requirements for aqueous samples. Solids samples require storage at 2 to 6^0 C. All QAPjP and regulatory authority requirements become priority over this requirement.

7.6 Sample hold times:

7.6.1 The hold time for solid and preserved aqueous (total and dissolved) samples, excluding Hg, is 6 months.

7.6.2 The hold time for solid and preserved aqueous (total and dissolved) samples for Hg is 28 days.

7.6.3 The hold time for biota samples, excluding Hg, is 6 months after removal from the freezer.

7.6.4 The hold time for biota samples for Hg is 28 days after removal from the freezer.

8. Equipment and Supplies

8.1 All reusable labware (glass, quartz, polyethylene, PTEFE, FEP, etc.) should be sufficiently clean for the task objectives.

8.2 **See Table B for a summary of Equipment.**

8.3 **See Table C for a summary of supplies.**

9. Reagents and Standards

9.1 Standards are used in the tuning of the instrument through the calibration, calibration verification, sample analysis, and continuing calibration verification. Standard solutions include: instrument tuning solutions, calibration and calibration check standards, ICSA/AB, internal standards, low level check standards (LLC or CRI), and spike standards. Please see Table D for a list of working standards. **Table F lists the directions to making intermediate standards from the stock standards listed in Table E.**

9.1.1 Mass Spectrometer Tuning Solution: A solution containing elements representing all of the mass regions of interest (for example, 10 µg/L of $^{23, 24, 25}$Mg and $^{206, 207, 208}$Pb) must be prepared to verify that the mass resolution and mass calibration of the instrument are within the required specifications. This solution is also used to verify that the instrument has reached thermal stability.

9.1.2 Cross Calibration Solution (X Cal): contains 50 ppb of most method analyte elements. This solution is used to calculate the concentration when the detector changes from pulse mode to analog mode. This enables a large linear range while protecting the detector.

9.1.3 Calibration Standards: These are an increasing gradient of concentration for the analytes of interest. These can be made in the laboratory or purchased from commercial suppliers.

9.1.4 Initial Calibration Verification (ICV): The quality control standard is the initial calibration verification solution (ICV), which must be prepared in the same acid matrix as the calibration standards. This solution must be an independent standard at approximately half of the concentration of the standard used for instrument calibration. An independent standard is defined as a standard composed of the analytes from a source different from those used in the standards for instrument calibration.

9.1.5 Reporting Limit Verification Standard (RLVS): With every Initial Calibration, a standard corresponding to the Pace reporting limit (PRL) must also be analyzed and meet established acceptance criteria. The RLVS is analyzed prior to any samples being analyzed and at the end of the analytical sequence. Additional RLVSs may be analyzed throughout the analytical sequence at the analyst's discretion. The limits for the RLVS are +/- 30% of the true concentration. These are standards that are at the reporting limit for the analytes of interest. The analysis of this standard demonstrates the instruments ability to report down to the reporting limit with known accuracy.

9.1.6 Interference Check Solutions (ICSA and ICSAB). The ICSA and ICSAB are prepared to contain known concentrations of interfering elements that will demonstrate the magnitude of interferences and provide an adequate test of any corrections. Chloride in the ICS provides a means to evaluate software corrections for chloride-related interferences such as ^{35}CI ^{16}O on ^{51}V, and ^{40}Ar ^{35}Cl on $^{75}As^{+}$. Iron is used to demonstrate adequate resolution of the spectrometer for the determination of manganese. Molybdenum serves to indicate oxide effects on cadmium isotopes. The other components are present to evaluate the ability of the measurement system to correct for various polyatomic isobaric interferences. The ICS is used to verify that the interference levels are corrected by the data system to within quality control limits. Table D provides a summary of the ICS-A and ICS-AB solution concentrations used.

9.1.7 Continuing Calibration Verification (CCV): This standard is near the midpoint of the curve and used to verify that the instrument is still in calibration.

9.2 Reagents: **Please see Table G for a list of reagents.**

9.3 All standards, reagents, and spiking solutions are kept at room temperature. Stock standards and reagents can be used until they expire. Refer to the most current version of S-GB-I-035 *Metals Stock Standards and Acid Expiration Date Rules* for metals stock standard and reagent expiration rules. Intermediate and working standards are given a six month expiration date. However the expiration date may not extend past the earliest expiration date of any stock standard used to create the solution. The use of any standard or reagent will be terminated if any contamination or problems arise prior to the expiration date.

9.4 Log-in of Standards, reagents, and standards are logged as follows:

9.4.1 Stock standards have a copy of their certificate of analysis logged onto a page in the ICPMS Stock Standard Log. The three-digit logbook number followed by a dash and the page number represent the stock standard number (e.g. 784-64).

9.4.2 Reagents are logged in the same manner, except they are logged into the Metals Reagent Logbook. Solutions (including standards, intermediates, and spikes) are logged into the ICPMS Standard Reference Log, by describing the directions in which they were made. They are logged as follows:

Logbook # - Page # - Line # (e.g. 785-62-08)

9.4.3 Stock standards can also be logged in to an electronic logbook. Refer to the most current version of T-GB-IT-003 *The Standard Log Program* for this procedure.

10. Set Up and Calibration

10.1 Calibration Curve: Demonstration and documentation of acceptable initial calibration is required before any samples are analyzed and is required periodically throughout sample analysis as dictated by results of continuing calibration verification standards. Refer to section 13 for calibration and standardization control criteria. Calibration consists of a calibration blank and four or five non-zero standards (analyte dependant) analyzed after a calibration blank. The ICPMS software creates a curve based on this data and the following equation: Y=a(x)+b. In calculating x(concentration) from y(response) the b is subtracted. The b represents the number of counts in the calibration blank.

10.2 Calibration Levels: **Please see Table D for directions on making the calibration standards and Table H to see the calibration levels used in the calculations.**

10.3 Internal Standards: Internal standardization must be used in all analyses to correct for instrument drift and physical interferences. For full mass range scans, a minimum of three internal standards must be used. Procedures described in this SOP for general applications detail the use of six internal standards; ^{45}Sc-CCT, ^{45}Sc-KED, ^{72}Ge, ^{89}Y, ^{115}In, ^{159}Tb, and ^{209}Bi. Additional internal standards such as Ho may be used if results indicate the presence of one or more of the internal standard elements in the samples or if recoveries for certain elements such as Zn or Cd are poor in some matrices. Internal standards must be present in all samples, standards and blanks at identical levels. This is achieved by directly adding the internal standard stock solution (200ppb in 2% HNO3) to all samples, standards and blanks by on-line addition prior to nebulization using a second channel of the peristaltic pump and a mixing Y-connector. The concentration of the internal standard should be sufficiently high that good precision is obtained in the measurement of the isotope used for data correction and to minimize the possibility of correction errors if the internal standard is naturally present in the sample. A final concentration at the nebulizer of approximately 100 ppb will result from the addition of a 200 ppb solution. **Table I provides a list of acceptable internal standards and their suggested associated elements.**

10.3.1 Due to matrix interferences one or more of the internal standards may not be suitable. It is up to the analyst to recognize and correct the problem by selecting another internal standard to reprocess the data or by diluting the sample(s) for reanalysis. NOTE: The interpolation between 2 internal standards is still possible when one internal standards needs to be removed to compensate for its presence in the samples, the next lightest or heaviest mass will replace the one removed.

10.3.2 During the determination, the software uses the ratio of analyte and internal standard intensities to adjust the final intensity values. Ratios are based on the calibration blank intensities.

10.3.3 An internal standard without Li must be used if Li is an analyte of interest.

10.3.4 Interference Calculations- Interference equations are used to correct for isobaric elemental and polyatomic interferences. All equations can be adjusted if necessary or added if the analyst determines that any particular correction is insufficient or if an equation is over correcting the data. **Table J shows the recommended Elemental Interference Equations**

10.3.4.1 Acquisition Mode:

Points per Mass: 1
Number Replicates: 3
Integration Time: 10 ms for all elements except Na, As, Se, Kr ; 5 ms for Na, and 50 ms for As, Se, Kr.

10.3.4.2 Example Peristaltic Pump Program:
Uptake time: 30 sec [1]
Stabilization Time (CCT pre experiment):45 sec
Stabilization Time (KED Changeover): 60 sec
Monitored Wash: 15Sec Minimum, 45Sec Maximum

10.3.4.3 **Acquisition masses and integration times can be found in Table K.**

11. Procedure

11.1 Solubilization and digestion procedures are presented in the Attachments I, II, and III (e.g. Methods 3010A and 3050B).

11.2 Instrument Startup:

11.2.1 Verify argon supply and pressure.

11.2.2 Turn on water chiller and exhaust fan.

11.2.3 Insure that the internal standard solution bottle is adequately full

11.2.4 Verify contents of auto sampler rinse port reservoir.

11.2.5 Empty waste reservoir.

11.2.6 Ignite the plasma and allow at least 15 minutes of warm-up while scanning the mass analyzer. The tuning procedures may then be carried out.

11.2.7 Insure that all peristaltic pump tubes are in good condition and correctly clamped into the peristaltic pumps. Verify that the flow of sample and internal standard solutions through the uptake lines and into nebulizer is free from extreme pulsations by introducing a bubble into each line and observing its progress.

11.3 Mass Tuning: Allow 15 minutes of scanning for the Instrument to achieve thermal stability. Aspirate the 10ppb Tuning Solution inserting both the sample and internal standard delivery lines into the tune solution so as not to dilute the tune solution. Run each of the following performance reports, print the passing report, and save the mode by month, day, year (no commas) into the configurations list by type (e.g. Standard Mode09052008, CCT Mode09052008, and KED Mode09052008).

11.3.1 EPA Performance Report (Xt Standard Mode)

11.1.3.1 Mass Resolution (10 Sweeps, 5 Reps)
Acquisition Parameters: Peak width measured at 5% peak maximum.
Dwell Time (mSec): 10
Point Spacing: 0.05amu
Mass Limits: 0.65 – 0.85 amu (Max error 0.10 amu)
Defined Masses: ^{24}Mg, ^{25}Mg, ^{26}Mg, ^{206}Pb, ^{207}Pb, ^{208}Pb

11.1.3.2 Sensitivity and Stability (35 Sweeps, 5 Reps)
Mass: Dwell (mSec) : %RSD : Counts
(NA=Not Applicable)
^{5}Bkg 500.0 : NA : <1
^{7}Li 10.0 : 2.0 : >60,000
^{24}Mg 10.0 : 2.0 : >10,000
^{25}Mg 10.0 : 2.0 : >10,000
^{26}Mg 10.0 : 2.0 : >10,000
^{59}Co 10.0 : 2.0 : >150,000
^{137}Ba++ 10.0 : NA : NA
^{115}In 10.0 : 2.0 : >400,000
^{137}Ba 10.0 : NA : NA
^{138}Ba 10.0 : NA : NA
^{140}Ce 10.0 : NA : NA
^{156}CeO 100.0 : NA : NA
^{206}Pb 10.0 : 2.0 : >10,000
^{207}Pb 10.0 : 2.0 : >10,000
^{208}Pb 10.0 : 2.0 : >10,000
^{220}Bkg 500.0 : NA : <1
^{238}U 10.0 : 2.0 : >800,000

11.1.3.3 Oxides and Doubly Charged (Ratio Results)
^{137}Ba++/^{137}Ba: <0.0300
^{156}CeO/^{140}Ce: <0.0200

11.3.2 CCT Performance Report (Xt CCT)
Sensitivity and Stability (45 Sweeps, 5 Reps)
Acquisition Parameters: Mass : Dwell (mSec) : %RSD : Counts ^{7}Li
10.0 : 2.0 : >10,000
^{9}Be 10.0 : 2.0 : >2,000
^{11}B 10.0 : 2.0 : >2,000

11.3.3 KED Performance Report (Xt CCT-KED)

11.3.3.1 Sensitivity and Stability (35 Sweeps, 5 Reps)
Acquisition Parameters: Mass : Dwell (mSec) : %RSD : Counts
^{78}Se 100.0 : NA : <20
^{115}In 10.0 : 2.0 : >100,000
^{140}Ce 10.0 : NA : NA
^{156}CeO 50.0 : NA : NA

11.3.3.2 Ratio Results
^{156}CeO/^{140}Ce <0.0200

11.3.4 Introduce the internal standard and aspirate a new rinse blank for 5-10 minutes to eliminate any carry-over into the calibration blank.

11.3.5 The Xcal solution does not need to be run unless deviations between the pulse counting and analog counting methods is observed in the spectra. The pulse counting will appear to sit above the pulse baseline in an observed spectra and indicates that the cross calibration needs to be performed. Aspirate the Xcal solution in Standard Mode, with both the sample delivery and internal standard lines (so as to not dilute the Xcal solution). Follow the options in 11.3.5.1 or 11.3.5.2. Step 11.3.5.3 needs to be followed after a detector change.

11.3.5.1 Cross Calibration Only. This is done when the deviation between the pulse and analog counting methods is observed and the minimum counts per second listed in the tuning section are achievable. Run the Instrument Calibration wizard in PlasmaLab when deviation of the analog spectra is observed. The detector cross calibration is selected by default in the wizard. This will reset the detector-gating plateau such that the analog spectra (dashed line in the spectra) will sit directly on top of the pulse baseline (solid line in the spectra).

11.3.5.2 Detector Setup and Cross Calibration. This is done when the minimum counts per second listed in the tune section are not achievable. Thus, the detector dynode value will be adjusted and a new cross calibration will be performed with the new detector voltage setting. Launch the Instrument Calibration wizard in PlasmaLab and select detector set up. The detector cross calibration will be checked by default, also select the detector set up portion in the wizard. The voltage applied to the detector will be set first to achieve acceptable sensitivity followed by a detector cross calibration with the new detector setting.

11.3.5.3 Dead Time Experiment. This experiment must be performed after a detector is replaced. The dead time experiment will identify the delay or "dead time" associated with a particular detector. The dead time is the delay between the pulse measurement and analog measurement when the detector gate is dropped. In the experiment a 1ppb and 10ppb solution of Uranium is run, and the ratios between ^{235}U and ^{238}U is calculated for both concentrations. The values for the ratios are adjusted such that the ratio values are as close to identical as possible and that value (dead time in nanoseconds) is entered into PlasmaLab software via the Advanced Page.

11.4 Automated Calibration, Quality Control and Sample Analysis:

11.4.1 Prepare calibration standards, blanks, spikes, samples, and QC samples. **Directions to make up the standards can be found in Tables D and F.**

11.4.2 Build a sequence in the sequence table and apply the repeat run rules to insert the CCV and CCB for every 10 unknowns.

11.4.3 When the sample list and QC checks have been verified for accuracy, queue the experiment to the Technician Queue. Each experiment will require a unique code (e.g. 0905208A, 0905208B, etc.).

11.4.4 **Expected values and limits for ICV, CCV, ICS-A, and ICS-AB can be found in Table L.**

11.5 Data Analysis and Calculations:

11.5.1 The Plasma Lab software performs all calculations necessary to convert raw counts per second data into quantitative concentration results.

11.5.2 Consideration should be given to the interference equations that are in the method. As a result of changing tune parameters over time, the equations may require adjustment periodically to ensure they are not over compensating or under compensating for the polyatomic or isobaric interferences. This is especially true of ^{52}Cr and ^{51}V as the CCT-KED tune can vary slightly from day to day operation. This variation (primarily in the add gas for the collision cell) will change the counts per second acquired for Cl and ClO ions. This can lead make the counts per second in the calibration blank for these isotopes artificially high or low (See Table J). In the case of Lead, quantitation is based on the sum of isotopes 206, 207, and 208 to compensate for any variation in naturally occurring isotope ratios. This is accomplished through the use of the interference correction equation for lead.

11.5.3 See the QA Manager for Isotopes and the respective laboratory specific method detection limits and reporting limits.

11.5.4 Aqueous Sample Calculation:

$$\frac{\text{Raw Data result (µg/L)} * DF * V_F}{V_I} = \text{Final Result (µg/L)}$$

Where:
DF = Dilution Factor
V_F = Final Volume (L)
V_I = Initial Sample Volume (L)

11.5.5 Soil Sample Calculation:

$$\frac{\text{Raw Data result (µg/L)} * DF * V_F}{W_S \times \%S} = \text{Final Result (mg/kg dry weight)}$$

Where:
DF = Dilution Factor
V_F = Final Volume (L)
V_I = Initial Sample Volume (L)
W_S = Sample weight (grams)

%S = Percent solids/ 100
Example: For a sample that is 97.6% solid use 0.976

11.5.6 Biota Sample Calculation

$$\frac{\text{Raw Data result (µg/L)} * DF * V_F}{W_S} = \text{Final Result (mg/kg)}$$

Where:
DF = Dilution Factor

V_F = Final Volume (L)
V_I = Initial Sample Volume (L)
W_S = Sample weight (grams)

NOTE: Results for biological samples are routinely reported on an "as is" or wet weight basis. Dry weight correction is available on request.

Hardness as $CaCO_3$ in mg/L = 2.497 * $[Ca_{\text{ in mg/L}}]$ + 4.118 * $[Mg_{\text{ in mg/L}}]$

12. Quality Control

There are three levels of quality control utilized in this SOP. They consist of Method QC, Instrument QC, and Prep/Batch QC.

12.1 Method QC consists of the instrument detection limits, linear ranges, method detection limits, the lower limit quantitation check, and demonstrations of capability. This QC must be completed prior to analyzing any samples.

12.1.1 Instrument Detection limits (IDLs): IDLs in ug/L are estimated by calculating the average of the standard deviations of the three runs on three non-consecutive days from the analysis of a reagent blank solution with seven consecutive measurements per day. Each measurement must be performed as though it were a separate analytical sample (i.e., each measurement must be followed by a rinse and/or any other procedure normally performed between the analysis of separate samples). IDLs must be determined at least every three months.

12.1.2 Linear Dynamic Ranges (LDR): The LDR is determined annually by analyzing a standard expected to be near the high end of the instruments range. The result must be within +/-10% of the expected concentration, or a lesser concentration tested until acceptable results are obtained.

12.1.3 Method Detection Limits (MDLs): Method detection limits were obtained by multiplying 3.143 by the standard deviation of seven spikes. The spikes went through the digestion procedures and were spiked at a concentration suspected to be within a factor of ten greater than the MDL. The most current version of the MDL SOP, ALL-Q-004, must be followed when determining MDLs. Note: The MDL determined by the MDL study is the theoretical MDL. The MDL used for reporting purposes may be higher than the theoretical MDL.

12.1.4 Lower Limit Quantitation Check (LLQC): The LLQC is a standard at the reporting limit concentration that has gone through all the prep procedures. It has control limits of +/-30% of the true value. It is analyzed to establish the lower limit of quantitation and whenever new limits are established.

12.1.5 Initial Demonstration of Capability (IDOC): An initial demonstration of capability (IDC) must be performed per S-ALL-Q-020, *Orientation and Training Procedure*s. A record of the IDC will be maintained in his/her QA file with written authorization from the Laboratory Manager and Quality Manager.

12.1.6 Instrument QC: Prior to the analysis of samples, and in some cases during the analysis run, the following quality control must be generated and/or within limits: Daily Performance Report for each mode of operation, Internal Standards, Interference Correction Solutions A and B (ICSA and ICSAB), Initial Calibration Verification (ICV), Continuing Calibration Verification (CCV), and Initial and Continuing Calibration Blanks (ICB and CCB).

12.1.5 The intensities of all internal standards must be monitored for every analysis. When the intensity of any internal standard fails to fall between 70 and 130 percent of the intensity of that internal standard in the blank of the calibration, one of the following procedures is followed. The sample is diluted appropriately and reanalyzed with the addition of appropriate amounts of internal standards. This procedure must be repeated until the internal standard intensities fall within the prescribed window. The internal standard for the element, or elements of interest, can also be changed to an internal standard that is within limits and the run reprocessed. If the supporting quality control passes, then the results can be reported.

12.1.6 The ICSA and ICSAB solution are used to verify the magnitude of elemental and molecular-ion isobaric interferences and the adequacy of any corrections at the beginning of an analytical run, prior to the analysis of any samples. The analyst should be aware that precipitation from solution AB may occur with some elements, specifically silver. The control limits for the elements in the ICSAB solution that are in the linear range must be within 80 to 120% of the expected recovery. If an element of interest does not meet these limits, then the problem must be corrected, the instrument recalibrated, and the run reanalyzed.

12.1.7 The ICV is analyzed to check the accuracy of the curve. It must be evaluated before any samples are analyzed. The ICV should be at or near the midpoint of the calibration curve, derived from a source independent of the calibration standards, and must quantitate within +/-10% of the expected value. If these limits are not met for an element of interest, the problem must be corrected, the instrument recalibrated, and the run reanalyzed. If the ICV fails high and the samples are non-detects, then they may be reported.

12.1.8 Reporting Limit Verification Standard (RLVS): With every Initial Calibration, a standard corresponding to the Pace reporting limit (PRL) must also be analyzed and meet established acceptance criteria. The RLVS is analyzed prior to any samples being analyzed and at the end of the analytical sequence. Additional RLVSs may be analyzed throughout the analytical sequence at the analyst's discretion. The limits for the RLVS are +/- 30% of the true concentration. These are standards that are at the reporting limit for the analytes of interest. The analysis of this standard demonstrates the instruments ability to report down to the reporting limit with known accuracy

12.1.9 The CCV is analyzed to check for calibration drift. The CCV is run after every 10 samples and again at the end of samples. It must quantitate within 10% of expected value. Any sample analyzed under out-of-control calibration must be reanalyzed, following the successful re-calibration of the instrument. If the CCV fails high and the samples are non-detects, then they may be reported.

12.1.10 The ICB is analyzed to check the accuracy of the curve. The CCBs are analyzed to check for calibration drift. In the absence of project specific reporting limits, the results of the calibration blanks must be less than the Reporting Limit. The ICB is run after the ICV and the CCBs are run after the CCVs. If the ICB or CCB fails high for an analyte and the samples are non-detects, then they may be reported.

12.2 A batch will consist of 20 or fewer samples. Batch Quality Control will include a Method Blank(MB), Laboratory Control Spike(LCS), Matrix Spike(MS), Matrix Spike Duplicate(MSD), Post Spike(PS), and a Serial Dilution(SDL). It may also include a Laboratory Control Spike Duplicate(LCSD) and/or Standard Reference Material (SRM).

12.2.1 The Method Blank is used to verify that interferences caused by contaminants in the solvents, reagents, glassware, etc. are known and minimized. The method blank is processed through all clean-ups, etc., which were performed on the samples in the batch. For a method blank to be acceptable, in the absence of project specific criteria, the concentration shall not be higher than the highest of the following: The reporting limit, or ten percent of the regulatory limit of concern for that analyte, or ten percent of the measured concentration in a particular sample of interest. See Flowcharts for a visual guide on applying flags to the above conditions. Each sample in the batch is assessed against the above criteria to determine if the sample results are acceptable. Any sample associated with an unacceptable blank is either flagged, re-prepped for analysis, or if re-prepping is not an alternative, the results are reported with the appropriate data qualifying codes.

12.2.2 A laboratory control sample (LCS) consists of a control matrix, which has been spiked, with the analytes(s) of interest or compounds representative of those analytes. Laboratory Control Samples are analyzed at a minimum of 1 per batch of 20 or fewer samples or preparation method. Results of the LCS are expressed in terms of percent recovery, and are used to determine batch acceptance. Acceptance limits are generated based on laboratory generated data and are not to exceed 80 to 120% of the expected recovery. If these limits are not met with the instrument in control, then the entire batch will be re-digested and re-analyzed.

An LCS Duplicate may be analyzed to evaluate laboratory precision. The LCSD must also meet the criteria for the LCS. The Relative Percent Difference (RPD) will be calculated between the LCS and LCSD. The RPD is calculated as outlined below:

$$RPD = \frac{| D_1 - D_2 |}{(D_1, + D_2,) /2} \times 100$$

where:
RPD = relative percent difference.
D_1 = first sample value.
D_2 = second sample value (duplicate)

The control limit for RPD is based on laboratory generated data and is not to exceed 20%. If outside this limit, all associated results are given a R1 data qualifier. Data generated with LCS samples that fall outside the established acceptance criteria are judged to be out-of-control. These data are considered suspect and the corresponding samples are reanalyzed or reported with qualifiers.

NOTE: In the event where adequate sample is not supplied by the client to perform a Matrix Spike/ Matrix Spike Duplicate, the LCS and duplicate can lend insight on the precision of the analysis.

12.2.3 Matrix spikes (MS and MSD) are performed to evaluate the effect of the sample matrix upon analytical methodology. A separate aliquot of sample is spiked with the analyte of interest and analyzed with the sample. MS and MSD are performed at a minimum frequency of one pair in 20 samples per matrix type per sample preparation method and are done more frequently where regulations require. Matrix spike recoveries are evaluated against in-house control limits. The recovery must not exceed 75 to 125% of the expected recovery. If outside this recovery, the parent is flagged with an M0 data qualifier. The RPD between the MS and MSD must be less than 20 %. If outside this limit, the parent is given a R1 data qualifier. The parent sample for the MS/MSD is chosen at random unless specified by a client. Poor performance in a matrix spike generally indicates a problem with the sample composition, and not the laboratory analysis, and results are used to assist in data assessment. A matrix effect is indicated if the LCS data are within acceptance criteria but the matrix spike data exceed the acceptance criteria. Prior to calculating recovery, the parent sample concentration (results <Reporting MDL = 0) is subtracted from the spike aliquot concentrations.

12.2.4 The Post Spike (PS) is run to verify matrix interferences. An analyte spike added to a portion of a prepared sample, or its dilution if above the LDR, should be recovered to within 80 to 120 percent of the known value. If the spike is not recovered within the specified limits with the instrument in control, then the sample has a confirmed matrix effect and the serial dilution test should be performed, and appropriate flags given to the matrix spike and duplicate data (e.g. M0, P6, and or R1). The post spike will be run per project specific requirements or per client request.

12.2.5 The Serial Dilution (SDL) is run to check for matrix interferences. If the analyte concentration is within the linear dynamic range (LDR) of the instrument and sufficiently high (minimally, a factor of at least 10 times greater than the lower limit of quantitation for the diluted sample, or 50 times the lower limit of quantitation for the parent sample) an analysis of a fivefold (1+4) dilution must agree within ± 10% of the original determination. If these limits are not met then an interference effect must be suspected and the data qualified with an SD flag. If the analytes of interest are greater than the LDR in the parent sample, the sample can be diluted and an SDL done off of the dilution. The serial dilution will be run per project specific requirements or per client request.

12.2.6 The SRM is typically prepped and analyzed upon client request. It is a sample of known concentration chosen to resemble the matrix being analyzed.

13. Method Performance

13.1 There are several requirements that must be met to insure that this procedure generates accurate and reliable data. A general outline of requirements has been summarized below. Further specifications may be found in the Laboratory Quality Manual.

13.2 The analyst must read and understand this procedure with written documentation maintained in his/her training file.

13.3 An initial demonstration of capability (IDC) must be performed per the most recent version of S-ALL-Q-020, *Orientation and Training Procedure*s. A record of the IDC will be maintained in his/her QA file with written authorization from the Laboratory Manager and Quality Manager.

13.4 An annual method detection limit (MDL) study will be completed per the most recent version of S-ALL-Q-004, *Method Detection Limit Studies*, for this method and whenever there is a major change in personnel or equipment. The results of these studies are retained in the quality assurance office.

13.5 Periodic performance evaluation (PE) samples are analyzed per the most recent version of S-ALL-Q-010, *PE/PT Program*, to demonstrate continuing competence. All results are stored in the QA office.

14. Pollution Prevention and Waste Management

14.1 The quantity of chemicals purchased is based on expected usage during its shelf life and disposal cost of unused material. Actual reagent preparation volumes reflect anticipated usage and reagent stability.

14.2 Excess reagents samples and method process wastes are characterized and disposed of in an acceptable manner. For further information on waste management consult the current version of ALL-S-002, *Waste Handling*.

15. References

15.1 USEPA, SW-846, Method 6020A "Inductively Coupled Plasma - Mass Spectrometry", February 2007.

15.2 USEPA, SW-846, Method 3010A, "Acid Digestion of Aqueous Samples and Extracts for Total Metals for Analysis by FLAA or ICP Spectrometry", December 1996.

15.3 USEPA, SW-846, Method 3050B, "Acid Digestion of Sediments, Sludges, and Soils", December 1996.

Tables, Diagrams, Flowcharts, Appendices, Addenda etc.

Attachment I - SW846 3010A DIGESTION
Attachment II - SW846 3050B DIGESTION
Attachment III - SW846 M3050B DIGESTION
Flow Chart A - ICPMS DETERMINATIVE METHOD
Flow Chart B - MDL or LOD FLAGGING and REPORTING
Flow Chart C - EQL or PSRL FLAGGING and REPORTING
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16. Revisions

Document Number	Reason for Change	Date
S-GB-M-006-REV.00	First Issue	22Sept2008

Attachment I:
SW846 3010A DIGESTION
- This prep is to be used for aqueous (Total and Dissolved) samples and sludges for the determination of Li, Be, B, Na, Mg, Al, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Sr, Mo, Ag, Cd, Sn, Sb, Ba, Hg, Tl, and Pb.
- See Table M for reporting limits, spike concentrations, and spike recovery limits.

1.0 Water Samples: All water samples must be digested as described in Method 3010A.

2.0 Turn on the Hot Block and allow it to warm up. Before placing samples in the block to digest, verify that the sample well temperature is in the range of 90-95 ^{0}C, adjust as required. Record the sample well temperature in the prep logbook. Verify that the hood is turned on.

3.0 Prepare the MB and LCS (an LCSD may also be required) by adding 50.0mL of Nanopure water into digestion vials. One MB and one LCS must be prepared for each batch of 20 samples or less.

4.0 Prepare the parent sample, duplicate and MS, or the MS and MSD by placing 50.0mL aliquots of a selected sample from each batch into digestion vials. One MS and one duplicate or MSD must be prepared for each analytical batch of 20 samples or less. The parent sample is chosen at random or per project specific requests– excluding rinse blanks, equipment blanks, and trip blanks.

5.0 Place 50.0mL of each sample in a digestion vial.

6.0 Spike the LCS (LCSD), MS, and MSD with 2.0 mL of ICP Spike solution.

7.0 Carefully add 3.0mL of concentrated HNO_3 to each sample, MB, LCS (LCSD), MS, and MSD vial, followed by 2.5mL of Concentrated HCl. Heat in the hot block for 4 hours or until the sample has been reduced to a minimum volume of approximately 5mLs. Do not let sample go to dryness, low sample recovery will result. If this occurs, discard sample and re-prep.

8.0 Remove the digestates from the hot block and allow to cool in the hood.

9.0 Dilute each vial to a final volume of 50.0mL with Nanopure water.

10.0 Place a screw cap on each vial and shake to mix thoroughly. Allow to settle before analysis.

11.0 If any digestate is turbid or there is a concern that insoluble materials may clog the nebulizer, centrifuge to settle the solids.

Attachment II:
SW846 3050B DIGESTION
- This prep is to be used for solid samples and sludges for the determination of Li, Be, B, Na, Mg, Al, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Sr, Mo, Ag, Cd, Ba, Hg, Tl, and Pb.
- See Table N for reporting limits, spike concentrations, and spike recovery limits.

1.0 Heat hot block at 95°C +/- 5°C (verify temperature with a calibrated thermometer). Typically, setting the temperature at 102 degrees will achieve this range. Record temperature in prep logbook.

2.0 Verify sample Station IDs and LIMs numbers on containers against backlog.

3.0 Lay out run in digestion logbook. Identify QC samples at frequency stated in the Quality Control Section of this SOP.

4.0 To the extent possible, mix and crush the sample as per SOP S-ALL-Q-021, *Sub-sampling (Sample Homogenization*), in the sample container with a spatula to achieve homogeneity.

5.0 Prepare Method Blank by weighing Teflon chips in digestion tube.

6.0 Prepare Laboratory Control Spike (LCS) by adding 2.0 mL of the ICP Spike to the LCS tube with Teflon chips.

7.0 Spike Duplicate (LCSD) if there is not enough volume for an MS/MSD or at client request. See Table E for spiking solutions.

8.0 Prepare Matrix Spike / Matrix Spike Duplicate (MS/MSD), by weighing 1.000 +/- 0.005 grams of parent sample into 3 separate digestion tubes. Record sample weight to nearest 0.01 gram on digestion log. Parent, matrix spike, and matrix spike duplicate must be the same weight. Add 2.0 mL of the ICPMS Spike to the MS/MSD digestion tubes. See Table E for spiking solutions.

9.0 Weigh 1.000 +/- 0.005 grams of homogenized sample into a labeled digestion tube. Record sample weight to nearest 0.01 gram on digestion log. Do this for each sample in the digestion group. For samples with high liquid content, a larger sample size may be used, as long as the digestion is complete. For sludges with % solids >10% and <50%, weigh out 2.5-5 grams. Record all information in the Metals Digestion Log (see attached example).

10.0 Preparing Paint Chips for Digestion

11.0 Transfer paint chips into labeled drying tins.

12.0 Dry samples at 103-105 degrees Celsius for 12-24 hours.

13.0 Remove samples from oven and desiccate for 1 hour.

14.0 Weigh out 0.5 gram of sample into a digestion tube. If the sample available is less than 0.5 gram, use the entire sample.

15.0 Always prepare an LCSD for paint Chips.

16.0 Results are always reported as mg/kg dry wt for paint chips.

17.0 CONTINUE DIGESTION IN HOOD.

18.0 Add small amount of Nanopure water (2mL) to digestion tube (to cover bottom). Swirl to keep sample from sticking to the tube.

19.0 Add 10 mL 1:1 HNO_3 using a calibrated repipettor. Cover with watch glass and swirl gently to mix.

20.0 To make 1:1 HNO_3, add 1 part HNO_3 to 1 part Nanopure water.

21.0 Heat the samples at 95°C +/- 5°C for 2 hours. Maintain a covering of solution over the bottom of the tube at all times. Remove from hot block and cool in hood.

22.0 CAUTION: DO NOT BOIL AT ANY TIME DURING DIGESTION.

23.0 This may result in metals volatilizing which would require starting the digestion over.

24.0 Add 2.5 mL 30% H_2O_2 using a calibrated repipettor.

25.0 CAUTION: DO NOT ALLOW LOSS OF SAMPLE DUE TO EXCESSIVE EFFERVESCENCE.

26.0 If sample loss occurs the sample must be re-digested.

27.0 Cover with watch glass, swirl gently to mix, and heat in hot block to start peroxide reaction. Heat the samples at 95°C +/- 5°C until effervescence subsides (no more bubbling). Maintain a covering of solution over the bottom of the tube at all times. Remove from hot block and cool in hood.

28.0 Add 2.5mL of Concentrated HCl and heat until the fuming subsides.

29.0 Rinse watch glass with Nanopure water into digestion tube.

30.0 Allow samples to cool to room temperature.

31.0 Bring samples to final volume of 50 mL with Nanopure water.

32.0 Centrifuge sample for 10 minutes at a setting between 20 and 25 or

33.0 Filter through Whatman #541(or equivalent) filter paper into a labeled digestion tube.

34.0 Rinse digestion tube with Nanopure water into filter paper.

35.0 Rinse filter paper with Nanopure water into specimen cup.

36.0 Bring to final volume of 50 mL with Nanopure water, cap, and mix well.

or

37.0 Samples may also be allowed to settle overnight if not filtered or centrifuged.

38.0 Samples are now ready for analysis.

Attachment III:

SW846 M3050B DIGESTION

- This prep is to be used for biota samples for the determination of Li, Be, B, Na, Mg, Al, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Sr, Ag, Mo, Cd, Ba, Hg, Tl, Pb, and U .

- See Table O for reporting limits, spike concentrations, and spike recovery limits.

1.0 Heat hot block at 95°C +/- 5°C (verify temperature with a calibrated thermometer). Typically, setting the temperature at 102 degrees will achieve this range. Record temperature in prep logbook.

2.0 Verify sample Station IDs and LIMs numbers on containers against backlog.

3.0 Lay out run in digestion logbook. Identify QC samples at frequency stated in the Quality Control Section of this SOP.

4.0 To the extent possible, mix and crush the sample as per SOP S-ALL-Q-021, *Sub-sampling (Sample Homogenization*), in the sample container with a spatula to achieve homogeneity.

5.0 Prepare Method Blank by leaving one digestion tube empty.

6.0 Prepare Chicken Blank by weighing 0.500 +/-.005 grams of catfish into one digestion tube for the control blank. Record sample weight in digestion log.

7.0 Prepare Laboratory Control Spike (LCS) by weighing 0.500 +/-.005 grams of Chicken into one digestion tube and adding 2.0 mL of the ICPMS Spike. Record sample weight in digestion log.

8.0 Spike Duplicate (LCSD) if there is not enough volume for an MS/MSD or at client request. Prepared the same as the LCS.

9.0 Prepare Standard Reference Material (SRM): If a SRM is requested, weigh out exactly 0.500 +/- .005 grams of appropriate reference material. Record in digestion log.

10.0 Prepare Matrix Spike / Matrix Spike Duplicate (MS/MSD), by weighing 0.5000 +/- 0.005 grams of parent sample into 3 separate digestion tubes. Record sample weight to nearest 0.01 gram in digestion log. Parent, matrix spike, and matrix spike duplicate must be the same weight. Add 2.0 mL of the ICPMS Biota Spike to the MS/MSD digestion tubes.

11.0 Weigh 0.500 +/- 0.005 grams of homogenized sample into a labeled digestion tube. Record sample weight to nearest 0.01 gram on digestion log. Do this for each sample in the digestion group. Record all information in the Metals Digestion Log (see attached example).

12.0 CONTINUE DIGESTION IN HOOD.

13.0 Add small amount of Nanopure water (2mL) to digestion tube (to cover bottom). Swirl to keep sample from sticking to the tube.

39.0 Add 10.0 mL of 1:1 HNO_3 using a calibrated repipettor. Cover with watch glass and swirl gently to mix.

14.0 To make 1:1 HNO_3, add 1 part HNO_3 to 1 part Nanopure water.

15.0 Heat the samples at 95°C +/- 5°C for 15 minutes.

CAUTION: DO NOT BOIL AT ANY TIME DURING DIGESTION.

This may result in metals volatilizing which would require starting the digestion over.

16.0 Remove from hot block and cool.

17.0 Add 2.5 mL of 30% H_2O_2 using a calibrated repipettor.

18.0 Swirl gently to mix, and heat in hot block to start peroxide reaction. Heat until effervescence subsides (about 15 min).

CAUTION: DO NOT ALLOW LOSS OF SAMPLE DUE TO EXCESSIVE EFFERVESCENCE.

19.0 Remove from hot block and cool.

20.0 Add 2.5 mL of 30% H_2O_2 using a calibrated repipettor.

21.0 Swirl gently to mix, and heat in hot block to start peroxide reaction. Heat until effervescence subsides (about 15 min).

22.0 **CAUTION: DO NOT ALLOW LOSS OF SAMPLE DUE TO EXCESSIVE EFFERVESCENCE**.

23.0 Remove from hot block and cool.

24.0 Add 2.5 mL Conc. HCl using a calibrated repipettor.

25.0 Bring samples to final volume of 50 mL with Nanopure water or go to step 27.0.

26.0 Centrifuge sample for 10 minutes at a setting between 20 and 25. OR

27.0 Filter through Whatman #541(or equivalent) filter paper into a labeled digestion tube.

28.0 Rinse digestion tube with Nanopure water into filter paper.

29.0 Rinse filter paper with Nanopure water into specimen cup.

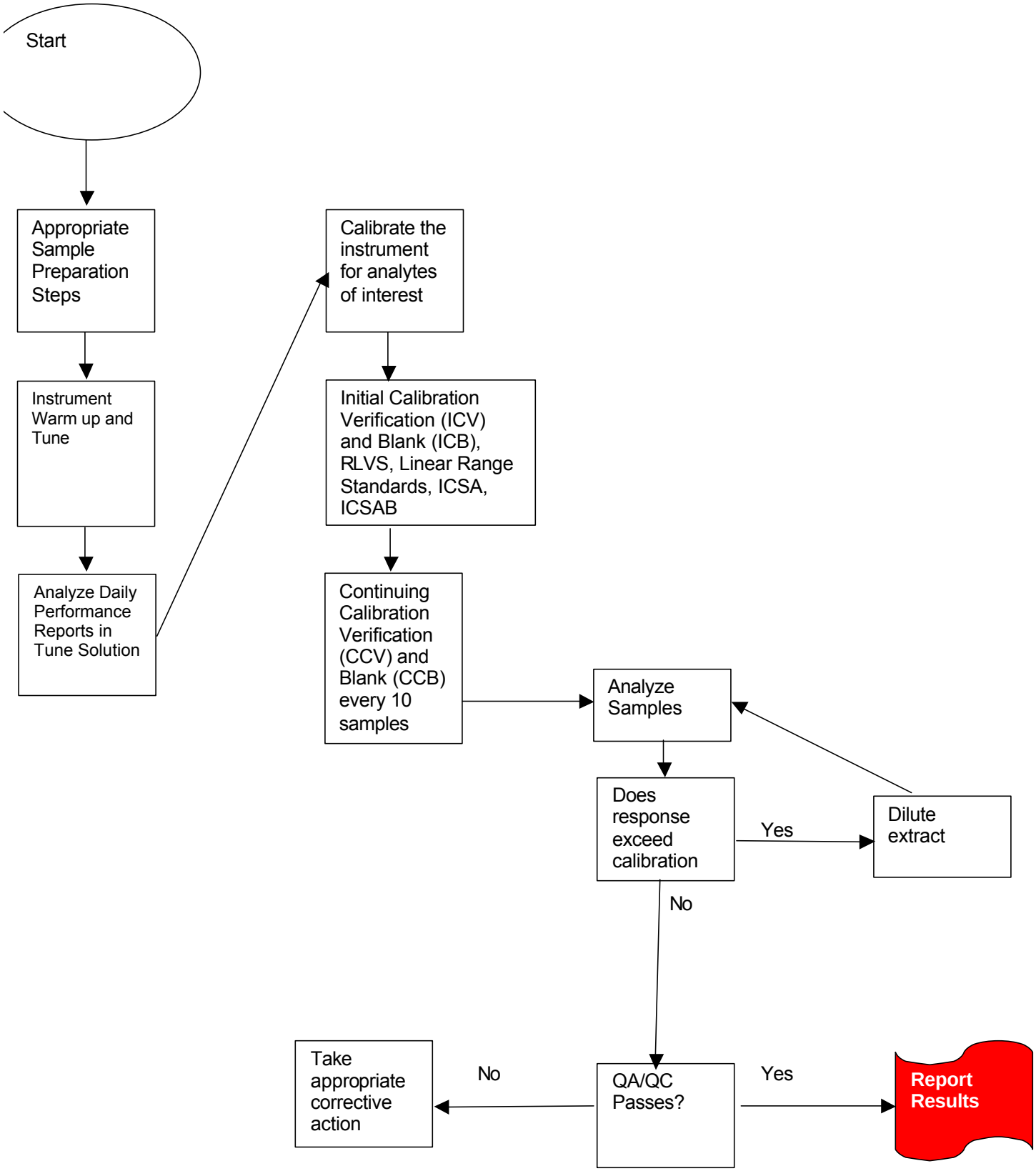
30.0 Bring to final volume of 50 mL with Nanopure water, cap, and mix well.
OR

31.0 Samples may also be allowed to settle overnight if not filtered or centrifuged.

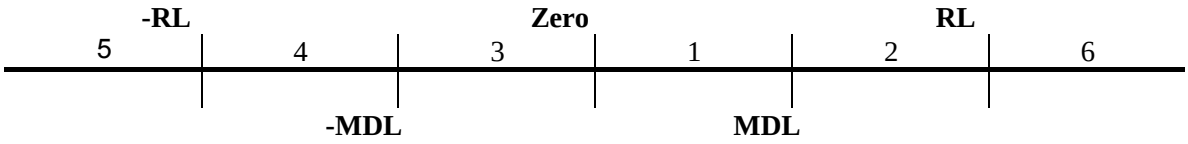
32.0 Samples are now ready for analysis.

Flowchart A

ICPMS DETERMINATIVE METHOD



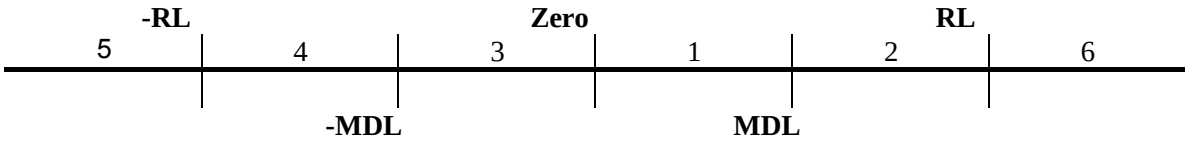
Flowchart B
MDL or LOD FLAGGING and REPORTING



Blank Position> **Sample Positionß**	5	4	3	1	2	6
1	R	A Flag Report < MDL	Report < MDL	Report < MDL	Report < MDL	Report < MDL
2	R	A Flag Report result w/10X Rule	Report result	Report result	A Flag Report result w/10X Rule	R
3	R	A Flag Report < MDL	Report < MDL	Report <MDL	Report < MDL	Report <MDL
4	R	A Flag Report <MDL	Report <MDL	Report <MDL	A Flag Report result w/10X Rule	Report <MDL
5	R	R	R	R	R	R
6	R	A Flag Report result w/10X Rule	Report result	Report result	A Flag Report result w/10X Rule	Report result w/10X Rule -or- R if result is not 10XMB

R= Analyst discretion to Re-run, Re-calculate, or Re-digest
X= Value in Method Blank (MB).

Flowchart C
EQL or PRSL FLAGGING and REPORTING



Blank Position> **Sample Positionß**	5	4	3	1	2	6
1	R	Report < RL	Report < RL	Report < RL	Report < RL	Report < RL
2	R	Report < RL	Report < RL	Report result	Report < RL	Report < RL
3	R	Report < RL	Report < RL	Report <RL	Report < RL	Report < RL
4	R	Report < RL	Report < RL	Report < RL	Report < RL	Report < RL
5	R	R	R	R	R	R
6	R	Report result	Report result	Report result	Report result	Report result w/10X Rule -or- R if result is not 10XMB

R= Analyst discretion to Re-run, Re-calculate, or Re-digest
RL= Reporting Limit

Table A: APPLICABLE ANALYTES

Isotope	Element	Symbol	Chemical Abstracts Service Registry Number (CASRN)
27	Aluminum	Al	7429-90-5
121	Antimony	Sb	7440-36-0
75	Arsenic	As	7440-38-2
137	Barium	Ba	7440-39-3
9	Beryllium	Be	7440-41-7
11	Boron	B	7440-42-8
111	Cadmium	Cd	7440-43-9
43	Calcium	Ca	7440-70-29
52	Chromium	Cr	7440-47-3
59	Cobalt	Co	7440-48-4
65	Copper	Cu	7440-50-8
57	Iron	Fe	7439-89-6
208	Lead	Pb	7439-92-1
24	Magnesium	Mg	7439-95-4
55	Manganese	Mn	7439-96-5
201	Mercury	Hg	7439-97-6
95	Molybdenum	Mo	7439-98-7
60	Nickel	Ni	7440-02-0
39	Potassium	K	9/7/7440
82	Selenium	Se	7782-49-2
107	Silver	Ag	7440-22-4
23	Sodium	Na	7440-23-5
88	Strontium	Sr	7440-24-6
205	Thallium	Tl	7440-28-0
118	Tin	Sn	7440-31-5
47	Titanium	Ti	7440-32-6
238	Uranium	U	7440-61-1
51	Vanadium	V	7440-62-2
66	Zinc	Zn	7440-66-6

Table B:
EQUIPMENT

Equipment	Manufacturer	Model(#)	Serial #
Thermo Xseries 2 ICPMS	ThermoFisher Scientific	XSeries 2	01301
Rough Pump	Edwards	E2 M28	086 105337
Computer	Dell	Optiplex 755	DJG5L3J
Autosampler	CETAC	ASX520	030867A520
Refrigerated Recirculator	NESLAB	Merlin M75	108009024
Uninterruptible Power Supply (UPS)	Toshiba	1600 EP Series UPS	080400330
Hot Block	Environmental Express	SC100	526CEC0714
Analytical Balance	Denver Instrument	XE-310	718860

Note: Equivalent substitutes may be used.

Table C:
SUPPLIES

Supplies	Manufacturer	Vendor	Catalog #*
Sample Per-Pump Tubing	Analytical West	Analytical West	PT-2100P
Internal Standard Per-Pump Tubing	Analytical West	Analytical West	PT-2100P
Waste Per-Pump Tubing	Analytical West	Analytical West	PT-2160P
Y Connectors	Hewlett-Packard	Hewlett-Packard	G1820-65106
Concentric Nebulizer	Thermo Electron Corp.	Thermo Electron Corp.	4600294-03
Quartz Torch	Thermo Electron Corp.	Thermo Electron Corp.	3601145
Screen and Bonnet	Thermo Electron Corp.	Thermo Electron Corp.	3601219
Ni Sample Cone	Thermo Electron Corp.	Thermo Electron Corp.	3600812
Ni Skimmer Cone	Thermo Electron Corp.	Thermo Electron Corp.	3600811
Graphite Sample Cone Seal	Thermo Electron Corp.	Thermo Electron Corp.	3004382
15 mL Polypropylene Test Tubes	Fisher Scientific	Fisher Scientific	14-956-7E
50-mL Disposable Digestion Cups	Environmental Express	Environmental Express	SC475
Calibrated Pipette 1000 uL	Eppendorf	Fisher Scientific	21-371-13
Calibrated Pipette 100-1000 uL	Eppendorf	Fisher Scientific	05-402-50
Calibrated Pipette 1000-5000 uL	Eppendorf	Fisher Scientific	05-402-91
Trace Metal Grade Pipette Tips 1 mL	Eppendorf	Fisher Scientific	21-372
Trace Metal Grade Pipette Tips 5 mL	Eppendorf	Fisher Scientific	21-381-198
N-DEX Nitrile Gloves	Best	Fisher Scientific	6005 PFM
pH Indicator Sticks	Whatman	MG Scientific	P114-26

Note: Equivalent substitutes may be used.

Table D:
WORKING STANDARDS

Standard	Stock or Intermediate Standard	Concentration	Elements	Amount Used	Final Volume (W/ Diluent)	Final Concentration	Elements
Cross Calibration (XCal)	ICP-MS-68A Solution A	10 ppm	Al, As, Ba, Be, Bi, B, Cd, Ca, Ce, Cs, Cr, Co, Cu, Dy, Er, Eu, Gd, Ga, Ho, In, Fe, La, Pb, Li, Lu, Mg, Mn, Nd, Ni, P, K, Pr, Re, Rb, Sm, Sc, Se, Na, Sr, Tb, Tl, Th, Tm, U, V, Yb, Y, Zn	0.5 mL	100 mL	50 ppb	All Elements
	ICP-MS-68A Solution B	10 ppm	Sb, Ge, Hf, Mo, Nb, Si, Ag, Ta, Te, Sn, Ti, W, Zr	0.5 mL			
Tune Solution	Tune Int	1 ppm	Mg, Bi, Ge, In, Sc, Tb, Y, Ba, B, Be, Ce, Co, Li, Ni, Pb, U	5 mL	500 mL	10 ppb	All Elements
ICB	Same as Cal. Level 1		------	------	------		------
CCB	Same as Cal. Level 1		------	------	------		------
Calibration Level 1 and Diluent/Blank Solution	Cal 1	1000 ppm	Au	0.1 mL	50 mL	2 ppm	Au
	Diluent / Blank	1000 ppm	Au	2.0 mL	1000 mL	2 ppm	Au
Calibration Level 2 and RLVS as applicable (See Table H)		1000 ppm	Au	0.1 mL	50 mL	2 ppm	Au
	Hg Int	1 ppm	Hg	0.010 mL		0.2 ppb	Hg
	T Int	1.25 ppm	As, Ba, Be, Cd, Co, Cr, Cu, Li, Mn, Ni, P, Pb, Se, Sr, Tl, V, Zn , B, Mo, Sb, Sn, Ti, Zr,	0.04		1 ppb	All Elements (not Ag, Si)
		0.75 ppm	Ag			0.5 ppb	Ag
		2.5 ppm	Si			2 ppb	Si
	M Int	500 ppm	Al, Ca, Fe, K, Mg, Na	0.025		250 ppb	Al, Ca, Fe, K, Mg, Na
Calibration Level 3 and RLVS as applicable (See Table H)		1000 ppm	Au	0.1 mL	50 mL	2 ppm	Au
	Hg Int	1 ppm	Hg	0.025 mL		0.5 ppb	Hg
	T Int	1.25 ppm	As, Ba, Be, Cd, Co, Cr, Cu, Li, Mn, Ni, P, Pb, Se, Sr, Tl, V, Zn , B, Mo, Sb, Sn, Ti, Zr,	0.2 mL		5 ppb	All Elements (not Ag, Si)
		0.75 ppm	Ag			2.5 ppb	Ag
		2.5 ppm	Si			10 ppb	Si
	M Int	500 ppm	Al, Ca, Fe, K, Mg, Na	0.025 mL		500 ppb	Al, Ca, Fe, K, Mg, Na
Calibration Level 4		1000 ppm	Au	0.1 mL	50 mL	2 ppm	Au
	Hg Int	1 ppm		0.05 mL		1 ppb	Hg
	T Int	1.25 ppm	As, Ba, Be, Cd, Co, Cr, Cu, Li, Mn, Ni, P, Pb, Se, Sr, Tl, V, Zn , B, Mo, Sb, Sn, Ti, Zr,	2 mL		50 ppb	All Elements (not Ag, Si)
		0.75 ppm	Ag			25 ppb	Ag
		2.5 ppm	Si			100 ppb	Si

	M Int	500 ppm	Al, Ca, Fe, K, Mg, Na	0.25 mL		2,500 ppb	Al, Ca, Fe, K, Mg, Na

Table D: Continued
WORKING STANDARDS

Standard	Stock or Intermediate Standard	Concentration	Elements	Amount Used	Final Volume (W/ Diluent)	Final Concentration	Elements
Calibration Level 5		1000 ppm	Au	0.1 mL	50 mL	2 ppm	Au
	Hg Int	1 ppm	Hg	0.5 mL		10 ppb	Hg
	T Int	1.25 ppm	As, Ba, Be, Cd, Co, Cr, Cu, Li, Mn, Ni, P, Pb, Se, Sr, Tl, V, Zn , B, Mo, Sb, Sn, Ti, Zr,	10 mL		250 ppb	All Elements (not Ag, Si)
		0.75 ppm	Ag			125 ppb	Ag
		2.5 ppm	Si			500 ppb	Si
	M Int	500 ppm	Al, Ca, Fe, K, Mg, Na	1.25 mL		12,500 ppb	Al, Ca, Fe, K, Mg, Na
Calibration Level 6		1000 ppm	Au	0.1 mL	50 mL	2 ppm	Au
	Hg Int	1 ppm	Hg	1.25 mL		25 ppb	Hg
	T Int	1.25 ppm	As, Ba, Be, Cd, Co, Cr, Cu, Li, Mn, Ni, P, Pb, Se, Sr, Tl, V, Zn , B, Mo, Sb, Sn, Ti, Zr,	20 mL		500 ppb	All Elements (not Ag, Si)
		0.75 ppm	Ag			250 ppb	Ag
		2.5 ppm	Si			1,000 ppb	Si
	M Int	500 ppm	Al, Ca, Fe, K, Mg, Na	2.5 mL		25,000 ppb	Al, Ca, Fe, K, Mg, Na
CCV		1000 ppm	Au	0.1 mL	50 mL	2 ppm Au	Au
	Hg Int	1 ppm	Hg	0.25 mL		5 ppb	Hg
	T Int	1.25 ppm	As, Ba, Be, Cd, Co, Cr, Cu, Li, Mn, Ni, P, Pb, Se, Sr, Tl, V, Zn , B, Mo, Sb, Sn, Ti, Zr,	4 mL		100 ppb	All Elements (not Ag, Si)
		0.75 ppm	Ag			50 ppb	Ag
		2.5 ppm	Si			200 ppb	Si
	M Int	500 ppm	Al, Ca, Fe, K, Mg, Na	0.5 mL		5,000 ppb	Al, Ca, Fe, K, Mg, Na
ICV		1000 ppm	Au	0.2 mL	100 mL	2 ppm	Au
		1000 ppm	U	0.011 mL		110 ppb	U
	PA-STD-1B	200 ppm	As, Ba, Be, Cd, Co, Cr, Cu, Li, Mn, Ni, P, Pb, Se, Sr, Tl, V, Zn	0.055 mL		110 ppb	As, Ba, Be, Cd, Co, Cr, Cu, Li, Mn, Ni, P, Pb, Se, Sr, Tl, V, Zn
	PA-STD-2B	1000 ppm	Si	0.055 mL		550 ppb	Si
			B, Mo, Sb, Sn, Ti, Zr			110 ppb	B, Mo, Sb, Sn, Ti, Zr
			Ag			55 ppb	Ag
	PA-STD-3B	2000 ppm	Al, Ca, Fe, K, Mg, Na	0.275 mL		5500 ppb	Al, Ca, Fe, K, Mg, Na
	Hg ICV Int	10 ppm	Hg	0.04 mL		4 ppb	Hg
ICSA	4400-061025MB01 Pace	500ug/mL	Al, Ca, Fe, K, Mg, Na, P, S,	1.0 mL	10 mL	50,000 ppb	Al, Ca, Fe, K, Mg, Na, S,
		1,000ug/mL	C			100,000 ppb	C
		3,600ug/mL	Cl			360,000 ppb	Cl
		10ug/mL	Mo, Ti			1,000 ppb	Mo, Ti
ICSAB	4400-061025MB01 Pace	500ug/mL	Al, Ca, Fe, K, Mg, Na, P, S,	1.0 mL	10 mL	50,000 ppb	Al, Ca, Fe, K, Mg, Na, S,
		1,000ug/mL	C			100,000 ppb	C
		3,600ug/mL	Cl			360,000 ppb	Cl
		10ug/mL	Mo, Ti			1,000 ppb	Mo, Ti (see Next Section)
	T Int	1.25 ppm	As, Ba, Be, Cd, Co, Cr, Cu, Li, Mn, Ni, P, Pb, Se, Sr, Tl, V, Zn , B, Mo, Sb, Sn, Ti, Zr,			100 ppb	As, Ba, Be, Cd, Co, Cr, Cu, Li, Mn, Ni, P, Pb, Se, Sr, Tl, V, Zn , B, Mo, Sb, Sn, Ti, Zr,
		0.75 ppm	Ag			50 ppb	Ag
		2.5 ppm	Si			200 ppb	Si
	Hg Int	1 ppm	Hg			5 ppb	Hg

Table D: Continued
WORKING STANDARDS

Standard	Stock or Intermediate Standard Used	Concentration	Elements	Amount Used	Final Volume (W/ Diluent)	Final Concentration	Elements
ICPMS Biota SPK [1]	PA-STD-1B	200 ppm	As, Ba, Be, Cd, Co, Cr, Cu, Li, Mn, Ni, P, Pb, Se, Sr, Tl, V, Zn	5 mL	100 mL	10 ppm	As, Ba, Be, Cd, Co, Cr, Cu, Li, Mn, Ni, P, Pb, Se, Sr, Tl, V, Zn
	PA-STD-2B	1000 ppm	Si	5 mL		50 ppm	Si
		200 ppm	B, Mo, Sb, Sn, Tl, Zr			10 ppm	B, Mo, Sb, Sn, Tl, Zr
		100 ppm	Ag			5 ppm	Ag
	PA-STD-3B	2000 ppm	Al, Ca, Fe, K, Mg, Na	25 mL		500 ppm	Al, Ca, Fe, K, Mg, Na
		10,000 ppm	K	15 mL		1500 ppm	K (2000 ppm Total)
		1000 ppm	U	1 mL		10 ppm	U
		1000 ppm	Hg	0.025		0.25 ppm	Hg
	Conc. HNO_3	69-70%		6.0 mL		6%	HNO_3
ICP Water / Soil Spike [2]	PA-STD-1B	200 ppm	As, Ba, Be, Cd, Co, Cr, Cu, Mn, Ni, Pb, Se, Sr, Tl, V, Zn	25 mL	200 mL	50 ppm	As, Ba, Be, Cd, Co, Cr, Cu, Mn, Ni, Pb, Se, Sr, Tl, V, Zn
	PA-STD-2B	1000 ppm	Si	25 mL		250 ppm	Si
		200 ppm	B, Mo, Sb, Sn, Ti			50 ppm	B, Mo, Sb, Sn, Ti
		100 ppm	Ag			25 ppm	Ag
	PA-STD-3B	2000 ppm	Al, Ca, Fe, K, Mg, Na	25 mL		500 ppm	Al, Ca, Fe, K, Mg, Na
Internal Standards (ISTD)	PACE-WI-CAL-4A	100 ppm	Bi, Ge, In, Sc, Tb, Y	2 mL	1000 mL	200 ppb	Bi, Ge, In, Sc, Tb, Y
	Conc. HNO_3	69-70%		3.0 mL		3%	HNO_3

Note: Equivalent substitutes may be used.

1 = 2 mL added to LCS/LCSD and MS/MSD, 0.2 mL to PS of 10 mL

2 = 1 mL added to LCS/LCSD and MS/MSD, 0.1 mL to PS of 10 mL

Table E:
STOCK STANDARDS

Standard Type	Manufacturer	Part #	Conc.	Analytes	Used In
Calibration Stocks	SPEX CertiPrep	XFSMN-26-250A	100mg/L	As, Ba, Be, Cd, Co, Cr, Li, Mn, Ni, P, Pb, Se, Sr, Tl, V, Zn	Calibration, CCVs, ICSAB
	SPEX CertiPrep	XFSMN-27-250A	500mg/L	Si	
			100mg/L	B, Mo, Sb, Sn, Ti, Zr	
			50mg/L	Ag	
	SPEX CertiPrep	XFSMN-28-250A	1,000mg/L	Al, Ca, Fe, K, Mg, Na	
	High-Purity Stds	100033-1	1,000ug/mL	Hg	
ICV/Spike Stocks	Inorganic Ventures	PA-STD-1B	200mg/L	As, Ba, Be, Cd, Co, Cr, Li, Mn, Ni, P, Pb, Se, Sr, Tl, V, Zn	ICV/Spike
	Inorganic Ventures	PA-STD-2B	1,000mg/L	Si	
			200mg/L	B, Mo, Sb, Sn, Ti, Zr	
			100mg/L	Ag	
	Inorganic Ventures	PA-STD-3B	2,000mg/L	Al, Ca, Fe, K, Mg, Na	
	Inorganic Ventures	CGHG1-1	1,000ug/mL	Hg	
	High Purity Standards	100064-1	1,000ug/mL	U	
Internal Standard Stocks	Inorganic Ventures	PACEWI-CAL-4A	10mg/L	Bi, Ge, In, Sc, Tb, Y	ISTD, Tune
Single Element Stocks	Ultra Scientific	ICP-112	10,000 mg/L	Mg	Tune / Int
	Ultra Scientific	ICP-056	1,000 mg/L	Ba	Tune
	Ultra Scientific	ICP-005	1,000 mg/L	B	Tune
	Ultra Scientific	ICP-004	1,000 mg/L	Be	Tune
	Ultra Scientific	ICP-058	1,000 mg/L	Ce	Tune
	Ultra Scientific	ICP-027	1,000 mg/L	Co	Tune
	Ultra Scientific	ICP-003	1,000 mg/L	Li	Tune
	Ultra Scientific	ICP-028	1,000 mg/L	Ni	Tune
	Ultra Scientific	ICP-082	1,000 mg/L	Pb	Tune
	Inorganic Ventures	AAU1-1	1,000 mg/L	U	Tune / Cal
	High Purity Standards	100033-1	1,000 mg/L	Hg	Cal
	Ultra Scientific	ICP-119	10,000 mg/L	K	Spike
ICSA	CPI	4400-061025MB01	500ug/mL	Al, Ca, Fe, K, Mg, Na, P, S,	ICSA & ICSAB
		Pace	1,000ug/mL	C	
			3,600ug/mL	Cl	
			10ug/mL	Mo, Ti	

Note: Equivalent substitutes may be used.

Note: Single element standards may be used.

Table F:
INTERMEDIATE STANDARDS

Intermediate Type	Name	Stock Standard(s) Used (Part #)	Concentration	Elements	Amount Used	Acid Used	Final Volume (W/Nanopure H_2O)	Final Concentration
Tune Solution Intermediates	Mg Tune Int		10,000 ppm	Mg	0.1 mL	3 mL HNO_3	100 mL	10 ppm
	Tune Int		10 ppm	Mg	10 mL	2 mL HNO_3	100 mL	1 ppm
			100 ppm	Bi, Ge, In, Sc, Tb, Y	1.0 mL			
			1000 ppm	Ba	0.1 mL			
			1000 ppm	B	0.1 mL			
			1000 ppm	Be	0.1 mL			
			1000 ppm	Ce	0.1 mL			
			1000 ppm	Co	0.1 mL			
			1000 ppm	Li	0.1 mL			
			1000 ppm	Ni	0.1 mL			
			1000 ppm	Pb	0.1 mL			
			1000 ppm	U	0.1 mL			
Calibration Intermediates	Hg Int		1000 ppm	Au	0.2 mL	3 mL HNO_3	100 mL	2 ppm
			1000 ppm	Hg	0.1 mL			1 ppm
	T Int		1000 ppm	U	0.125 mL	3 mL HNO_3 2 mL HCl	100 mL	1.25 ppm
			100 ppm	As, Ba, Be, Cd, Co, Cr, Cu, Li, Mn, Ni, P, Pb, Se, Sr, Tl, V, Zn	1.25 mL			0.75 ppm
			100 ppm Ag 50 ppm Si 500 ppm	Si, B, Mo, Sb, Sn, Ti, Zr, Ag	1.25 mL			2.5 ppm
	M Int		1000 ppm	Al, Ca, Fe, K, Mg, Na	50 mL	3 mL HNO_3	100 mL	500 ppm
ICV Intermediate	Hg ICV Int	CGHG1-1	1000 ppm	Hg	1.0 mL	1 mL HNO_3	100 mL	10 ppm

Table G:
REAGENTS

Reagent/Stock Std	**Used In**	**Purity**	**Vendor**	**Order #**
Hydrochloric Acid, (36.5-38.0% HCL)	Std. And Prep	Trace Metals Grade	MG Scientific	9530-33
Nitric Acid (69.0-70.0% HNO_3)	Std. And Prep	Trace Metals Grade	MG Scientific	9598-34
Nanopure or Milli-Q Water	all	18 Meg Ohms	On-Site	On-Site
Hydrogen Peroxide (30% H_2O_2)	Prep	Trace Metals Grade	Fischer Scientific	H325-4

Table H:
CALIBRATION LEVELS

Element	Cal Blank	Calibration Standard 2 and RLVS as applicable	Calibration Standard 3 and RLVS as applicable	Calibration Standard 4	Calibration Standard 5	Calibration Standard 6
Aluminum	0 ppb	250 ppb	500 ppb	2,500 ppb	12,500 ppb	25,000 ppb
Antimony	0 ppb	1 ppb	5 ppb	50 ppb	250 ppb	500 ppb
Arsenic	0 ppb	1 ppb	5 ppb	50 ppb	250 ppb	500 ppb
Barium	0 ppb	1 ppb	5 ppb	50 ppb	250 ppb	500 ppb
Beryllium	0 ppb	1 ppb	5 ppb	50 ppb	250 ppb	500 ppb
Boron	0 ppb		5 ppb	50 ppb	250 ppb	500 ppb
Cadmium	0 ppb	1 ppb	5 ppb	50 ppb	250 ppb	500 ppb
Calcium	0 ppb	250 ppb	500 ppb	2,500 ppb	12,500 ppb	25,000 ppb
Chromium	0 ppb	1 ppb	5 ppb	50 ppb	250 ppb	500 ppb
Cobalt	0 ppb	1 ppb	5 ppb	50 ppb	250 ppb	500 ppb
Copper	0 ppb	1 ppb	5 ppb	50 ppb	250 ppb	500 ppb
Iron	0 ppb	250 ppb	500ppb	2,500 ppb	12,500 ppb	25,000 ppb
Lead	0 ppb	1 ppb	5 ppb	50 ppb	250 ppb	500 ppb
Magnesium	0 ppb	250 ppb	500 ppb	2,500 ppb	12,500 ppb	25,000 ppb
Manganese	0 ppb	1 ppb		50 ppb	250 ppb	500 ppb
Mercury	0 ppb	0.2 ppb	0.5 ppb	1.0 ppb	10 ppb	25 ppb
Molybdenum	0 ppb	1 ppb	5 ppb	50 ppb	250 ppb	500 ppb
Nickel	0 ppb	1 ppb	5	50 ppb	250 ppb	500 ppb
Potassium	0 ppb	250 ppb	500 ppb	2,500 ppb	12,500 ppb	25,000 ppb
Selenium	0 ppb	1 ppb	5 ppb	50 ppb	250 ppb	500 ppb
Silver	0 ppb	0.5 ppb	2.5 ppb	25 ppb	125 ppb	250 ppb
Sodium	0 ppb	250 ppb	500 ppb	2,500 ppb	12,500 ppb	25,000 ppb
Strontium	0 ppb	1 ppb	5 ppb	50 ppb	250 ppb	500 ppb
Thallium	0 ppb	1 ppb	5 ppb	50 ppb	250 ppb	500 ppb
Tin	0 ppb		5 ppb	50 ppb	250 ppb	500 ppb
Titanium	0 ppb	1 ppb	5 ppb	50 ppb	250 ppb	500 ppb
Vanadium	0 ppb	1 ppb	5 ppb	50 ppb	250 ppb	500 ppb
Zinc	0 ppb		5 ppb	50 ppb	250 ppb	500 ppb
Internal Standards	100 ppb each	100 ppb each	100 ppb each	100 ppb each	100 ppb each	100 ppb each

Note: Calibration levels may change if noted. All solutions in 2ppm Au and matrix matched acid concentrations.

Table I:
INTERNAL STANDARDS
(Multiple Listing Indicates Interpolation Between the Surrounding Internal Standards)

ISTD	Analytes
^{45}Sc-CCT	Li, Be, B
^{45}Sc-KED ^{72}Ge	Na – Zn
^{72}Ge ^{89}Y	As – Sr
^{89}Y ^{115}In	Mo – Cd
^{115}In ^{159}Tb	Sn – Ba
^{159}Tb ^{209}Bi	Hg – Pb
^{209}Bi	U

Table J:
EQUATIONS

Analyte	Recommended Elemental Interference Equations
^{43}Ca	-0.00110 * ^{88}Sr
^{51}V $_{1}$	-2.16995 * ^{53}ClO
^{53}ClO	–0.11400 * ^{52}Cr
^{52}Cr $_{1}$	–0.00032 * ^{35}Cl
^{54}Fe	–0.02841 * ^{52}Cr
^{60} Ni	–0.00020 * ^{43}Ca
^{78}Se	–0.03065 * ^{83}Kr
^{111}Cd	–0.00134 * ^{95}Mo
^{115}In	–0.01416 * ^{118}Sn
^{201}Hg	-0.04155 * ^{184}W
^{208}Pb	1.00000 * ^{206}Pb + 1.00000 * ^{207}Pb

1 – The equation may require periodic adjustment based on the KED add gas and tuning parameters. The mean value in counts per second (cps) for the calibration blank **MUST** be > 0 cps (ideally, all replicates should be > 0 cps). The normal operating range in cps is 10 – 700cps for the calibration blank and must be inspected by the analyst.

Table K:
INTEGRATION TIMES

Mass	Element	Resolution Mode	Dwell Time Per Mass (mSec)	Mass	Element	Resolution Mode	Dwell Time Per Mass (mSec)
7	Li	Standard	10	66	Zn	Standard	10
9	Be	Standard	10	72	Ge	Standard	10
10	B	Standard	10	75	As	Standard	50
23	Na	High	5	78	Se	Standard	50
24-26	Mg	Standard	10	83	Kr	Standard	50
27	Al	Standard	10	89	Y	Standard	10
31	P	High	10	95	Mo	Standard	10
34	S	High	10	107	Ag	Standard	10
35	Cl	High	10	111	Cd	Standard	10
39	K	High	10	115	In	Standard	10
43-44	Ca	Standard	10	118	Sn	Standard	10
45	Sc-KED	Standard	10	121	Sb	Standard	10
45	Sc-CCT	High	10	137	Ba	Standard	10
47	Ti	Standard	10	159	Tb	Standard	10
51	V	Standard	10	184	W	Standard	10
52	Cr	Standard	10	201	Hg	Standard	10
54	Fe	Standard	10	205	Tl	Standard	10
55	Mn	Standard	10	206	Pb	Standard	10
59	Co	Standard	10	207	Pb	Standard	10
60	Ni	Standard	10	208	Pb	Standard	10
63	Cu	Standard	10	209	Bi	Standard	10
66	Zn	Standard	10				

Table L:
INSTRUMENT QC LIMITS

Element	ICV (ppb)	CCV (ppb)	ICV/CCV Limits	ICSA (ppb)	ICSAB (ppb)	ICSAB Limits	RLVS (ppb)	RLVS Limits
Aluminum	11000	10000	90%-110%	50,000	50,000	80%-120%	250	70-130%
Antimony	110	100	90%-110%		100	80%-120%	1	70-130%
Arsenic	110	100	90%-110%		100	80%-120%	1	70-130%
Barium	110	100	90%-110%		100	80%-120%	1	70-130%
Beryllium	110	100	90%-110%		100	80%-120%	1	70-130%
Boron	110	100	90%-110%		100	80%-120%	5	70-130%
Cadmium	110	100	90%-110%		100	80%-120%	1	70-130%
Calcium	11000	10000	90%-110%	50,000	50,000	80%-120%	250	70-130%
Chromium	110	100	90%-110%		100	80%-120%	1	70-130%
Cobalt	110	100	90%-110%		100	80%-120%	1	70-130%
Copper	110	100	90%-110%		100	80%-120%	1	70-130%
Iron	11000	10000	90%-110%	50,000	50,000	80%-120%	250	70-130%
Lead	110	100	90%-110%		100	80%-120%	1	70-130%
Magnesium	110	100	90%-110%	50,000	50,000	80%-120%	250	70-130%
Manganese	11000	10000	90%-110%		100	80%-120%	1	70-130%
Mercury	4	5	90%-110%		5	80%-120%	0.2	70-130%
Molybdenum	110	100	90%-110%	1,000	1,100	80%-120%	1	70-130%
Nickel	110	100	90%-110%		100	80%-120%	1	70-130%
Potassium	11000	10000	90%-110%	50,000	50,000	80%-120%	250	70-130%
Selenium	110	100	90%-110%		100	80%-120%	1	70-130%
Silver	55	50	90%-110%		50	80%-120%	0.5	70-130%
Sodium	11000	10000	90%-110%	50,000	50,000	80%-120%	250	70-130%
Strontium	110	100	90%-110%		100	80%-120%	1	70-130%
Thallium	110	100	90%-110%		100	80%-120%	1	70-130%
Tin	110	100	90%-110%		100	80%-120%	5	70-130%
Titanium	110	100	90%-110%	1,000	1,100	80%-120%	1	70-130%
Uranium	110	100	90%-110%		100	80%-120%	1	70-130%
Vanadium	110	100	90%-110%		100	80%-120%	1	70-130%
Zinc	110	100	90%-110%		100	80%-120%	5	70-130%

Table M:
AQUEOUS BATCH QC
ON INSTRUMENT
CONCENTRATIONS AND LIMITS

Element	Method Blank (RL in ppb)	LCS/ LCSD (ppb)	LCS/LCSD Limits (%)	MS/MSD Amount (ppb)	MS/MSD Limits (%)	PS Amount (ppb)	PS Limits (%)
Aluminum	250	5,000	80-120	5,000	75-125	5,000	80-120
Antimony	1	500	80-120	500	75-125	500	80-120
Arsenic	1	500	80-120	500	75-125	500	80-120
Barium	1	500	80-120	500	75-125	500	80-120
Beryllium	1	500	80-120	500	75-125	500	80-120
Boron	5	500	80-120	500	75-125	500	80-120
Cadmium	1	500	80-120	500	75-125	500	80-120
Calcium	250	5,000	80-120	5,000	75-125	5,000	80-120
Chromium	1	500	80-120	500	75-125	500	80-120
Cobalt	1	500	80-120	500	75-125	500	80-120
Copper	1	500	80-120	500	75-125	500	80-120
Iron	250	5,000	80-120	5,000	75-125	5,000	80-120
Lead	1	500	80-120	500	75-125	500	80-120
Magnesium	250	5,000	80-120	5,000	75-125	5,000	80-120
Manganese	1	500	80-120	500	75-125	500	80-120
Mercury	0.2	5	80-120	5	75-125	5	80-120
Molybdenum	1	500	80-120	500	75-125	500	80-120
Nickel	1	500	80-120	500	75-125	500	80-120
Potassium	250	5,000	80-120	5,000	75-125	5,000	80-120
Selenium	1	500	80-120	500	75-125	500	80-120
Silver	0.5	250	80-120	250	75-125	250	80-120
Sodium	250	5,000	80-120	5,000	75-125	5,000	80-120
Strontium	1	500	80-120	500	75-125	500	80-120
Thallium	1	500	80-120	500	75-125	500	80-120
Tin	5	500	80-120	500	75-125	500	80-120
Titanium	1	500	80-120	500	75-125	500	80-120
Uranium	1	500	80-120	500	75-125	500	80-120
Vanadium	1	500	80-120	500	75-125	500	80-120
Zinc	5	500	80-120	500	75-125	500	80-120

Please see the QA manager for the most current MDLs.

Table N:

SOLIDS BATCH QC
ON INSTRUMENT
CONCENTRATIONS AND LIMITS

Element	Method Blank (RL in ppb)	LCS/ LCSD (ppb)	LCS/LCSD Limits (%)	MS/MSD Amount (ppb)	MS/MSD Limits (%)	PS Amount (ppb)	PS Limits (%)
Aluminum	250	5000	80-120	5000	75-125	5000	80-120
Antimony	1	500	80-120	500	75-125	500	80-120
Arsenic	1	500	80-120	500	75-125	500	80-120
Barium	1	500	80-120	500	75-125	500	80-120
Beryllium	1	500	80-120	500	75-125	500	80-120
Boron	5	500	80-120	500	75-125	500	80-120
Cadmium	1	500	80-120	500	75-125	500	80-120
Calcium	250	5000	80-120	5000	75-125	5000	80-120
Chromium	1	500	80-120	500	75-125	500	80-120
Cobalt	1	500	80-120	500	75-125	500	80-120
Copper	1	500	80-120	500	75-125	500	80-120
Iron	250	5000	80-120	5000	75-125	5000	80-120
Lead	1	500	80-120	500	75-125	500	80-120
Magnesium	250	5000	80-120	5000	75-125	5000	80-120
Manganese	1	500	80-120	500	75-125	500	80-120
Mercury	0.2	5	80-120	5	75-125	5	80-120
Molybdenum	1	500	80-120	500	75-125	500	80-120
Nickel	1	500	80-120	500	75-125	500	80-120
Potassium	250	5000	80-120	5000	75-125	5000	80-120
Selenium	1	500	80-120	500	75-125	500	80-120
Silver	0.5	250	80-120	250	75-125	250	80-120
Sodium	250	5000	80-120	5000	75-125	5000	80-120
Strontium	1	500	80-120	500	75-125	500	80-120
Thallium	1	500	80-120	500	75-125	500	80-120
Tin	10	500	80-120	500	75-125	500	80-120
Titanium	1	500	80-120	500	75-125	500	80-120
Uranium	1	500	80-120	500	75-125	500	80-120
Vanadium	1	500	80-120	500	75-125	500	80-120
Zinc	10	500	80-120	500	75-125	500	80-120

Please see the QA manager for the most current MDLs.

Table O:
BIOTA BATCH QC
ON INSTRUMENT
CONCENTRATIONS AND LIMITS

Element	Method Blank (RL in ppb)	LCS/ LCSD (ppb)	LCS/LCSD Limits (%)	MS/MSD Amount (ppb)	MS/MSD Limits (%)	PS Amount (ppb)	PS Limits (%)
Aluminum	250	10,000	80-120	10,000	75-125	10,000	80-120
Antimony	1	200	80-120	200	75-125	200	80-120
Arsenic	1	200	80-120	200	75-125	200	80-120
Barium	1	200	80-120	200	75-125	200	80-120
Beryllium	1	200	80-120	200	75-125	200	80-120
Boron	5	200	80-120	200	75-125	200	80-120
Cadmium	1	200	80-120	200	75-125	200	80-120
Calcium	250	10,000	80-120	10,000	75-125	10,000	80-120
Chromium	1	200	80-120	200	75-125	200	80-120
Cobalt	1	200	80-120	200	75-125	200	80-120
Copper	1	200	80-120	200	75-125	200	80-120
Iron	250	10,000	80-120	10,000	75-125	10,000	80-120
Lead	1	200	80-120	200	75-125	200	80-120
Magnesium	250	10,000	80-120	10,000	75-125	10,000	80-120
Manganese	1	200	80-120	200	75-125	200	80-120
Mercury	0.2	5	80-120	5	75-125	5	80-120
Molybdenum	1	200	80-120	200	75-125	200	80-120
Nickel	1	200	80-120	200	75-125	200	80-120
Potassium	250	40,000	80-120	40,000	75-125	40,000	80-120
Selenium	1	200	80-120	200	75-125	200	80-120
Silver	0.5	100	80-120	100	75-125	100	80-120
Sodium	250	10,000	80-120	10,000	75-125	10,000	80-120
Strontium	1	200	80-120	200	75-125	200	80-120
Thallium	1	200	80-120	200	75-125	200	80-120
Tin	5	200	80-120	200	75-125	200	80-120
Titanium	1	200	80-120	200	75-125	200	80-120
Uranium	1	200	80-120	200	75-125	200	80-120
Vanadium	1	200	80-120	200	75-125	200	80-120
Zinc	5	200	80-120	200	75-125	200	80-120

Note: Biota spikes are fortified for K as a result of its natural presence in the Chicken blank. **Please see the QA manager for the most current MDLs.**

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STANDARD OPERATING PROCEDURE

Soil/Semisolid Sample Preparation for the Analysis of Gasoline Range Organics and Petroleum Volatile Organics by Wisconsin Modified GRO.

Reference Methods:
WI Modified Method for the Determination of Gasoline Range Organics
SW-846 Method 5030B
SW-846 Method 5035

SOP NUMBER:	S-GB-O-005-Rev.1
EFFECTIVE DATE:	Date of Final Signature
SUPERSEDES:	GB-O-005 Rev.0

APPROVAL

Nils Melberg, Laboratory Manager — Date: 12/05/07

Arthur F. Lautenbach, Quality Manager — Date: 12/05/07

ANNUAL REVIEW

SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE APPROVAL. SOP IS VALID FOR ONE YEAR FROM DATE OF LAST SIGNATURE.

Signature	Title	Date

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1. Purpose

1.1 This SOP details the steps and conditions involved in preparing soil/semisolid samples for the determination of gasoline range organics (GRO) and petroleum volatile organic compounds (PVOCs) following The Method for Determining Gasoline Range Organics (Wisconsin DNR 1995).

1.2 Samples prepared by this SOP are analyzed by the latest revisions of SOPs S-GB-O-006 *Modified Method for Determination of Gasoline Range Organics*, S-GB-O-008 *Total Petroleum Hydrocarbons – Gasoline by Gas Chromatography Using Flame-ionization Detectors*, and S-GB-O-009 *Aromatic Volatiles by Gas Chromatography Using Photo-ionization Detectors*.

2. Scope and Application

2.1 The policies and procedures contained in this SOP are applicable to all personnel involved in the preparation of soil/semisolid samples for the determination of GRO and PVOCs using a purge and trap, Gas Chromatography procedure.

3. Summary of Method

3.1 Samples are collected in methanol or using En Core™ samplers. Prior to sample introduction to the GC system for analysis, the samples are weighed to determine mass, homogenized physically, and batched for quality control measurements to assess the precision and accuracy of the prep and analytical procedures. It is specified in the method that a maximum weight of 35 grams in a 2 oz jar or 20 grams in a 40 mL VOC vial can be collected and considered valid.

4. Interferences

4.1 The primary introductions of laboratory interferences come from dirty glassware or impure reagents. Clean laboratory apparatus, quality reagents and conscientious laboratory personnel are essential in the production of high quality data.[1]

5. Safety

5.1 The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable. Cautions are included for known extremely hazardous materials.

5.2 A reference file of Material Safety Data Sheets (MSDS) is made available to all personnel involved in the chemical analysis, and is located in Sample Receiving. A formal safety plan has been prepared and is distributed to all personnel with documented training

[1] Pace Analytical Services, Inc – Green Bay Laboratory purchases high quality solvents to eliminate this potential of contaminations and require these vendors to stand behind claims made on the solvents purchased.

6. Definitions

6.1 Refer to Section 10.0 of the most current version of the Pace Quality Manual for the terms used at Pace Analytical. When definitions are not consistent with NELAC defined terms, an explanation will be provided in this SOP.

7. Responsibilities and Distribution

7.1 Personnel

7.1.1 All personnel involved with sample preparation and analysis are responsible for adherence to this SOP. A controlled copy will be available for review and consultation within the area methods manual.

7.1.2 Personnel are responsible for ensuring that any deviations to this SOP are reported to the laboratory manager.

7.2 Laboratory Manager

7.2.1 The laboratory manager is responsible for ensuring adherence to this SOP and will receive a controlled copy of this SOP.

7.2.2 The laboratory manager is responsible for performing an annual review of the SOP and reporting any required revisions to the Quality Assurance Office.

7.3 Quality Assurance Office

7.3.1 The QA Office is responsible for performing an annual review of the SOP in conjunction with the purchasing department and revising as needed.

7.3.2 The QA Office is responsible for ensuring that all revisions to the SOP are implemented.

7.4 Revisions

7.4.1 This SOP will be reviewed on an annual basis at a minimum, and any required revisions will be incorporated.

8. Sample Collection, Preservation and Handling

8.1 Wisconsin has promulgated a 21 day hold time for volatile soil samples preserved in the field with methanol. If an En Core™ is used for sample, the sample must be preserved within 48 hours of collection with methanol.

8.2 After reception in the laboratory, samples are to be stored at 4° ± 2° Celsius at all times when not being prepared.

8.3 A maximum weight of 35.4 grams can be collected and considered valid using an En Core™ sampler, a 2 oz. certified clean jar, or 20.4 grams if collected in a 40 mL VOC vial.

9. Equipment and Supplies

9.1 Microsyringes: 10-µL, 25-µL, 50-µL, 100-µL, 250-µL, 500-µL, and 1,000-µL:

9.2 Shaker Table

9.3 Syringe, 50 mL, for holding sample aliquot and diluent solution.

9.4 Balance: Analytical, capable of accurately weighing 0.01 g.

9.5 Sonication bath

9.6 40 mL VOC vials for GC autosampler.

9.7 En Core™ samplers

9.8 Computer

9.9 Balance to Computer Interface Connection

9.10 Autoprogram (GRO), most current version.

9.11 Repipettor, to dispense methanol

9.12 10 mL Graduated Cylinder, to measure dispensed methanol.

10. Reagents and Standards

10.1 Reagent water: Reagent water is defined as water in which an interferent is not observed at the method detection limit of the compounds of interest.

10.2 Methanol (MeOH): Purge and Trap grade. Store away from other solvents.

10.3 10,000 ppm – 10 component Gasoline Range Organics Standard.

10.4 100 µg/mL ααα-Trifluorotoluene surrogate solution added by the autosampler.

11. Calibration

11.1 Not Applicable.

12. Procedure

12.1 The balance is to be leveled before calibration. Calibration verification of the analytical balance is done with S-class weights of 2.0g, 5.0g, 20.0g, and 200.0g. These values are to be noted in the Balance calibration logbook. The frequency of balance calibration verification is once per day before the balance is used or when the balance is moved.

12.2 Zero the balance.

12.3 Place the vial or jar on the balance and write the weight on the vial or jar and in the Soil Prep Logbook.

12.4 In most instances, 40 mL sample vials and 2 oz jars are prepared at Pace Analytical Services Inc. – Green Bay Laboratory and sent to the client prior to sampling. See SOP S-ALL-GB-C-004 *Bottle Preparation* for the specifics on the preparation of sample bottles. (40 mL vials contain 10 mL of Methanol (MeOH) and have an average weight of 25.62 g without MeOH. 2 oz. jars contain 20 mL of MeOH and have an average weight of 87.32 g including MeOH.) If you are unsure of the amount of MeOH or the weight of the client sampling containers, you must contact the Project Manager before proceeding with the samples.

12.4.1 Preserved 40 mL vials generally have a weight range of 32.XX g to 34.XX g. (with 10 mL of MeOH). The specific weight prior to sampling should be recorded on the vial and is a measurement of the vial, cap and MeOH.

12.4.1.1 A 1:1 ratio of soil weight (g) to MeOH volume (mL) is required. The amount of soil in the sample may be calculated as follows for 40 mL vials:

where:

$W_S = W_T - W_J$

W_s = Weight of soil in the sample (g)
W_t = Total weight of the sample including vial, cap, soil, and MeOH (g)
W_J = Weight of the jar including the vial, cap, and MeOH (g)

12.4.1.2 The volume of MeOH required to achieve the 1:1 ratio of soil weight (g) to MeOH (mL) may be calculated as follows:

where:

$V_M = W_S - 10mL$

V_M = Volume of MeOH required to achieve 1:1 ratio of soil (g):MeOH (mL)
W_S = Weight of soil in the sample (g)
10 = Volume of MeOH initially added (mL)

12.4.2 2 oz jars generally have a weight range of 83.XX g to 87.XX g. (with 20 mL of MeOH). The specific weight of the jar prior to sampling should be recorded on the jar and is a measurement of the jar and cap.

12.4.1.1 A 1:1 ratio of soil weight (g) to MeOH (mL) is required. The amount of soil in the sample may be calculated as follows for 2oz jars:

where:

$W_S = W_T - W_J - 15.8$

W_s = Weight of soil in the sample (g)
W_t = Total weight of the sample including vial, cap, soil, and MeOH (g)
W_J = Weight of the jar including the vial, and cap (g)
15.8 = Weight of 20 mL of MeOH added to the jar (g)

12.4.1.2 The volume of MeOH required to achieve the 1:1 ratio of soil weight to MeOH may be calculated as follows:

where:

$V_M = W_S - 20$ mL

V_M = Volume of MeOH required to achieve 1:1 ratio of soil (g):MeOH (mL)
W_S = Weight of soil in the sample (g)
20 = Volume of MeOH initially added (mL)

12.5 If 1:1 ratio cannot be achieved, write the sample weight and volume of Methanol in the prep logbook, you must contact the Project Manager before proceeding with the samples. If the sample is analyzed, the appropriate data qualifier and comment is entered into LIMS.

12.6 Add the appropriate amount of Methanol using a graduated cylinder or syringe.

12.7 Place prep sheet in the SOILS PREP BOOK.

12.8 Sign over the face of the printout and page to insure removal of page will be noticeable. Date the top of the page of the notebook and sign and date the bottom of the notebook.

12.9 The QC set blank is made for the set, which includes 10 grams of Ottawa sand and 10 mL of methanol placed in a 40 mL VOA Vial.

12.10 The QC set laboratory control spike and laboratory control spike duplicate (LCS/LCSD) are made for the set which includes 10 grams of Ottawa sand, 10 mL of methanol, and 10 µL of the 10,000 ppm revised WISC PVOC/GRO mix standard placed in 40 mL VOA Vial.

12.11 Samples and QC set are then shaken on shaker table for two minutes to pre-homogenize the samples.

12.12 Samples are then placed in the sonicator, which is set at the sixth (6) setting for power and the coldest temperature setting. The samples are sonicated for 20 minutes to finish the homogenization process.

12.13 Samples are pre-screened using a rapid GC headspace technique. See SOP GB-O-001 *Sample Screening Volatile Organics Prior to Preparation* for the specifics on the pre-screening of samples.

12.14 A standard analytical dilution is 1:50. Add 1.0 mL of the sample extract measured with a microsyringe of appropriate volume to 49 mL of reverse osmosis water in a 50 mL syringe. Non-standard dilutions are made from the results of the screening analysis.[2]

12.15 To make dilutions other than a standard 1:50 dilution, fill a 50 mL syringe to a volume of 49 mL with reverse osmosis water. Using a 1.0 mL syringe, inject methanol into the 50 mL syringe to bring the total volume of sample and methanol to equal 1.0 mL. Using an appropriate volume syringe, inject the sufficient amount of sample to reach desired dilution. See Table 1 for dilutions.

12.16 The 50 mL syringe contents are place into a 40 mL VOC vial by slowly deploying the plunger and injecting on the side of the vial to eliminate cavitation and loss of analytes to volatilization or sparging. Enough of the contents are injected to created a meniscus at the top of the vial that when capped will produce a no headspace sample.

12.17 The vial is capped and checked for headspace. If vial is free of headspace, it is ready for analysis.

13. Quality Control

13.1 A maximum of 20 samples define a QC set. One method blank (MB), laboratory control spike (LCS), laboratory control spike duplicate (LCSD), matrix spike (MS) and matrix spike duplicate (MSD), are necessary per 20 samples OR per extraction batch whichever is more frequent.

13.2 A maximum weight of 35.4 grams can be collected and considered valid using an En Core™ sampler or a 2 oz. certified clean jar, or 20.4 grams if collected in a 40 mL VOC vial.

14. Method Performance

14.1 There are several requirements that must be met to insure that this procedure generates accurate and reliable data. A general outline of requirements has been summarized below. Further specifications may be found in the Laboratory Quality Manual.

14.1.1 The analyst must read and understand this procedure with written documentation maintained in his/her training file.

[2] On instrument values are to be above 500 ppm GRO. This is the point considered the midpoint of the analysis curve. Samples containing heavy petroleum products can be lower than 500 ppm GRO on column to prevent contamination carryover effects. The cut off is 300 ppm GRO in these instances. The top calibration point is 3000/5000 ppm (instrument dependent) for GRO and 300/500 ppb (instrument dependent) for individual PVOC components. Linear results are possible out to 3000/5000 ppm (instrument dependent) and 300/500 ppb (instrument dependent) respectively.

14.1.2 An initial demonstration of capability (IDOC) must be performed per ALL-Q-020, *Training Procedures*. A record of the IDOC will be maintained in his/her QA file with written authorization from the Laboratory Manager and Quality Manager.

14.1.3 An annual method detection limit (MDL) study will be completed per S-ALL-Q-004, *Method Detection Limit Studies*, for this method and whenever there is a major change in personnel or equipment. The results of these studies are retained in the quality assurance office.

14.1.4 Periodic performance evaluation (PE) samples are analyzed per S-ALL-Q-010, *PE/PT Program*, to demonstrate continuing competence. All results are stored in the QA office.

15. Pollution Prevention and Waste Management

15.1 The quantity of chemicals purchased is based on expected usage during its shelf life and disposal cost of unused material. Actual reagent preparation volumes reflect anticipated usage and reagent stability.

15.2 Excess reagents, samples and method process wastes are characterized and disposed of in an acceptable manner. For further information on waste management consult the current version of ALL-S-002, *Waste Handling*..

16. References

SW-846 5030B Purge and Trap for Aqueous Samples
Revision 2, December 1996
SW-846 5035 Closed System Purge and Trap and Extraction for Volatile Organics in Soil and Waste Samples. Revision 0, December 1996
Modified GRO, Method for Determining Gasoline Range Organics
Wisconsin DNR, WI-PUB-SW-141, September 1995
S-GB-O-006 *Modified Method for Determination of Gasoline Range Organics*
S-GB-O-008 *Total Petroleum Hydrocarbons – Gasoline by Gas Chromatography Using Flame-ionization Detectors*
S-GB-O-009 *Aromatic Volatiles by Gas Chromatography Using Photo-ionization Detectors*
S-GB-O-001 *Sample Screening Volatile Organics Prior to Preparation*
S-ALL-GB-C-004 *Bottle Preparation*

17. Tables, Diagrams, Flowcharts, Appendices, Addenda etc.

Table 1. Methanol Dilutions (All dilutions are performed in 49 mLs of water in a 50 mL syringe)

Dilutions	Volume of Sample (µL)	Volume of Methanol (µL)
50	1000	0
100	500	500
125	400	600
200	250	750
250	200	800
400	125	880
500	100	900
625	80	920
1000	50	950
1250	40	1000
2000	25	1000
2500	20	1000
4000	12.5	1000
5000	10	1000
6250	8	1000
10000	5	1000
25000	2	1000

18. Revisions

Document Number	Reason for Change	Date
GB-O-005-Rev.0	Reformatted SOP body to Pace analytical format	08Apr2005
S-GB-O-005-Rev.1	Up-dated cover page to new format. Up-dated instances of "EnChem" to Pace Analytical Services, Inc. – Green Bay Laboratory, throughout document. Up-dated Section 12 Procedures. Section 12/13 – Up-dated Blank Spike/Blank Spike Duplicate (BS/BSD) to Laboratory Control Spike/Laboratory Control Spike Duplicate (LCS/LCSD) Section 15.2: Up-dated to current SOP nomenclature. Section 16: Updated references	04Dec2007

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STANDARD OPERATING PROCEDURE

Aromatic Volatiles By Gas Chromatography Using Photoionization Detectors

Reference Methods:
SW-846 8021B / EPA 602

SOP NUMBER:	S-GB-O-009-Rev.1
EFFECTIVE DATE:	Date of Final Signature
SUPERSEDES:	GB-O-009-Rev.0

APPROVAL

Nils Melberg, General Manager — Date: 10/4/07

Arthur F. Lautenbach, Quality Manager — Date: 10/4/07

ANNUAL REVIEW

SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE APPROVAL. SOP IS VALID FOR ONE YEAR FROM DATE OF LAST SIGNATURE.

Signature	Title	Date

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S-GB-O-009-Rev.1

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1. Purpose

1.1 This SOP details the steps and conditions involved in analyzing aqueous, solid, and semi-solid samples for the determination of volatile organic compounds following SW-846 8021B and EPA 602. The samples analyzed by this SOP are prepared by the current versions of GB-O-005, *Soil/Semisolid Sample Preparation for the Analysis of Gasoline Range Organics and Petroleum Volatile Organics by Wisconsin Modifies GRO*, and GB-O-010, *Aqueous Sample Preparation for the Analysis of Gas Range Organics and Petroleum Volatile Organics*

2. Scope and Application

2.1 This method is used to determine volatile organic compounds in a variety of matrices. This method is applicable to nearly all types of samples, regardless of water content, including Aqueous, Solids, Non-Aqueous and Air Matrices. The compounds found in Appendix A, Table A can be determined but more compounds can be added with proper and acceptable demonstration.

2.2 Method detection limits (MDLs) are compound dependent and vary with compound properties. The applicable concentration range of this method is compound and instrument dependent but is approximately 0.1 to 500 ppb. Analytes that are inefficiently purged from water will not be detected when present at low concentrations, but they can be measured with acceptable accuracy and precision when present in sufficient amounts. Determination of some structural isomers (i.e., Xylenes) may be hampered by co-elution. These are presented as a summation of the isomers.

2.3 In the absence of Project or Accrediting Authority Specified requirements the estimated quantitation limit (EQL) for an individual compound is approximately 5 µg/kg (wet weight) for solids, and between 1 and 2 µg/L for aqueous matrices. EQLs will be proportionately higher for sample extracts and samples that require dilution or reduced sample size to avoid saturation of the detector. Solid extraction EQLs are 50 µg/kg for all compounds except Benzene at 20 µg/kg and m/p-Xylene at 100 µg/kg. For the State of Wisconsin the reporting limits are 25 µg/kg for all compounds with the exception of m/p-Xylene, which is 50 µg/kg.

2.4 This method is restricted for use by, or under the supervision of, analysts experienced in the use of gas chromatographs for measurement of purgeable organics at low ppb concentrations and skilled in the interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method.

3. Summary of Method

3.1 This method provides gas chromatographic conditions for the detection of aromatic volatile organic compounds. Five mL aliquots of sample will be analyzed using purge-and-trap. A temperature program is used in the gas chromatograph to separate the organic compounds. For aromatic volatile compound analysis, detection is achieved by a photoionization detector (PID).

3.2 Identification is obtained by analyzing standards under the same conditions used for samples and comparing resultant GC retention times. Concentrations of the identified components are measured by relating the response produced for that compound to the response produced by a compound that is used as an internal standard.

3.3 Soil samples are collected in wide mouth VOC vials, 40 mL VOC vials, or in 25 g Encore samplers. Aqueous samples are collected in 40 mL VOC vials preserved with HCl. See section entitled "Sample Collection, Preservation, Shipment and Storage." Minimum handling is required to reduce VOC loss.

4. Interferences

4.1 Major contaminant sources are volatile materials in the laboratory and impurities in the inert purging gas and in the sorbent trap. The use of non polytetrafluoroethylene (PTFE) thread sealants, plastic tubing, or flow controllers with rubber components should be avoided, since such materials outgas organic compounds which will be concentrated in the trap during the purge operation. Analyses of calibration and reagent blanks provide information about the presence of contaminants.

4.2 Subtracting blank values from sample results is not permitted. If reporting values without correcting for the blank results in what the laboratory feels is a false positive result for a sample, the analyst should fully explained this in text accompanying the uncorrected data.

4.3 Contamination may occur when a sample containing low concentrations of volatile organic compounds is analyzed immediately after a sample containing high concentrations of volatile organic compounds. A technique to prevent this problem is to rinse the purging apparatus and sample syringes with portions of organic free reagent water between samples. After the analysis of a sample containing high concentrations of volatile organic compounds, one or more blanks should be analyzed to check for cross-contamination. A low concentration sample (i.e., not detected) following the injection of a high concentration sample is also used to check for cross contamination.

4.4 For samples containing large amounts of water-soluble materials, suspended solids, high boiling compounds, or high concentrations of compounds being determined, it may be necessary to wash the purging device with a soap solution, rinse it with organic free reagent water, and then dry the purging device in an oven at 105°C. In extreme situations, the entire purge-and-trap device may require dismantling and cleaning. Screening of the samples prior to purge-and-trap GC analysis is highly recommended to prevent contamination of the system.

> Note: This is especially true for soil and waste samples. Screening may be accomplished with an automated headspace technique.

4.5 Samples can be contaminated by diffusion of volatile organics through the septum seal of the sample container into the sample during shipment and storage. A trip blank prepared from organic free reagent water and carried through the sampling, handling, and storage protocols can serve as a check on such contamination.

> Note: For some Accrediting Authorities, the use of methanol for a trip blank is required.

5. Safety

5.1 The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable. Cautions are included for known extremely hazardous materials.

5.2 A reference file of Material Safety Data Sheets (MSDS) is made available to all personnel involved in the chemical analysis, and is located in Sample Receiving. A formal safety plan has been prepared and is distributed to all personnel with documented training

6. Definitions

6.1 Refer to Section 10.0 of the most current version of the Pace Quality Manual for the terms used at Pace Analytical. When definitions are not consistent with NELAC defined terms, an explanation will be provided in this SOP.

7. Responsibilities and Distribution

7.1 Personnel

7.1.1 All personnel involved with sample preparation and analysis are responsible for adherence to this SOP. A controlled copy will be available for review and consultation within the area methods manual.

7.1.2 Personnel are responsible for ensuring that any deviations to this SOP are reported to the laboratory manager.

7.2 Laboratory Manager

7.2.1 The laboratory manager is responsible for ensuring adherence to this SOP and will receive a controlled copy of this SOP.

7.2.2 The laboratory manager is responsible for performing a biennial review of the SOP and reporting any required revisions to the Quality Assurance Office.

7.3 Quality Assurance Office

7.3.1 The QA Office is responsible for performing a biennial review of the SOP in conjunction with the purchasing department and revising as needed.

7.3.2 The QA Office is responsible for ensuring that all revisions to the SOP are implemented.

7.4 Revisions

7.4.1 This SOP will be reviewed on a biennial basis at a minimum, and any required revisions will be incorporated.

8. Sample Collection, Preservation and Handling

8.1 Aqueous samples should be collected in triplicate without agitation and without headspace in contaminant-free 40 mL glass VOC vials with Teflon-lined septa in the caps. The Teflon liner must contact the sample. Samples must be preserved with 500 µL of Hydrochloric Acid (HCl) at the time of collection (acid should be added to the vial prior to adding the sample).

Note: Pace Analytical Services, Inc., uses pre-cleaned, Level 3 certified, 40 mL VOC vials purchased from QEC. These vials contain 0.5 mL of 18 % HCL.

Note: If targeted compounds breakdown with the addition of HCl, samples must be collected unpreserved. Unpreserved samples have a 7-day holding time. The pH of the samples are taken using pH indicator paper and recorded in the prep logbook. Chlorine testing will be performed on samples requiring EPA Method 602 using chlorine indicator paper strips and recorded in the prep logbook.

8.2 The samples will need to be cooled to 4°C after collection. Aqueous samples will be stored in refrigerators at Pace Analytical Services, Inc., and must be held at 4°C (+/- 2°C). Preserved samples have a 14 day holding time or as specified by the Accrediting Authority.

8.3 One trip blank is required per sampling event and site.

8.4 Solid samples for SW846 5035 should be collected with the ENCORE sampler or other sampling technique if approved by method. A sufficient number of samplers should be collected to provide for backup analyses in the event of breakage or instrument malfunctions and to allow for screening. One vial should be collected for dry weight determination.

8.5 Soil samples for volatile analysis that are preserved with the sodium bisulfate preservative solution are to be cooled to approximately 4°C, packed in appropriate containers, and shipped to the laboratory on ice. These are to be analyzed within 14 days of sample collection. Samples receiving no preservation other than cooling to 4°C must be shipped to the laboratory the same day that they are collected. Once in the laboratory, the samples must be analyzed or frozen within 48 hours of sample collection. All samples need to be analyzed as soon as practical, but within the designated holding time of 14 days from sample collection for preserved samples or 48 hours for unpreserved samples.

Note: Unpreserved ENCORE samplers will be frozen by Pace Analytical Services, Inc., personnel upon receipt to the lab or prepared for analysis immediately.

8.6 Solid samples for SW846 5030 are routinely collected in a 2 oz. jar containing 20 mL of methanol, or 40 – mL VOA vials containing 10 mL of methanol. A separate vial should be collected for dry weight determination.

Note: Zero headspace jar sampling can only be used and is limited to projects where it is approved by the Accrediting Authority.

8.7 Samples need to be shipped to the lab as soon as the samples are collected.

8.8 Sample temperature must be determined upon receipt to the lab.

Note: Sample temperature is recorded by use of a temperature blank. The temperature must be between 4°C (+/- 2°C) unless superseded by the accrediting authority. For certain authorities recording sample temperature as "received on ice (ROI)" is acceptable.

8.9 Samples will be stored at Pace Analytical Services, Inc., at 4°C (+/- 2°C).

8.10 All preserved samples must be analyzed within 14 days from the date of collection unless project or authority specific holding times differ.

8.11 See Appendix A Table G for a summary.

9. Equipment and Supplies

9.1 See the following Tables in Appendix A for a summary:

Equipment	Table C
Supplies	Table D

10. Reagents and Standards

10.1 See the following Tables in Appendix A for a summary:

Reagents	Table E
Standards	Table F

10.1.1 Intermediate standards will have a shelf life of 6 months from the date prepared, or the expiration date of the stock standard, whichever is less.

11. Calibration

11.1 Demonstration and documentation of acceptable initial calibration is required before any samples are analyzed and is required periodically throughout sample analysis as dictated by results of a Calibration Verification Standard (CVS). After initial calibration is successful, a calibration check is required at the beginning and end of each period during which analyses are performed, not to exceed 12 hours, and at requisite intervals.

11.2 Initial calibration accuracy must be evaluated before any samples are analyzed through the analysis of a Quality Control Sample called a Calibration Verification Standard (CVS), which includes all compounds of interest. The CVS should be at or near the midpoint of the calibration range, must be derived from a source independent of the calibration standard (i.e., second source), and must quantitate within +/- 15 % of the expected value. Where the recovery of individual compounds is greater than +/- 15% in the CVS, the compound may be reported if the average recovery in the CVS of all the calibrated compounds is +/- 15% and all compound recoveries are within 70 to 130 %. Water and soil extracts will analyze a CVS at 20 µg/L on column for each compound of interest (m/p-Xylene will be at 40 µg/L). Low-level soil CVSs will be analyzed at 50 µg/L on column (m/p-Xylene will be at 100 µg/L).

11.3 Calibration drift is monitored through the analysis of additional Calibration Verification Standards (CVSs) at periodic intervals during the analytical sequence (See Appendix A, Table H for frequency). These additional CVSs should also quantitate within 15 % of the expected value.

Note: South Carolina CVS limit is +/- 15%. This must be assessed by individual compound. Averaging is not allowed.

11.4 Calibrate the instrument at a minimum of five concentration levels.

11.5 See the following Tables in Appendix A for a summary:

Standards	Table F
Calibration and Standardization	Table I
Directions for Standards	Table P

11.6 Internal standard is added automatically by the autosampler to each calibration standard. Surrogate standards are added to medium level MeOH calibration standards and low-level calibration standards at the same concentration as the compounds. Use IS only when **calibrating** these two matrices. Use IS/SS for low-level sample **analysis** and IS only for medium level sample **analysis.**

11.7 Internal standard and Surrogate are added automatically by the autosampler to each calibration standard for Wisconsin methanol extractions and aqueous curve. Use IS/SS for sample analysis.

11.8 Internal standard/Surrogate standard (IS/SS) mix is added automatically by the autosampler for aqueous matrices and low-level soil matrices.

11.9 The vial autosampler will inject 5 mL of each calibration standard into the sparge tube or will purge the sample in the vial for the low level analysis. Calibrated compounds will use average response factors providing they pass the criteria in Appendix A, Table I. The average response factors are determined by a ratio of amount/area. Amount being the concentration in µg/L and area being the integrated area of the individual compounds. The average response factors are then determined by taking the amount/area ratio for all calibration levels and averaging them. The response factor is calculated as follows:

$$RF = \frac{\text{Response of Compound}}{\text{Response of IS}} \times \frac{\text{Concentration of IS}}{\text{Concentration of Compound}}$$

Where: **RF** is the response factor
IS is the internal standard

The RF is calculated for each calibration point and then all calibration points are averaged for a mean relative response factor (RRF). The percent relative standard deviation (% RSD) is then calculated as follows:

$$\% \text{ RSD} = \frac{\text{SD}}{\text{Mean RRF}} \times 100$$

Where: **SD** is the standard deviation of the averaged response factors

11.10 Linear regression may also be used. The working calibration curve will be verified by the criteria in Appendix A, Table I.

12. Procedure

12.1 Verify the initial calibration. A sequence will begin and end with the analysis of a calibration verification standard (CVS). The calibration shall be verified at a frequency of every 10 analytical samples (not to exceed a 12-hour period).

12.2 A method blank must be analyzed after the CVS to ensure that the total system (introduction device, transfer lines and GC system) is free of contaminants. If the method blank indicates contamination, then it may be appropriate to analyze another method blank to demonstrate that the contamination is not a result of carryover from standards or samples.

12.3 If the second blank confirms contamination, the analyst must stop the analytical sequence determine the source of the contamination, eliminate the contamination if it involves a compound of interest, and begin the 12-hour sequence again.

12.4 Update retention times. The retention times will be adjusted daily from the first CVS standard analyzed at the start of an analytical sequence and after every CVS in the analytical sequence. Pace will default to +/- 0.05* minutes on either side of the apex (retention time) for standard deviation 3x values less than or equal to 0.05 minutes. This is a value that the analysts, QC department, and Lab Manager agreed upon to reduce the false positives by using windows that are too wide and to reduce false negatives by using windows that are too narrow. Data may not be reported when a new column has been installed until the retention time windows have been established. Any data analyzed while the retention time study was conducted will have to be reprocessed using the new retention time window value obtained before the data may be released to our clients. It will be acceptable to use the retention times from the highest standard of a calibration curve to reprocess data for that day that the curve was run.

* Instruments equipped with Electronic Pressure Control (EPC) shall use a +/- 0.03 default.

12.5 Update Internal Standard area limits. Internal Standard area limits established from the area of the first CVS starting a sequence or method. Limits are -50% to +50% of the CVS** area. The CVS must also be compared to the corresponding calibration point and may not vary by more than -50% to +50% from the initial calibration response.

** Experience with samples has led Pace to tighten the limits to avoid Calibration Verification Standard failures during the analysis.

12.6 Volatile compounds are introduced into the gas chromatograph by purge-and-trap. Purge-and-trap will be used directly on aqueous samples and for low-level soil samples. Medium level soils and solids should be analyzed by methanol extraction followed by purge-and-trap. Soil concentrations MUST be reported on a dry weight basis unless local regulations require different.

12.7 Introduce volatile compounds into the gas chromatograph using the purge-and-trap method. Adjust the purge gas flow rate (helium) to 40-45 mL/min on the purge-and-trap device.

12.8 Load the autosampler rack with samples that correspond with the order written up in the instrument logbook. Samples need to be written in logbooks and keyed into the sample log tables in HPCHEM as follows for automated data processing:

800001B001SA50

Where, 800001-001 = ten digit lab number (including the dash)
B = prep/analytical code in the 7th character position replacing the "-"
S = matrix code in the 11th character position
A = test code in the 12th character position
50 = dilution factor, up to a 4 digit dilution factor in the 13-16th character position

12.9 Dilutions requiring more than four digits can be done by using the letter H as a 100x multiplier and the letter K as a 1000x multiplier. Spaces are not allowed in any of the 16 available character positions. See Appendix A, Table Q for additional codes and examples. The analyst performing the analysis will check the logbook, as well as the autosampler. A second analyst will also check the logbook, as well as the autosampler. Both individuals will initial the sample log table, which is a computer-generated hard copy of the analysis written in the logbook. The second analyst will initial the logbook indicating that the autosampler has been double-checked. The initial check of the autosampler was done when the samples were loaded.

12.10 Samples not requiring dilutions will be loaded directly into the autosampler rack. In the event of insufficient vials, or if one needs to use the last vial, the analysis should be performed during the shift that an analyst is present. The data will need to be reviewed and reset as needed. 20 mL vials can be filled (no headspace) with sample and stored in case additional analysis is needed. Diluted samples are prepared in 50 mL syringes and then transferred into 40 mL VOC vials for the autosampler rack. The following procedure is appropriate for diluting purgeable samples. All steps must be performed without delay until the diluted sample is in a gas-tight 40 mL VOC vial.

12.11 Dilutions are made in 50 mL syringes. Choose a syringe that will deliver the proper aliquot for the desired dilution. Adjust the volume in the 50 mL syringe to accommodate the sample aliquot. Introduce a bubble into the 50 mL syringe to allow for the sample aliquot. Inject the aliquot into the 50 mL syringe keeping the syringe needle tip below the surface of the water. Invert the 50 mL syringe three times and transfer the diluted sample to a labeled 40 mL VOC vial. Methanol (MEOH) extracts will contain 2 % MEOH or 1 mL total MEOH to 49 mL of water (x50), which is for clean extracts. Samples requiring larger dilutions will have aliquots of sample and purge and trap grade MEOH to equal 1 mL (2 % by volume) total. Aliquots of less than 1 µL are not recommended.

12.12 The vial autosampler will automatically add the IS/SS mix (or IS mix only) when it transfers the 5 mL of sample to the sparge tube or to the low-level soil vials.

12.13 Start the vial autosampler (see operating and instruction manuals for the different types of autosamplers). The purge time is 11 minutes and will be at ambient temperature for aqueous matrices and MeOH extracts. Low level soils will employ a heated purge at 40°C for 11 minutes. The sample syringe is then flushed 1-3 times during purge.

12.14 At the conclusion of the purge time, dry purge the sample for 5 minutes for the Tekmar 3000 with 0.53 mm id column, 3 minutes for the DynaWaters/Dynatrap systems, and no dry purge for instruments with DB-624 0.32 mm id columns. The purge and trap will step to desorb ready. When the GC is ready at 30°C (50°C for instruments with DB-624 0.32 mm id columns), the purge and trap will step to desorb. The desorb mode (2 minutes) will begin the gas chromatographic temperature program and GC data acquisition. Concurrently, the trapped materials are introduced to the gas chromatographic column by rapidly heating the trap to 180°C (245°C for instruments with DB-624 0.32 mm id columns) and back flushing the trap with Helium between 20 and 60 mL/min for 2 minutes. The sparge tube is also drained at this time. See Table R for instrument specific purge parameters.

12.15 After the sample has been desorbed and steps into the bake mode, the vial autosampler will automatically flush the sparge tube, plumbing lines and sample syringe 3-5 times between samples. This cleans the plumbing lines, sample syringe and sparge tube.

12.16 After desorbing the sample, the purge and trap also steps into the bake mode. This reconditions the trap. During bake, the trap temperature will be brought to 180-270°C (depending on the system used), while being flushed with helium. The bake cycle is for 7- 10 minutes (depending on the system used). After bake, the trap cools, and then the next sample is introduced. Vial autosamplers will continue to cycle through the programmed auto-sampler position.

12.17 If the initial analysis of a sample or a dilution of the sample has a concentration of analytes that exceeds the initial calibration range, the sample must be reanalyzed at a higher dilution. Monitor carry-over by carefully looking at the sample (or samples) immediately following a high range sample. If carryover is suspected, blanks may be run and the sample(s) in question should be reanalyzed if needed.

12.18 Samples that are diluted higher than the normal dilution (x1 for waters and low level soils and x50 for medium level MeOH soils) will require a value near the upper half of the calibration curve. However, since a large portion of our work is done analyzing Total Petroleum Hydrocarbons (TPH) and due to MDL reporting, Aromatic compound water samples will be reported if the response of one of the Aromatics or the TPH value from the FID is in the upper half of the curve. Since samples are screened, the TPH midpoint is used as guidance. The midpoint will be 700 µg/L for gasoline samples (30 % less than the midpoint of our calibration curve), and 500 µg/L for diesel contaminated samples. Aromatics will be at 70 µg/L for the midpoint of the curve.

12.19 Medium level methanol extraction for Soil/Sediment: This procedure is based on extracting the solid/sediment/soil with methanol. An aliquot of the extract is added to reagent water and purged at the conditions previously described.

12.20 Low level soils or solids are weighed out at 5 g and put in 5 mL of water with a disposable stir bar. Samples collected in the field in VOA vials and received in Encore Samplers will have to have the weight determined. The weight and volume will need to be corrected in LIMS to account for the discrepancies.

12.21 For the preparation of samples please refer to the most current version of GB-O-005, *Soil/Semisolid Sample Preparation for the Analysis of Gasoline Range Organics and Petroleum Volatile Organics by Wisconsin Modified GRO.*

12.22 Calculations:

12.22.1 The concentration of compounds in the sample is determined from a linear regression curve to develop average response factors (RF) using the Internal Standard calculation technique. The RF is the slope of the linear regression line using the response ratio (y) and the amount ratio (x) and the origin.

The response ratio is calculated as follows:

Sp ratio = (a / b) / c

Where:

a = average of the responses of the internal standard in the calibration curve level 1
b = average of the responses of the compound/surrogate in the calibration curve level 1
c = concentration of the internal standard in ppb

12.22.2 The amount ratio is calculated as follows:

Amt ratio = D/E

Where:

D = concentration of the compound/surrogate level 1
E = concentration of the internal standard (in the same curve point as "D")

A linear regression model is developed using the amount and response ratios from above with the origin point (0, 0)

NOTE: Linearity through zero is a statistical assumption and not a rationale for reporting results below the calibration range demonstration by the analysis of the calibration standards.

12.22.3 Calculate the concentration of each identified analyte in the sample as follows:

Aqueous samples concentration (µg/L) =

$$\frac{(A_{(x)} / A_{(is)})}{RF} * C_{(is)} * DF$$

where:

$A_{(x)}$ = Area of the compound being measured.
$A_{(is)}$= Area of the internal standard.
RF = Response factor for compound being measured
DF = Dilution Factor of the sample
$C_{(is)}$ = Concentration of the Internal Standard

Sediment/Soil and Sludge samples concentration (µg/kg) =

$$\frac{(A_{(x)} / A_{(is)}) * C_{(is)} * DF}{RF * \%D_{(TS)}}$$

where:

$A_{(x)}$ = Area of the compound being measured.
$A_{(is)}$= Area of the internal standard.
RF = Response factor for compound being measured
DF = Dilution Factor of the sample calculated as:
(Volume of extract in mL / weight of sample in grams)
%D = % dry weight of sample/100, or 1 for a wet-weight basis.

12.22.4 Peak areas measured from blanks may not be subtracted from sample peak areas.

13. Quality Control

13.1 Quality control procedures are taken to ensure the proper production and operation in all of the various sample preparation and/or sample introduction techniques. The laboratory must also maintain records to document the quality of the data generated.

13.2 Reference samples are purchased from a NIST certified vendor. Results of these studies are made available to analysts, management and accrediting authorities.

13.3 Retention time windows are crucial to the identification of target compounds. Retention time windows are established to compensate for minor shifts that occur as a result of sample loading and normal chromatographic variability. Establishment of the width of this window is of considerable importance. A window that is "tight" may lead to the reporting of both false negative and false positive results. Re-analysis occurs in this situation due to the non-identification of surrogate and spike components in the analysis. "Wide" retention times lead to false positive results that cannot be confirmed upon re-analysis.

13.4 Before establishing retention time windows, make sure that the chromatographic system is operating reliably and that the system conditions have been optimized for the target analytes and surrogates in the sample matrix to be analyzed. Make three injections of all single component standard mixtures over the course of a 72-hour period.

13.5 Record the retention time for each single component analyte and surrogate to three decimal places (e.g., 0.007). Calculate the mean and standard deviation of the three absolute retention times for each single component analyte and surrogate.

13.6 If the standard deviation of the retention times for a target compound is much smaller than the default deviation (i.e., no difference between the absolute retention times), then the laboratory may use a default standard deviation of 0.1 minutes for the 0.53 mm id column, and 0.06 minutes for the 0.32 mm id column.

13.7 Pace has in place procedures for documenting the effect of the matrix on method performance (precision and accuracy). Development of limits is done by randomly choosing points by matrix from the previous year. When new compounds are added for analysis, default limits are utilized until new limits can be established. The average percent recovery (p) and standard deviation (s) are calculated and the upper and lower warning and control limits are established by the following equations:

Warning Limits-

Upper Warning Limit (UWL) = p+2s
Lower Warning Limit (LWL) = p-2s

Control Limits-

Upper Control Limit (UCL) = p+3s
Lower Control Limit (LCL) = p-3s

Relative Percent Difference Limits -

%RPD = p'+3s'

where:

p = is the average relative percent difference
s = is the standard deviation of the relative percent difference.

NOTE: If %RPD control limits are calculated to be below 10%, the limit for that individual compound will be set at 10%. This limit allows for assessment of the data without compromising the known quality in a production setting. Most samples received are not for research.

13.8 Continuous charting for precision and accuracy is done. Limits are set yearly for Lab Control Spikes (LCS) and Matrix Spikes (MS) and surrogates.

13.9 Surrogate recoveries - The laboratory must evaluate surrogate recovery data from individual samples against the surrogate control limits developed by the laboratory. Development of limits is done by randomly choosing a minimum of 20 points by matrix from the previous year. The average percent recovery (p) and standard deviation (s) are calculated and the upper and lower control limits are established by the following equations:

Control Limits-

Upper Control Limit (UCL) = p+3s
Lower Control Limit (LCL) = p-3s

NOTE: Remember that even for a 95% confidence interval, 1 out of every 20 observations is likely to fall outside of the control limits established.

13.10 For each analytical batch, not to exceed 20 environmental samples, a method blank, matrix spike and matrix spike duplicate must be analyzed (the frequency of the spikes may be different for different monitoring programs but no less than 1 per 20 samples). The blank and spiked samples must be carried through all stages of the sample preparation and measurement steps. (This can be superseded by Accrediting or Project Specific Requirements.) A matrix spike and matrix spike duplicate will be analyzed provided the client has submitted enough sample.

13.11 A Lab Control Spike (LCS) and Duplicate (LCSD) pair is also included with each analytical batch. The pair consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. The pair is spiked with the same analytes at the same concentrations as the matrix spike. When the results of the matrix spike analysis indicate a potential problem due to the sample matrix itself, these results are used to verify that the instrument was in control.

13.12 See Appendix A Table H for a summary of frequency by method citation.

13.13 When results of sample spikes indicate atypical method performance, if possible the sample is reanalyzed to confirm matrix interferences.

NOTE: Remember that even for a 95% confidence interval, 1 out of every 20 observations is likely to fall outside of the control limits established.

13.14 See Appendix A Tables listed below for limit summaries:

Surrogate Limits	Table J2
Matrix Spike Limits	Table J
Lab Control Spike	Table J1

13.15 See Appendix A Tables listed below for summaries of review and corrective actions:

Analyst/Technician Data Assessment	Table K
Analyst/Supervisor Data Assessment	Table L
Report Reviewer/Project Management Data Assessment	Table M
Corrective Actions	Table N
Contingencies for Out of Control Data	Table O

13.16 Before processing any samples, the analyst shall demonstrate, through the analysis of a method blank, that interferences from the analytical system, glassware, and reagents are under control. Each time a set of samples is analyzed or there is a change in reagents, a method blank shall be analyzed as a safeguard against chronic laboratory contamination. The blanks shall be carried through all stages of sample preparation and measurement.

13.17 The calibration shall be verified at a frequency of every 10 analytical samples (not to exceed a 12 hour period) with the analysis of a Calibration Verification Standard (CVS). A sequence will begin with the analysis of a CVS followed by a blank. CVSs will be analyzed at the end of a set of samples and the end of a sequence. Changing of a trap is not considered a major change and may not require the system to be recalibrated.

13.18 A Lab Control Spike and Duplicate (LCS/D) should be analyzed for each analyte using the same sample preparations, analytical methods and QA/QC procedures employed for the test samples. One LCS/D pair should be prepared and analyzed for each sample batch at a frequency of one LCS/D pair for each 20 samples or less for SW846 citations and one LCS/D pair for each 10 samples or less for EPA citations. Limits are attained from the cited method references, until established by the lab where method citations allow.

13.19 Documenting the effect of the matrix shall include the analysis of at least one matrix spike/matrix spike duplicate pair. The sample used for the MS/D pair is either determined by the client or selected at random from client samples, as sample volume allows. One MS/D pair should be prepared and analyzed for each sample batch at a frequency of one MS/D pair for each 20 samples or less for SW846 citations and one MS/D pair for each 10 samples or less for EPA citations. In-house laboratory limits are developed from samples analyzed during the previous year. A minimum of 40 spike samples' recoveries, 10 from each of the previous years four quarters will represent the data pool. The laboratory must evaluate surrogate recovery data from individual samples. Limits are established the same as matrix spikes described above. All samples prepared and analyzed by this method are spiked with surrogate standard. All quality control data should be maintained and be available for easy reference or inspection.

13.20 See Appendix A Table H for a summary.

14. Method Performance

14.1 There are several requirements that must be met to insure that this procedure generates accurate and reliable data. A general outline of requirements has been summarized below. Further specifications may be found in the Laboratory Quality Manual.

14.1.1 The analyst must read and understand this procedure with written documentation maintained in his/her training file.

14.1.2 An initial demonstration of capability (IDOC) must be performed per ALL-Q-020, *Training Procedures*. A record of the IDOC will be maintained in his/her QA file with written authorization from the Laboratory Manager and Quality Manager.

14.1.3 An annual method detection limit (MDL) study will be completed per ALL-Q-004, *Method Detection Limit Studies*, for this method and whenever there is a major change in personnel or equipment. The results of these studies are retained in the quality assurance office.

14.1.4 Periodic performance evaluation (PE) samples are analyzed per ALL-Q-010, *Proficiency Testing Program*, to demonstrate continuing competence. All results are stored in the QA office.

15. Pollution Prevention and Waste Management

15.1 The quantity of chemicals purchased is based on expected usage during its shelf life and disposal cost of unused material. Actual reagent preparation volumes reflect anticipated usage and reagent stability.

15.2 Excess reagents, samples and method process wastes are characterized and disposed of in an acceptable manner. For further information on waste management consult the current version of ALL-S-002, *Waste Handling*.

16. Data Assessment and Acceptance Criteria for Quality Control Measures:

16.1 At a minimum there are three levels of data review:

16.2 Analyst/Technician verification at the bench top are looking at instrument performance as it relates to initial calibration, calibration verification, cleanliness.

16.3 Supervisor/Analyst verification after analysis are looking for sample concentration versus linear range of the instrument, typical patterns resulting from the compounds or elements in question, and quality control measure criteria. Data is either accepted without qualification, accepted with qualification, or rejected with samples reprocessed.

16.4 Report Reviewer/Project Management personnel look at the presentation of the data on final reports. The reports are verified for holding time compliance, receipt conditions, method citation and reasonableness, which may include field duplicate analysis, analytical comments and qualifications presented by the previous reviews, and comparing results of similar analytical techniques as it relates to the project site information when available.

16.5 A fourth level of review , data validation is determined from a project or program scope of laboratory services and encompasses the generation Quality Control summaries in the media of "Form Generation."

16.6 See the following Tables in Appendix A for a summary:

Analyst/Technician	Table K
Supervisor/Analyst	Table L
Report Reviewer/Project Management	Table M

17. Corrective Actions for Out-of-Control Data

17.1 Assessment of Quality Control measures is done to provide a level of confidence in the data generated. The measures provide documentation that the instrument conditions were reliable during the analysis.

17.2 See Table N for corrective actions taken in cases where statistical goals were not achieved.

18. Contingencies for Handling Out-of-Control or Unacceptable Data

18.1 During analysis, events occur specific to the physical and chemical characteristics of the environmental sample. When possible, with received sample volumes, data generated along with measures that do not meet statistical goals are re-analyzed again to see if the statistical goal can be achieved. When environmental samples do not meet statistical goals, unacceptable data is generated. These events are different from those pertaining to instrument operating conditions. These events occur when the instruments are operating under ideal conditions.

18.2 The tables list routine assessment and not those specific to a project/program where data validation is determined from a project or program scope of laboratory services and encompasses the generation Quality Control summaries in the media of "Form Generation",

18.3 Contingencies for handling sample out-of-control quality control assessments are found in Table O.

19. References

Method SW846 8000B, December 1996
Method SW486 8021B, December 1996
EPA 602, EPA_600_4_79_020_March 1983
GB-O-005, *Soil/Semisolid Sample Preparation for the Analysis of Gasoline Range Organics and Petroleum Volatile Organics by Wisconsin Modified GRO.*
GB-O-010, *Aqueous Sample Preparation for the Analysis of Gas Range Organics and Petroleum Volatile Organics.*
GB-O-009, *Aromatic Volatiles by Gas chromatography Using Photoionization Detectors.*

20. Tables, Diagrams, Flowcharts, Appendices, Addenda etc.

Table A
REPORTING LIMITS - 2003

COMPOUND NAME Effective Date: 3-1-2004	Aqueous		Low Level Solids		Medium Level Solids *	
	Units µg/L		Units µg/kg		Units µg/kg	
	MDL	EQL	MDL	EQL	MDL	EQL
MTBE	0.36084	1.0	0.48754	5.0	4.4	50
BENZENE	0.13786	1.0	0.55588	5.0	2.7	20
TOLUENE	0.35737	1.0	0.56980	5.0	6.0	50
ETHYLBENZENE	0.40127	1.0	0.56106	5.0	3.5	50
M/P-XYLENE	0.74127	2.0	1.1432	10	3.7	100
O-XYLENE	0.35855	1.0	0.52865	5.0	2.2	50
1,3,5-TRIMETHYLBENZENE	0.39537	1.0	0.63962	5.0	4.8	50
1,2,4-TRIMETHYLBENZENE	0.39160	1.0	0.54100	5.0	4.2	50
NAPHTHALENE	0.46679	1.0	0.32096	5.0	3.6	50

* EQL for Wisconsin = 25 µg/kg for all analytes with the exception of m/p-Xylene, which is 50 µg/kg

Table B
REQUIRED SAFETY EQUIPMENT

Item:	Safety Apparel Description	Mandatory for Procedure	Optional
1	Safety Goggles or Glasses	x	
2	Lab Coat		x
3	Gloves		x
4	Face Shield		x

Table C
EQUIPMENT

Equipment	Manufacturer	Model(s)	Serial #	Date In Service
GRO # 1	Hewlett Packard	5890A Series II	3310A48054	3/92
GRO # 2	Hewlett Packard	5890A Series II	3140A39241	6/93
GRO # 3	Hewlett Packard	5890A Series II	3203A40701	6/93
GRO # 4	Hewlett Packard	5890A Series II	3336A57281	4/95
GRO # 5	Hewlett Packard	5890A Series II	3310A47921	7/95
GRO # 6	Hewlett Packard	5890A Series II	3336A61359	2/96
GRO # 7	Hewlett Packard	5890A Series II	2950A28043	10/02
P&T # 1	Tekmar	Tekmar 3000	94005013	6/02
P&T # 2	Tekmar	Tekmar 3000	94067018	1/04
P&T # 3	Tekmar	Tekmar 3000	95296017	4/95
P&T # 4	Tekmar	Tekmar 3000	99042009	6/00
P&T # 5	Tekmar	Tekmar 3000	95198009	9/00
P&T # 6	Tekmar	Tekmar 3000	94005013	9/03
P&T # 7	Dyna Tech	Dynatrap	11192-593	10/02
Autosampler # 1	DynaTech	Archon 5100A	11911-496A	6/02
Autosampler # 2	DynaTech	Archon 5100A	11950-696A	5/95
Autosampler # 3	Varian	Archon	12561	12/98
Autosampler # 4	DynaTech	Archon 5100A	11930-596A	4/03
Autosampler # 5	Varian	Archon	13300	9/00
Autosampler # 6	DynaTech	PTA-30 W/S	11717-395	4/03
Autosampler # 7	DynaTech	Dynatrap	11192-593	10/02

Table D
SUPPLIES

Supplies	Manufacturer	Vendor	Catalog #
Syringes			
10µL Gastight 1701	Hamilton	Fisher Scientific	14-815-1
25µL Gastight 1702	Hamilton	Fisher Scientific	14-815-29
50µL Gastight 1705	Hamilton	Fisher Scientific	14-824-30
100µL Gastight 1710	Hamilton	Fisher Scientific	13-684-100
250µL Gastight 1725	Hamilton	Fisher Scientific	13-684-102
500µL Gastight 1750	Hamilton	Fisher Scientific	13-684-106
1mL Gastight 1001	Hamilton	Fisher Scientific	14-824-25
5mL Gastight 1005	Hamilton	Fisher Scientific	13-684-96
50mL Gastight 1050	Hamilton	Fisher Scientific	14-815-195
Columns			
DB-624 Capillary column, 30 m x 0.53 mm id x 3 µm film	J&W Scientific	VWR Scientific	125-1334
DB-624 Capillary column, 30 m x 0.32 mm id x 1.8 µm film	J&W Scientific	VWR Scientific	123-1334
Traps			
Purge Trap A DynaTech	Supelco	Supelco	21075-U
Purge Trap A for Tekmar 3000 Concentrator	Supelco	Supelco	24910-U
Purge Trap K for Tekmar 3000 Concentrator	Supelco	Supelco	24920-U
Sparge Tubes			
Fritless 5-mL Sparge Tube	Supelco	Supelco	22780
Septa			
IceBlue Septa, 11mm	Restek	Restek	22392
Ferrules			
0.8mmVespel/Graphite ferrules	Restek	Restek	20213
1/16" x 0.5mm id Vespel/Graphite ferrules	Restek	Restek	20231
Sample Vessels and Stir Bars			
Stir Bar	Fisher Brand	Fisher Brand	14-511-60A
2 oz. jars	QEC	QEC	2114-0002
40 mL VOA vials	QEC	QEC	3112-40HCL
40 mL VOA vials	QEC	QEC	3112-40mL
10 mL volumetric	Kimax Brand	Fisher Scientific	10-212AA
25 mL volumetric	Kimax Brand	Fisher Scientific	10-212BB
50 mL volumetric	Kimax Brand	Fisher Scientific	10-212A
100 mL volumetric	Kimax Brand	Fisher Scientific	10-212B
200 mL volumetric	Kimax Brand	Fisher Scientific	10-212C
500 mL volumetric	Kimax Brand	Fisher Scientific	10-218D
1.8 mL amber vials & caps	Restek	Restek	24637

Table D - Continued
SUPPLIES

Supplies	Manufacturer	Vendor	Catalog #
Volumetric Devices			
Pasteur Pipettes	Fisher Scientific	Fisher Scientific	13-678-20A
Spatula with spoon	Fisher Scientific	Fisher Scientific	14-375-10
Pipette bulb	Fisher Scientific	Fisher Scientific	14-065B
0.1-2.5 mL Repipettor	Brinkmann	Fisher Scientific	13-688-130
1-5 mL Repipettor	Brinkmann	Fisher Scientific	13-688-131
2-10 mL Repipettor	Brinkmann	Fisher Scientific	13-688-133
5-25 mL Repipettor	Brinkmann	Fisher Scientific	13-688-134
10 mL graduate cylinder	Kimex Brand	Fisher Scientific	08-554B "to deliver"
10 mL pipette "to deliver" (TD)	Kimex Brand	Kimex Brand	13-6644G
pH Indicator Paper		School Masters Science	46809W2

Table E
REAGENTS

Reagent	Purity	Concentration	Manufacturer	Vendor	Catalog #
WISC PVOC/GRO MIX	99 %	1000 µg/mL each PVOC	Restek Corp.	Restek Corp	30095
WISC PVOC/GRO MIX	99 %	1000 µg/mL each PVOC	Supelco	Supelco	4-8167
Fluorobenzene (IS)	99.9 %	20 mg/mL	AccuStandard Inc.	AccuStandard Inc.	M-524-IS-2-10X
α,α,α–Trifluorotoluene (SS), (TFT)	99.4 %	20 mg/mL	AccuStandard Inc.	AccuStandard Inc.	M-602-Ss-100X
Ottawa Sand Standard	ASTM C-190 and Method T-132	20-30 Mesh	Fisher Scientific	Fisher Scientific	S23-3
Methanol	Purge & Trap Grade		Burdick & Jackson	Burdick & Jackson	232-1
Sodium Bisulfate	Certified Grade	---	Fisher Scientific	Fisher	S-240-3
Reverse Osmosis Water (ROW)	Organic Free	---	Flowmatic	Water Care	

Table F
STANDARDS

Standard	Acronym	Concentration	Direction found in Section:	Alias
Aqueous / WI Modified MeOH				
Level 1 Calibration Standard (water)	CAL STD	1.0 ppb	Table P	Level 1
Level 2 Calibration Standard (water)	CAL STD	5.0 ppb	Table P	Level 2
Level 3 Calibration Standard (water)	CAL STD	10 ppb	Table P	Level 3
Level 4 Calibration Standard (water)	CAL STD	20 ppb	Table P	Level 4
Level 5 Calibration Standard (water)	CAL STD	50 ppb	Table P	Level 5
Level 6 Calibration Standard (water)	CAL STD	200 ppb	Table P	Level 6
Level 7 Calibration standard (water)	CAL STD	500 ppb or 300ppb*	Table P	Level 7
PVOC Intermediate (Verification)	100 ppm GRO	10 ppm each PVOC	Table P	
PVOC Intermediate (Curve)	100 ppm GRO Curve std.	10 ppm each PVOC	Table P	
Internal Standard and Surrogate Standard Mix	IS/SS	100 ppm each compound	Table P	
Calibration Verification Standard (Water)	CVS	20 ppb each PVOC	Table P	Check, CCV
Lab Control Spikes (Water)	LCS/LCSD	20 ppb each PVOC	Table P	
Lab Control Spikes (Wisconsin MeOH)	LCS/LCSD	20 ppb each PVOC	Table P	
Matrix Spikes (Water)	MS/MSD	20 ppb each PVOC	Table P	

* Instrument specific criteria due to linearity capability.

Table F - Continued

STANDARDS

Standard	Acronym	Concentration	Direction found in Section:	Alias
Low Level Solids				
Level 1 Calibration Standard (Low Level)	CAL STD	5.0 ppb	Table P	Level 1
Level 2 Calibration Standard (Low Level)	CAL STD	10 ppb	Table P	Level 2
Level 3 Calibration Standard (Low Level)	CAL STD	20 ppb	Table P	Level 3
Level 4 Calibration Standard (Low Level)	CAL STD	50 ppb	Table P	Level 4
Level 5 Calibration Standard (Low Level)	CAL STD	200 ppb	Table P	Level 5
Level 6 Calibration Standard (Low Level)	CAL STD	500 ppb	Table P	Level 6
PVOC Intermediate (Verification)	100 ppm GRO	10 ppm each PVOC	Table P	
PVOC/ α,α,α–Trifluorotoluene mixed Curve Intermediate std.	100 ppm GRO Curve/10 ppm SS Mix	10 ppm each PVOC + 10 ppm α,α,α–Trifluorotoluene	Table P	
Internal Standard and Surrogate Standard Mix	IS/SS	100 ppm each compound	Table P	
Internal Standard Only	IS Only	100 ppm	Table P	
Surrogate Spike Solution	1000 ppm SS	1000 ppm	Table P	
Calibration Verification Standard (Low Level)	CVS	50 ppb each PVOC	Table P	
Lab Control Spikes (Low Level)	LCS/LCSD	50 ppb each PVOC	Table P	
Matrix Spikes (Low Level)	MS/MSD	50 ppb each PVOC	Table P	

Table F – Continued

STANDARDS

Standard	Acronym	Concentration	Direction found in Section:	Alias
Medium Level Solid				
Level 1 Calibration Standard (MeOH)	CAL STD	0.4 ppb	Table P	Level 1
Level 2 Calibration Standard (MeOH)	CAL STD	1.0 ppb	Table P	Level 2
Level 3 Calibration Standard (MeOH)	CAL STD	5.0 ppb	Table P	Level 3
Level 4 Calibration Standard (MeOH)	CAL STD	10 ppb	Table P	Level 4
Level 5 Calibration Standard (MeOH)	CAL STD	20 ppb	Table P	Level 5
Level 6 Calibration Standard (MeOH)	CAL STD	50 ppb	Table P	Level 6
Level 7 Calibration Standard (MeOH)	CAL STD	200 ppb	Table P	Level 7
Level 8 Calibration Standard (MeOH)	CAL STD	500 ppb	Table P	Level 8
PVOC Intermediate (Verification)	100 ppm GRO	10 ppm each PVOC	Table P	
PVOC/ α,α,α–Trifluorotoluene mixed Curve Intermediate std.	100 ppm GRO Curve/10 ppm SS Mix	10 ppm each PVOC + 10 ppm α,α,α–Trifluorotoluene	Table P	
Internal Standard Only	IS Only	100 ppm	Table P	
Surrogate Spike Solution	100 ppm SS	100 ppm	Table P	
Surrogate Spike Solution	2500 ppm SS	2500 ppm	Table P	
Surrogate Spike Solution	1000 ppm SS	1000 ppm	Table P	
Calibration Verification Standard (MeOH)	CVSBTX	50 ppb each PVOC, 50 ppb Surrogate Std.	Table P	Surrogated BTEX Check
Lab Control Spikes (MeOH)	LCS/LCSD	20 ppb each PVOC, 50 ppb Surrogate Std (both on column after x50 dilution)	Table P	
Matrix Spikes (MeOH)	MS/MSD	20 ppb each PVOC, 50 ppb Surrogate Std (both on column after x50 dilution)	Table P	

Table G
SAMPLE COLLECTION, PRESERVATION, SHIPMENT AND STORAGE

Matrix	Prep Method	Container(s)	Preservation	Shipment Conditions	Lab Storage Conditions
Aqueous	SW846 5030B	40 mL VOC Vials (3)	0.5 mL of 1:1 HCl	On ice 4+/- 2° Celsius	Refrigerate 4+/- 2° Celsius
Solid	SW846 5035A	Encore samplers (two 5 gram samplers and one 25 gram sampler) or 40 mL unpreserved VOC vial	1 Effervescence 2 Non Effervescence 3 Screen > 200 ppb	On ice 4+/- 2° Celsius	Refrigerate 4+/- 2° Celsius
Solid	SW846 5030B	4 oz ZH packed tight or 40 mL VOC vial	Water and/or MeOH	On ice 4+/- 2° Celsius	Refrigerate 4+/- 2° Celsius

1 - If sample exhibits effervescence, then 5 mL RO WATER.
2 - Non-effervescence = 5 mL RO WATER containing 1 g Sodium Bisulfate.
3 – Preserve with methanol

Table H
QUALITY CONTROL

Preparation Method ⇨ Quality Control Measure ⇩	SW846 5030	SW846 5030B	SW846 5035	EPA 601/602	WI Modified Waters	WI Modified Soils
Initial Calibration	Minimum of five levels; lowest level near but above MDL	Minimum of five levels; lowest level near but above MDL	Minimum of five levels; lowest level at the EQL	Minimum of five levels; lowest level near but above MDL	Minimum of five levels; lowest level near but above MDL	Minimum of five levels; lowest level near but above MDL
Method Blank	One per batch of samples, up to 20 environmental samples, whichever is more frequent.	One per batch of samples, up to 20 environmental samples, whichever is more frequent.	One per batch of samples, up to 20 environmental samples, whichever is more frequent.	One per batch of samples, up to 10 environmental samples, whichever is more frequent.	One per batch of samples, up to 20 environmental samples, whichever is more frequent.	One per batch of samples, up to 20 environmental samples, whichever is more frequent.
Calibration Verification Standard (CVS)	1 CVS at the beginning of an analytical sequence and 1 CVS per 10 analytical samples not to exceed a 12 hour time clock. The analytical sequence should end with a CVS. A batch of 20 samples should end with a CVS.	1 CVS at the beginning of an analytical sequence and 1 CVS per 10 analytical samples not to exceed a 12 hour time clock. The analytical sequence should end with a CVS. A batch of 20 samples should end with a CVS	1 CVS at the beginning of an analytical sequence and 1 CVS per 10 analytical samples not to exceed a 12 hour time clock. The analytical sequence should end with a CVS. A batch of 20 samples should end with a CVS	1 CVS at the beginning of an analytical sequence and 1 CVS per 10 analytical samples not to exceed a 12 hour time clock. The analytical sequence should end with a CVS. A batch of 20 samples should end with a CVS	1 CVS at the beginning of an analytical sequence and 1 CVS per 10 analytical samples not to exceed a 12 hour time clock. The analytical sequence should end with a CVS. A batch of 20 samples should end with a CVS	1 CVS at the beginning of an analytical sequence and 1 CVS per 10 analytical samples not to exceed a 12 hour time clock. The analytical sequence should end with a CVS. A batch of 20 samples should end with a CVS

Table H- Continued
QUALITY CONTROL

Preparation Method ⇨ Quality Control Measure ⇩	SW846 5030	SW846 5030B	SW846 5035	EPA 601/602	WI Modified Waters	WI Modified Soils
Independent Calibration Verification	The initial calibration curve is made from Supelco provided stock standards which is verified with Restek provided stock standards.	The initial calibration curve is made from Supelco provided stock standards which is verified with Restek provided stock standards.	The initial calibration curve is made from Supelco provided stock standards which is verified with Restek provided stock standards.	The initial calibration curve is made from Supelco provided stock standards which is verified with Restek provided stock standards.	The initial calibration curve is made from Supelco provided stock standards which is verified with Restek provided stock standards.	The initial calibration curve is made from Supelco provided stock standards which is verified with Restek provided stock standards.
Lab Control Spike and Duplicate	One pair per batch of samples, up to 20 environmental samples, whichever is more frequent.	One pair per batch of samples, up to 20 environmental samples, whichever is more frequent.	One pair per batch of samples, up to 20 environmental samples, whichever is more frequent.	One pair per batch of samples, up to 10 environmental samples, whichever is more frequent.	One pair per batch of samples, up to 20 environmental samples, whichever is more frequent.	One pair per batch of samples, up to 20 environmental samples, whichever is more frequent.
Matrix Spike and Duplicate	One pair per batch of samples, up to 20 environmental samples, whichever is more frequent.	One pair per batch of samples, up to 20 environmental samples, whichever is more frequent.	One pair per batch of samples, up to 20 environmental samples, whichever is more frequent.	One pair per batch of samples, up to 10 environmental samples, whichever is more frequent.	One pair per batch of samples, up to 20 environmental samples, whichever is more frequent.	Not Applicable
Internal Standards	Added to every sample.	Added to every sample.	Added to every sample.	Added to every sample.	Added to every sample.	Added to every sample.
Surrogate Standards	Added to every sample.	Added to every sample.	Added to every sample.	Added to every sample.	Added to every sample.	Added to every sample.

Table I
CALIBRATION AND STANDARDIZATION

Analytical Method Acceptance Criteria⇨ Calibration Measure ⇩	**Frequency**	**Acceptance Criteria**
Initial Calibration	• Installation of new column • Installation of new FID or jet • Creation of new analytical method • CVS fails criteria	• % RSD ≤ 15% for every compound • Use of Average Response factors if: % RSD is ≤ 15% for any reportable compounds Otherwise, use Linear Regression and Correlation Coefficient is > 0.9900. • EPA 602 - % RSD ≤ 10 % for every compound. • EPA 602 - Use of Average Response factors if: % RSD is ≤ 10% for any reportable compounds Otherwise, use Linear Regression and Correlation Coefficient is > 0.9900.
Independent Calibration Verification Standard	• Same as CVS See Table H	• RF of CVS must be ≤ 15% difference from initial calibration.
Continuing Calibration Verification Standard (CVS)	• See Table H	• RF of CVS must be ≤ 15% difference from initial calibration.
Lab Control Spike and Duplicate	• One pair per batch of samples, up to 20 environmental samples, whichever is more frequent.*	• See Table J1 under Lab Control Spike Recovery Limits
Matrix Spike and Duplicate	• One pair per batch of samples, up to 20 environmental samples, whichever is more frequent.*	• See Table J under Matrix Spike Recovery Limits

* EPA Method 602 requires one pair per batch of 10 samples.

Table I - Continued
CALIBRATION AND STANDARDIZATION

Analytical Method Acceptance Criteria⇨ Calibration Measure ⇩	**Frequency**	**Acceptance Criteria**
Internal Standards	• Added to every sample.	• Retention times monitored from the first CVS IS retention time. • Internal Standard area limits established from the area of the first CVS starting a sequence or method. Limit is 50%-100%
Surrogate Standards	• Added to every sample.	• In house limits determined. See Table J2 under Surrogate recovery Limits

Table J
Matrix Spike Recovery Limits

Preparation Method ⇨ Effective Date:05/17/2004	Aqueous Preps			Extractable Soil Preps[a]			Low Level Soil Preps		
Matrix Spike Recovery Parameters ⇩	LCL	UCL	RPD	LCL	UCL	RPD	LCL	UCL	RPD
Methyl Tert-butyl ether	79	120	20	67	113	20	72	131	30
Benzene	80	120	20	67	112	20	64	132	30
Toluene	80	120	20	67	108	20	72	126	30
Ethylbenzene	80	120	20	70	109	20	68	128	30
M/P-Xylene	78	124	20	69	109	20	59	136	30
O-Xylene	80	120	20	69	111	20	60	132	30
1,3,5-Trimethylbenzene	71	124	20	63	113	20	-	-	-
1,2,4-Trimethylbenzene	72	123	20	57	113	20	-	-	-
Naphthalene	72	123	20	49	117	20	-	-	-
Xylene – Total	78	124	20	69	111	20	59	136	30

a – The WI Modified GRO method omits the use of matrix spikes, however, it does rely on a Lab Control Spike pair to determine extraction efficiency, accuracy and precision.

Table J1
Lab Control Spike Recovery Limits

Preparation Method ⇨ Effective Date:05/17/2004	Aqueous Preps[b]			Extractable Soil Preps[b]			Low Level Soil Preps			Carbon Tubes		
Lab Control Spike Recovery Parameters ⇩	LCL	UCL	RPD	LCL	UCL	RPD	LCL	UCL	RPD	LCL	UCL	RPD
Methyl Tert-butyl ether	82	116	20	84	116	20	83	123	20	71	119	20
Benzene	85	115	20	85	115	20	85	115	20	81	113	20
Toluene	85	115	20	85	117	20	85	117	20	75	107	20
Ethylbenzene	85	115	20	85	118	20	85	119	20	77	106	20
M/P-Xylene	85	115	20	85	119	20	85	117	20	63	92	20
O-Xylene	85	115	20	85	119	20	85	119	20	57	95	20
1,3,5-Trimethylbenzene	83	115	20	85	123	20	-	-	-	50	150	50
1,2,4-Trimethylbenzene	82	115	20	85	122	20	-	-	-	50	150	50
Naphthalene	75	120	20	82	125	20	-	-	-	50	150	50
Xylene – Total	85	115	20	85	119	20	85	119	20			

'b – The WI Modified GRO method allows 80-120% Recovery in a LCS for all PVOCNAP compounds.

Table J2
Surrogate Standard Recovery Limits

Preparation Method ⇨ Effective Date: 07/01/2002	SW846 5030 Soils		SW846 5030B		SW846 5035		WI Modified Waters		WI Modified Soils		EPA 602	
Surrogate Spike Recovery Parameters ⇩	LCL	UCL	LCL	UCL	LCL	UCL	LCL	UCL	LCL	UCL	LCL	UCL
α,α,α–Trifluorotoluene	69	146	80	124	65	139	80	124	80	119	85	115

Table K
ANALYST/TECHNICIAN DATA ASSESSMENT

Analytical Method Acceptance Criteria⇨ Data Assessment Measure ⇩	Method Citation SW If these conditions are not achieved ⇒	Method Citation EPA If these conditions are not achieved ⇒
Initial Calibration	• 1	• 1
Initial Calibration Verification	• 1	• 1
Calibration Blank	• 1	• 1
Method Blank	• 2	• 2
Internal Standard Area	• 3	• 3
Continuing Calibration Verifications	• 4	• 4
Surrogate Recovery	• 5	• 5
Accuracy & Precision Laboratory Control Spikes	• 6	• 6
Accuracy & Precision Matrix Spikes	• 7	• 7

1. Check instrumentation/equipment condition; enter maintenance in instrument log; perform another initial calibration. No data can be reported. Generate on Non-Conformance Memo.

2. In the absence of project specific requirements, sample detects greater than 20 times the method blank contamination level are reported with those not exceeding 20 times re-analyzed or qualified. Values less than the MDL (or EQL when reporting to the EQL) are reported. Generate on Non-Conformance Memo.

3. In the absence of project specific requirements, check to be sure that there are no errors in the calculations. If errors are found, recalculate the data accordingly. Examine chromatograms for interfering peaks and integrated peak areas. Re analyze sample if volume allows. Generate on Non-Conformance Memo.

4. In the absence of project specific requirements, where the recovery of individual compounds is greater than +/- 15% in the CVS, the compound may be reported if the average recovery in the CVS of all the calibrated compounds is -/+ 15% and all compound recoveries are within 70 to 130 %. Generate on Non-Conformance Memo.

5. In the absence of project specific requirements, check to be sure that there are no errors in the calculations. If errors are found, recalculate the data accordingly. Examine chromatograms for interfering peaks and integrated peak areas. If the program allows report the concentrations noting the surrogate recovery is most likely due to co-elution with target compounds. Some samples may require dilution in order to bring one or more target analytes within the calibration range or to overcome significant interferences with some analytes. Re analyze sample if volume allows. If the surrogate recoveries are available from a less-diluted or undiluted aliquot of the sample or sample extract, those recoveries may be used to demonstrate that the surrogates were within the in-house QC limits, and no further action is required. If, upon re-analysis the recovery is again not within limits, report the data as an "estimated concentration." If the recovery is within the limits in the re-analysis, provide the re-analysis data to the data user. Generate on Non-Conformance Memo.

6. In the absence of project specific requirements, the LCS and LCSD are spiked with the same analytes at the same concentrations as the matrix spike. When the results of the matrix spike analysis indicate a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix. If the LCS and LCSD recoveries do not meet those limits as required in the method or program, the samples shall be re-analyzed. If sample volume does not allow re-analysis the entire prep/analytical batch of samples shall be flagged to reflect the deficiencies. Generate on Non-Conformance Memo.

7. In the absence of project specific requirements, when the results of the matrix spike analysis indicate a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix. If sample volume allows re-analysis, it shall be performed to verify the matrix effect. When sample volume does not allow for re-analysis, the parent sample shall be flagged to reflect the deficiencies. Generate a Non- Conformance Memo.

Table L
ANALYST/SUPERVISOR DATA ASSESSMENT

Analytical Method Acceptance Criteria⇨ Data Assessment Measure ⇩	**Method Citation SW If these conditions are not achieved ⇒**	**Method Citation EPA If these conditions are not achieved ⇒**
Initial Calibration	• 1	• 1
Initial Calibration Verification	• 1	• 1
Calibration Blank	• 1	• 1
Method Blank	• 2	• 2
Internal Standard Area	• 3	• 3
Continuing Calibration Verifications	• 4	• 4
Surrogate Recovery	• 5	• 5
Accuracy & Precision Laboratory Control Spikes	• 6	• 6
Accuracy & Precision Matrix Spikes	• 7	• 7

1. Check instrumentation/equipment condition; enter maintenance in instrument log; perform another initial calibration. No data can be reported. Generate on Non-Conformance Memo.

2. In the absence of project specific requirements, sample detects greater than 20 times the method blank contamination level are reported with those not exceeding 20 times re-analyzed or qualified. Generate on Non-Conformance Memo.

3. In the absence of project specific requirements, check to be sure that there are no errors in the calculations. If errors are found, recalculate the data accordingly. Examine chromatograms for interfering peaks and integrated peak areas. Re analyze sample if volume allows. Generate on Non-Conformance Memo.

4. In the absence of project specific requirements, immediately after the flawed CCV analyze another CCV or re-analyzed all samples set after the last acceptable CCV. Generate on Non-Conformance Memo.

5. In the absence of project specific requirements, check to be sure that there are no errors in the calculations. If errors are found, recalculate the data accordingly. Examine chromatograms for interfering peaks and integrated peak areas. If the program allows report the concentrations noting the surrogate recovery is most likely due to co-elution with target compounds. Some samples may require dilution in order to bring one or more target analytes within the calibration range or to overcome significant interferences with some analytes. Re analyze sample if volume allows. If the surrogate recoveries are available from a less-diluted or undiluted aliquot of the sample or sample extract, those recoveries may be used to demonstrate that the surrogates were within the in-house QC limits, and no further action is required. If, upon re-analysis the recovery is again not within limits, report the data as an "estimated concentration." If the recovery is within the limits in the re-analysis, provide the re-analysis data to the data user.

6. In the absence of project specific requirements, the LCS and LCSD are spiked with the same analytes at the same concentrations as the matrix spike. When the results of the matrix spike analysis indicate a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix. If the LCS and LCSD recoveries do not meet those limits as required in the method or program, the samples shall be re-analyzed. If sample volume does not allow re-analysis the entire prep/analytical batch of samples shall be flagged to reflect the deficiencies. Generate on Non-Conformance Memo.

7. In the absence of project specific requirements, when the results of the matrix spike analysis indicate a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix. If sample volume allows re-analysis, it shall be performed to verify the matrix effect. When sample volume does not allow for re-analysis, the parent sample shall be flagged to reflect the deficiencies. Generate a Non- Conformance Memo.

Table M
REPORT REVIEWER/PROJECT MANAGEMENT DATA ASSESSMENT

Analytical Method Acceptance Criteria⇨ Data Assessment Measure ⇩	**Method Citation SW If these conditions are not achieved ⇒**	**Method Citation EPA If these conditions are not achieved ⇒**
Holding Time Compliance	• 1	• 1
Sample Receipt Conditions and Preservation	• 2	• 2
Method Citation	• 3	• 3
Reasonableness: Field Duplicate	• 4	• 4
Reasonableness: Analytical Comments Qualifications	• 5	• 5

1. Flag results with an H and comment on the number of days past hold in LIMS.
2. In prose describe the receipt conditions as they relate to the acceptance criteria list in Table G
3. Compare to regulatory program in QAPP or Chain of Custody.
4. Are duplicate with 40% agreement. If not, internally flag for review.
5. Do related suites of tests agree or are reasonable.

Table N
CORRECTIVE ACTIONS

Analytical Method Acceptance Criteria⇨ Quality Control Measure ⇩	Method Citation SW If these conditions are not Achieved ⇒	Corrective Action (Key below)	Method Citation EPA If these conditions are not Achieved ⇒	Corrective Action (Key below)
Initial Calibration		• 1	•	• 1
Method Blank		• 2	•	• 2
Continuing Calibration Verification		• 3	•	• 3

1. Check instrumentation/equipment condition; enter maintenance in instrument log; perform another initial calibration

2. Samples that are "non-detect", or have detects greater than 20 times the method blank contamination level are reported without qualification. Sample detects less than 20 times the method blank contamination are re-analyzed or qualified.

3. Immediately after the flawed CCV analyze another CCV or re-analyzed all samples set after the last acceptable CCV.

Table O
CONTINGENCIES FOR HANDLING
OUT-OF-CONTROL OR UNACCEPTABLE DATA

Analytical Method Acceptance Criteria⇨ Quality Control Measure ⇩	Method Citation SW If these conditions are not achieved ⇒	Corrective Action (Key below)
Lab Control Spike and Duplicate	•	• 1
Matrix Spike and Duplicate	•	• 2
Internal Standards	•	• 3
Surrogate Standards	•	• 4

1. If Lab Control Spike/Duplicate fail on water analysis, the entire batch is re-analyzed with new QC, sample volume permitting. Inadequate sample volume results in flagging with "&" all associated samples. If Lab Control Spike/Duplicate fails on MeOH analysis, the LCS/LCSD is reanalyzed to confirm failure. Confirmation of failure results in flagging with "&" all associated samples. If non-confirmation of failure, reanalyze all samples with the valid QC.

2. If Lab Control Spikes pass acceptance criteria, flag parent sample with "N" to indicate matrix effects.

3. When sample volume is available reanalyze the samples at a higher dilution. If the second analysis indicates the same internal standard recoveries add analytical comments and effects on data.

4. When sample volume is available reanalyze the samples. If the second analysis indicates the same surrogate standard recoveries add analytical comments and flag with an "F" to demonstrate the matrix effects on data. High failures for Wisconsin do not necessitate reanalysis. Flag with an "F" and comment on co-elution effects.

Table P
Directions for Standards

Standard	Acronym	Concentration	REAGENTS USED:	Final Volume
Aqueous / WI Modified MeOH				
Level 1 Calibration Standard (water)	CAL STD	1.0 ppb	5 µL of 100 ppm curve std. to 50 mL RO WATER	50 mL RO WATER
Level 2 Calibration Standard (water)	CAL STD	5.0 ppb	25 µL of 100 ppm curve std. to 50 mL RO WATER	50 mL RO WATER
Level 3 Calibration Standard (water)	CAL STD	10 ppb	50 µL of 100 ppm curve std. to 50 mL RO WATER	50 mL RO WATER
Level 4 Calibration Standard (water)	CAL STD	20 ppb	100 µL of 100 ppm curve std. to 50 mL RO WATER	50 mL RO WATER
Level 5 Calibration Standard (water)	CAL STD	50 ppb	250 µL of 100 ppm curve std. to 50 mL RO WATER	50 mL RO WATER
Level 6 Calibration Standard (water)	CAL STD	200 ppb	10 µL of Restek Wisc PVOC/GRO Mix curve std to 50 mL RO WATER	50 mL (RO WATER)
Level 7 Calibration Standard (water)	CAL STD	500 ppb	25 µL of Restek Wisc PVOC/GRO Mix curve std to 50 mL RO WATER	50 mL (RO WATER)
PVOC Intermediate (Verification)	100 ppm GRO	10 ppm each PVOC	500 µL of Restek Wisc PVOC/GRO Mix to 49.5 mL MeOH	50 mL (MeOH)
PVOC Intermediate (Curve)	100 ppm GRO Curve std.	10 ppm each PVOC	100 µL of Supelco UST Modified GRO Mix Curve std to 9.9 mL MeOH	10 mL (MeOH)
Internal Standard and Surrogate Standard Mix	IS/SS	100 ppm each compound	1000 µL of 20 mg/mL Fluorobenzene + 1000 µL of 20 mg/mL α,α,α–Trifluorotoluene to 198 mL MeOH	200 mL (MeOH)
Calibration Verification Standard (Water)	CVS	20 ppb each PVOC	1000 µL of 100 ppm GRO to 499 mL RO WATER	500 mL (RO WATER)
Lab Control Spikes (Water)	LCS/LCSD	20 ppb each PVOC	1000 µL of 100 ppm GRO to 499 mL RO WATER	500 mL (RO WATER)
Lab Control Spikes Wisconsin (MeOH)	LCS/LCSD	20 ppb each PVOC	10 µL of Wisc PVOC/GRO Mix to 10 mL MeOH and 10 g Ottawa Sand. (Do a x50 Dilution for analysis)	10 mL MeOH in 10 g Ottawa Sand
Matrix Spike (Water)	MS/MSD	20 ppb each PVOC	86 µL of 100 ppm GRO standard to 43 mL of sample.*	43 mL Sample

*** It has been determined gravimetrically through a laboratory study that that the 40 mL VOC vials from QEC have a final volume of 43 mL.**

Table P - Continued
Standards

Standard	Acronym	Concentration	REAGENTS USED:	Final Volume
Low Level Solids				
Level 1 Calibration Standard (Low Level)	CAL STD	5.0 ppb	25 µL of 100 ppm curve std. To 50 mL RO WATER. Take a 5 mL Aliquot and put in a 40 mL VOA vial with a stir bar. Secure Cap tightly.	50 mL (RO WATER)
Level 2 Calibration Standard (Low Level)	CAL STD	10 ppb	50 µL of 100 ppm curve std. To 50 mL RO WATER. Take a 5 mL Aliquot and put in a 40 mL VOA vial with a stir bar. Secure Cap tightly.	50 mL (RO WATER)
Level 3 Calibration Standard (Low Level)	CAL STD	20 ppb	100 µL of 100 ppm curve std. to 50 mL RO WATER. Take a 5 mL Aliquot and put in a 40 mL VOA vial with a stir bar. Secure Cap tightly.	50 mL (RO WATER)
Level 4 Calibration Standard (Low Level)	CAL STD	50 ppb	250 µL of 100 ppm curve std. to 50 mL RO WATER. Take a 5 mL Aliquot and put in a 40 mL VOA vial with a stir bar. Secure Cap tightly.	50 mL (RO WATER)
Level 5 Calibration Standard (Low Level)	CAL STD	200 ppb	10 µL of Supelco UST Modified GRO Mix curve std to 50 mL RO WATER. Take a 5 mL Aliquot and put in a 40 mL VOA vial with a stir bar. Secure Cap tightly.	50 mL (RO WATER)
Level 6 Calibration Standard (Low Level)	CAL STD	500 ppb	25 µL of Supelco UST Modified GRO Mix curve std to 50 mL RO WATER. Take a 5 mL Aliquot and put in a 40 mL VOA vial with a stir bar. Secure Cap tightly.	50 mL (RO WATER)
PVOC Intermediate (Verification)	100 ppm GRO	10 ppm each PVOC	500 µL of Restek Wisc PVOC/GRO Mix to 49.5 mL MeOH	50 mL (MeOH)
PVOC/ α,α,α–Trifluorotoluene mixed Curve Intermediate std.	100 ppm GRO Curve/10 ppm SS Mix	10 ppm each PVOC + 10 ppm α,α,α-Trifluorotoluene	100 µL of Supelco UST Modified GRO Mix curve std + 100 µL of 1000 ppm α,α,α–Trifluorotoluene to 9.8 mL MeOH	10 mL (MeOH)
Internal Standard and Surrogate Standard Mix	IS/SS	100 ppm each compound	1000 µL of 20 mg/mL Fluorobenzene + 1000 µL of 20 mg/mL α,α,α–Trifluorotoluene to 198 mL MeOH	200 mL (MeOH)
Internal Standard Only	IS Only	100 ppm	1000 µL of 20 mg/mL α,α,α–Trifluorotoluene to 199 mL MeOH	200 mL (MeOH)
Surrogate Spike Solution	1000 ppm SS	1000 ppm	50 µL of 20 mg/mL α,α,α–Trifluorotoluene to 950 µL MeOH	1 mL (MeOH)
Calibration Verification Standard (Low Level)	CVS	50 ppb each PVOC	25 µL of 100 ppm GRO to 5 mL RO WATER and a disposable stir bar in a 40 mL VOA Vial, Secure cap tightly.	5 mL RO WATER
Lab Control Spikes (Low Level)	LCS/LCSD	50 ppb each PVOC	25 µL of 100 ppm GRO to 5 mL RO WATER and 5 g Ottawa Sand and a disposable stir bar in a 40 mL VOA Vial, Secure cap tightly.	5 mL RO WATER in 5 g Ottawa Sand
Matrix Spike (Low Level)	MS/MSD	50 ppb each PVOC	25 µL of 100 ppm GRO to 5 mL RO WATER and 5 g sample and a disposable stir bar in a 40 mL VOA Vial, Secure cap tightly.	5 mL RO WATER in 5 g sample

Table P - Continued
Standards

Standard	Acronym	Concentration	REAGENTS USED:	Final Volume
Medium Level Solid				
Level 1 Calibration Standard (MeOH)	CAL STD	0.4 ppb	2.0 µL of 100 ppm GRO/10 ppm TFT curve std + 1000 µL of MeOH to 49 mL RO WATER	50 mL (RO WATER)
Level 2 Calibration Standard (MeOH)	CAL STD	1.0 ppb	5 µL of 100 ppm GRO/10 ppm TFT curve std + 1000 µL of MeOH to 49 mL RO WATER	50 mL (RO WATER)
Level 3 Calibration Standard (MeOH)	CAL STD	5.0 ppb	20 µL of 100 ppm GRO/10 ppm TFT curve std + 980 µL of MeOH to 49 mL RO WATER	50 mL (RO WATER)
Level 4 Calibration Standard (MeOH)	CAL STD	10 ppb	50 µL of 100 ppm GRO/10 ppm TFT curve std + 950 µL of MeOH to 49 mL RO WATER	50 mL (RO WATER)
Level 5 Calibration Standard (MeOH)	CAL STD	20 ppb	100 µL of 100 ppm GRO/10 ppm TFT curve std + 900 µL of MeOH to 49 mL RO WATER	50 mL (RO WATER)
Level 6 Calibration Standard (MeOH)	CAL STD	50 ppb	250 µL of 100 ppm GRO/10 ppm TFT curve std + 750 µL of MeOH to 49 mL RO WATER	50 mL (RO WATER)
Level 7 Calibration Standard (MeOH)	CAL STD	200 ppb	10 µL of Supelco UST Modified GRO Mix curve std + 10 µL of 1000 ppm α,α,α-Trifluorotoluene + 980 µL MeOH to 49 mL RO WATER.	50 mL (RO WATER)
Level 8 Calibration Standard (MeOH)	CAL STD	500 ppb	25 µL of Supelco UST Modified GRO Mix curve std + 25 µL of 1000 ppm α,α,α-Trifluorotoluene + 950 µL MeOH to 49 mL RO WATER.	50 mL (RO WATER)
PVOC Intermediate (Verification)	100 ppm GRO	10 ppm each PVOC	500 µL of Restek Wisc PVOC/GRO Mix to 49.5 mL MeOH	50 mL (MeOH)
PVOC/α,α,α-Trifluorotoluene mixed Curve Intermediate std.	100 ppm GRO Curve/10 ppm SS Mix	10 ppm each PVOC + 10 ppm α,α,α-Trifluorotoluene	100 µL of Supelco UST Modified GRO Mix curve std + 100 µL of 1000 ppm α,α,α-Trifluorotoluene to 9.8 mL MeOH	10 mL (MeOH)
Internal Standard Only	IS Only	100 ppm	1000 µL of 20 mg/mL α,α,α-Trifluorotoluene to 199 mL MeOH	200 mL (MeOH)
Surrogate Spike Solution	100 ppm SS	100 ppm	50 µL of 20 mg/mL α,α,α-Trifluorotoluene to 9.95 mL MeOH	10 mL (MeOH)
Surrogate Spike Solution	2500 ppm SS	2500 ppm	1250 µL of 20mg/mL α,α,α-Trifluorotoluene to 8.750 mL MeOH	10 mL (MeOH)
Surrogate Spike Solution	1000 ppm SS	1000 ppm	50 µL of 20 mg/mL α,α,α-Trifluorotoluene to 950 µL MeOH	1 mL (MeOH)
Calibration Verification Standard (MeOH)	CVSBTX	50 ppb each PVOC, 50 ppb Surrogate Std.	1000 µL of 100 ppm GRO + 100 µL of 100 ppm α,α,α-Trifluorotoluene to 196 mL RO WATER plus 2.9 mL MeOH	200 mL
Lab Control Spikes (MeOH)	LCS/LCSD	20 ppb each PVOC, 50 ppb Surrogate Std (both on column after x50 dilution)	10 µL of Restek Wisc PVOC/GRO Mix + 10 µL of 2500 ppm α,α,α-Trifluorotoluene to 10 mL MeOH and 10 g Ottawa Sand. (Do a x50 Dilution for analysis)	10 mL MeOH in 10 g Ottawa Sand
Matrix Spikes (MeOH)	MS/MSD	20 ppb each PVOC, 50 ppb Surrogate Std (both on column after x50 dilution)	10 µL of Restek Wisc PVOC/GRO Mix + 10 µL of 2500 ppm α,α,α-Trifluorotoluene to 10 mL MeOH and 10 g sample. (Do a x50 Dilution for analysis)	10 mL MeOH in 10 g sample

Table Q
DATA TRANSFER CODES

831234F001SD50

Letter occupying position of "F"

F WI EXTRACTABLE SOLID LIMITS (5030B)
B ALL WATERS REPORTED W/PID (5030B)
Out of state Soils received in ZHE for PID in MeOH (5030/5030B)
Low level soil received in ZHE (5030)
N Out of state Soils received in Encore/MeOH for PID (5035/5030B)
A Low level soils received in Encore or in water (5035)
D TPHGAS BY OA-1 (WATER AND SOIL) (OA-1)
J TPHGAS C6 – C12 BY 8015
E TPHGAS C6 – C10 BY 8015 (WATER AND SOIL in ZHE) (5030B)
T TPHGAS C6 – C10 BY 8015 (SOIL in Encore/MeOH) (5035/5030B)

Letter occupying position of "S"

S MEDIUM LEVEL EXTRACTABLE SOLID IF LOGGED IN -S-ME
W AQUEOUS
I IMPINGER
C CHARCOAL TUBE
M METHANOL BLANK
L LOW LEVEL SOIL
MEDIUM LEVEL EXTRACTABLE SOLID IF LOGGED IN -S

Letter occupying position of "D"

A GRO, TPHGAS, OA-1 ONLY
B BENZENE ONLY
C BTEX W/ MTBE
D BTEX
E BTEX &MTBE W/ NAPH
F MTBE ONLY
G NAPH ONLY
H PVOC
I PVOC W/ NAPH
J BTEX W/ MTBE 602
K BTEX 602
L PVOC 602
N BTEX W/ NAPH
P BTEX W/ TOTAL XYLENES
R BTEX &MTBE W/ TOTAL XYLENES

if lower case no rear FID analysis

NUMBER occupying position of "50"

DILUTION FACTOR (up to 4 digits) 10K = 10,000 (10 x 1000)
1HK = 100,000 (1 x 100 x 1000)
10HK = 1,000,000 (10 x 100 x 1000)

TABLE R

PURGE AND TRAP OPERATING PROCEDURES

Analysis Method
(Current Edition of 8021B)

Parameter	Dynatrap	Tekmar 3000	Tekmar 3000
Trap	Purge Trap A For Dynatech	Purge Trap A For Tekmar 3000	Purge Trap K For Tekmar 3000
Trap contents	Tenax	Tenax	Carbopack B/Carboxen 1000 & 1001
Column *	0.53mm ID x 3.0µm film	0.53mm ID x 3.0µm film	0.32mm ID x 1.8µm film
Electric Pressure Control (EPC)	No	No	Yes
Purge Gas	He	He	He
Purge Gas Flow Rate (mL/Min)	40-45	40-45	40-45
Purge Time (min)	11	11	11
Purge Temp	Ambient	Ambient	Ambient
Desorb Temp (°C)	180	200	250
Desorb Time (min)	2	2	2
Dry Purge Time (min)	3	5	None
Bake Temp (°C)	220	220	270
Backflush Gas Flow (mL/min)	20-60	20-60	20-60

* All columns are DB-624 and 30 meters

21. Revisions

Document Number	Reason for Change	Date
GB-O-009-Rev.0	Reformatted SOP body to Pace analytical format	12Apr2005
S-GB-O-009-Rev.1	Biennial Review. Changed SOP number to conform to latest Pace SOP naming convention, added Annual Review signoff section.	04Oct2007

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STANDARD OPERATING PROCEDURE

Aqueous Sample Preparation for the Analysis of Gas Range Organics and Petroleum Volatile Organics

Reference Methods:
WI Modified Method for the Determination of Gasoline Range Organics
SW-846 Method 5030B

SOP NUMBER:	S-GB-O-010-Rev.1
EFFECTIVE DATE:	Date of Final Signature
SUPERSEDES:	GB-O-010 Rev. 0

APPROVAL

Nils Melberg, Laboratory Manager — Date: 11/28/07

Arthur F. Lautenbach, Quality Manager — Date: 11/28/07

ANNUAL REVIEW

SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE APPROVAL. SOP IS VALID FOR ONE YEAR FROM DATE OF LAST SIGNATURE.

Signature	Title	Date

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1. Purpose

1.1 This SOP details the steps and conditions involved in preparing aqueous samples for the determination of gasoline range organics (GRO) and petroleum volatile organic compounds (PVOCs) following The Method for Determining Gasoline Range Organics (Wisconsin DNR 1995) and SW-846 5030B.

1.2 Samples prepared by this SOP are analyzed by the latest revisions of SOPs S-GB-O-006 *Modified Method for Determination of Gasoline Range Organics*, S-GB-O-008 *Total Petroleum Hydrocarbons – Gasoline by Gas Chromatography Using Flame-ionization Detectors*, and S-GB-O-009 *Aromatic Volatiles by Gas Chromatography Using Photo-ionization Detectors*.

2. Scope and Application

2.1 The policies and procedures contained in this SOP are applicable to all personnel involved in the preparation of aqueous samples for the determination of GRO and PVOCs using a purge and trap, Gas Chromatography procedure

3. Summary of Method

3.1 Water samples are collected and stored at 4°C ± 2°C in an area free of solvent fumes. All samples should be analyzed within 14 days of collection for preserved samples; 7 days for unpreserved. Water samples can be analyzed directly for volatile organic compounds by purge-and-trap extraction and gas chromatography. Higher concentrations of these analytes in water can be determined by dilution of the sample prior to the purge-and-trap process. Screening of the samples prior to purge-and-trap analysis may provide guidance on whether sample dilution is necessary. Pace routinely screens samples to eliminate exceedances of the calibration curve and to protect sensitive instruments from damage.

4. Interferences

4.1 The primary introduction of laboratory interference comes from dirty glassware or impure reagents. Clean laboratory apparatus, quality reagents and conscientious laboratory personnel are essential in the production of high quality data.[1]

[1]Pace Analytical Services, Inc. – Green Bay Laboratory purchases high quality solvents to eliminate this potential of contaminations and requires these vendors to stand behind claims made on the solvents purchased.
Pace Analytical Services, Inc. – Green Bay Laboratory has adopted and implemented SOP's addressing proper glassware cleaning techniques, tailored to the department using the apparatus.

4.2 Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride and fluorocarbons) through the septum seal of the sample vial during shipment and storage. A trip blank prepared from organic-free reagent water is carried through sampling and handling protocols to serve as a check on such contamination

5. Safety

5.1 The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable. Cautions are included for known extremely hazardous materials.

5.2 A reference file of Material Safety Data Sheets (MSDS) is made available to all personnel involved in the chemical analysis, and is located in Sample Receiving. A formal safety plan has been prepared and is distributed to all personnel with documented training

6. Definitions

6.1 Refer to Section 10.0 of the most current version of the Pace Quality Manual for the terms used at Pace Analytical. When definitions are not consistent with NELAC defined terms, an explanation will be provided in this SOP.

7. Responsibilities and Distribution

7.1 Personnel

7.1.1 All personnel involved with sample preparation and analysis are responsible for adherence to this SOP. A controlled copy will be available for review and consultation within the area methods manual.

7.1.2 Personnel are responsible for ensuring that any deviations to this SOP are reported to the laboratory manager.

7.2 Laboratory Manager

7.2.1 The laboratory manager is responsible for ensuring adherence to this SOP and will receive a controlled copy of this SOP.

7.2.2 The laboratory manager is responsible for performing a biennial review of the SOP and reporting any required revisions to the Quality Assurance Office.

7.3 Quality Assurance Office

7.3.1 The QA Office is responsible for performing a biennial review of the SOP in conjunction with the purchasing department and revising as needed.

7.3.2 The QA Office is responsible for ensuring that all revisions to the SOP are implemented.

7.4 Revisions

7.4.1 This SOP will be reviewed on a biennial basis at a minimum, and any required revisions will be incorporated.

8. Sample Collection, Preservation and Handling

8.1 Aqueous samples should be collected in triplicate without agitation and without headspace in contaminant-free 40 ml glass VOC vials with Teflon-lined septa in the caps. The Teflon liner must contact the sample. Samples must be preserved with 500 µL of Hydrochloric Acid (HCl) at the time of collection, (acid should be added to the vial prior to adding the sample).

Note: Pace Analytical Services, Inc. – Green Bay Laboratory uses pre-cleaned, level 3 certified, 40 ml VOC vials purchased from QEC. These vials contain 0.5 ml of 18 % HCL.

Note: If targeted compounds breakdown with the addition of HCl, samples must be collected unpreserved. Unpreserved samples have a 7-day holding time. The pH of the samples are taken using pH indicator paper and recorded in a logbook.

8.2 The samples will need to be cooled to 4° C after collection. Aqueous samples will be stored in refrigerators at Pace Analytical Services, Inc. – Green Bay Laboratory and must be held at 4° C (+/- 2C). Preserved samples have a 14-day holding time or as specified by the Accrediting Authorities.

8.3 One trip blank is required per sampling event and site.

8.4 Samples need to be shipped to the lab as soon as the samples are collected.

8.5 Sample temperature must be determined upon receipt to the lab.

Note: Sample temperature is recorded by use of a temperature blank. The temperature must be between 4° C (+/- 2C) unless superseded by the accrediting authority. For certain authorities recording sample temperature as "received on ice (ROI)" is acceptable.

9. Equipment and Supplies

9.1 Microsyringes: 10-µL, 25-µL, 50-µL, 100-µL, 250-µL, 500-µL, and 1,000-µL:

9.2 Syringe: 50 mL, for holding sample aliquot and diluent solution.

9.3 40 mL VOC vials for GC autosampler.

10. Reagents and Standards

10.1 Reverse Osmosis Water

10.2 10,000 ppm – 10 component Gasoline Range Organics Standard from Restek or Supelco.

10.3 100 ug/mL ααα-Trifluorotoluene surrogate solution added by the autosampler.

11. Calibration

11.1 Not Applicable.

12. Procedure

12.1 Print GRO Waters Backlog.

12.1.1 Login to windows

12.1.2 Click on the conifer icon.

12.1.3 Enter your last name and password, click ok.

12.1.4 In conifer select User Extension.

12.1.5 Select Gas Backlogs.

12.1.6 Select Waters Prep Backlog - Print Report. This will display the backlog on the screen.

12.1.7 Select File-Print-OK. This will print the backlog.

12.1.8 Repeat this process for the Waters Prep Sheet.

12.1.9 Repeat this process for MN Water Prep Backlog and Prep worksheet.

12.2 Arrange the samples on the prep sheet into QC sets of 19 samples or less (this allows room for one sample to be added to the set at the time of analysis to serve as the MS/MSD parent sample while still remaining within the maximum of 20 samples per set). Pull the samples from the volatiles water refrigerator.

12.3 Higher concentration samples are pre-screened using a rapid GC headspace technique. See latest revision of SOP S-GB-O-001 *Sample Screening Volatile Organics Prior to Preparation* for the specifics on the pre-screening of samples.

12.4 Dilute samples according to screen data.

12.4.1 Samples that screen clean can be analyzed directly from the original sample vials free of headspace.

12.4.2 Dilutions of higher concentration samples are made based on the results of the screen data.

12.5 If the samples are not to be analyzed immediately, store the set in the appropriate section of the sample refrigerator.

12.6 For each analytical batch, not to exceed 20 environmental samples, a method blank, matrix spike and matrix spike duplicate must be analyzed (the frequency of the spikes may be different for different monitoring programs but no less than 1 per 20 samples). The blank and spiked samples must be carried through all stages of the sample preparation and measurement steps. (This can be superseded by Accrediting or Project Specific Requirements.) The sample used for the MS/D pair is either determined by the client or selected at random from client samples, as sample volume allows. See the analytical SOP for spike concentration and instructions.

12.7 A Laboratory Control Spike and Duplicate (LCS/LCSD) pair is also included with each analytical batch. The pair consists of an aliquot of reverse osmosis water. The pair is spiked with the same analytes at the same concentrations as the matrix spike. When the results of the matrix spike analysis indicate a potential problem due to the sample matrix itself, these results are used to verify that the instrument was in control. See the analytical SOP for spike concentration and instructions.

12.8 All diluted samples, the blank, laboratory control spike, laboratory control spike duplicate, matrix spike and matrix spike duplicate must be free of headspace.

12.9 Place prep sheet in the WATER PREP BOOK.

12.10 Sign over the face of the printout and page to insure removal of page will be noticeable. Date the top of the page of the notebook and sign and date the bottom of the notebook.

13. Quality Control

13.1 A maximum of 20 samples define a QC set. One method blank, laboratory control spike, laboratory control spike duplicate, matrix spike and matrix spike duplicate are necessary per 20 samples or per extraction batch whichever is more frequent.

13.2 After reception in the laboratory, samples are to be stored at 4°C ± 2°C at all times when not being prepared.

13.3 All water samples that are preserved should be analyzed within 14 days of collection or 7 days for unpreserved water samples.

13.4 The size of any bubble caused by degassing upon cooling the sample should not exceed 5-6 mm. When a bubble is present, also observe the cap and septum to ensure that a proper seal was made at the time of sampling. If the sample was improperly sealed or if the bubble exceeds 5-6mm, the sample should not be used for analysis. If insufficient sample vials are received, the sample is analyzed and the appropriate flag is entered into LIMS.

14. Method Performance

14.1 There are several requirements that must be met to insure that this procedure generates accurate and reliable data. A general outline of requirements has been summarized below. Further specifications may be found in the Laboratory Quality Manual.

14.1.1 The analyst must read and understand this procedure with written documentation maintained in his/her training file.

14.1.2 An initial demonstration of capability (IDOC) must be performed per ALL-Q-020, *Training Procedures*. A record of the IDOC will be maintained in his/her QA file with written authorization from the Laboratory Manager and Quality Manager.

14.1.3 An annual method detection limit (MDL) study will be completed per S-ALL-Q-004, *Method Detection Limit Studies*, for this method and whenever there is a major change in personnel or equipment. The results of these studies are retained in the quality assurance office.

14.1.4 Periodic performance evaluation (PE) samples are analyzed per S-ALL-Q-010, *PE/PT Program*, to demonstrate continuing competence. All results are stored in the QA office.

15. Pollution Prevention and Waste Management

15.1 The quantity of chemicals purchased is based on expected usage during its shelf life and disposal cost of unused material. Actual reagent preparation volumes reflect anticipated usage and reagent stability.

15.2 Excess reagents, samples and method process wastes are characterized and disposed of in an acceptable manner. For further information on waste management consult the current version of ALL-S-002, *Waste Handling*..

16. References

SW-846 5030B Purge and Trap for Aqueous Samples
Revision 2, December 1996
Modified GRO, Method for Determining Gasoline Range Organics
Wisconsin DNR, WI-PUB-SW-141, September 1995
S-GB-O-006 *Modified Method for Determination of Gasoline Range Organics*
S-GB-O-008 *Total Petroleum Hydrocarbons – Gasoline by Gas Chromatography Using Flame-ionization Detectors*
S-GB-O-009 *Aromatic Volatiles by Gas Chromatography Using Photo-ionization Detectors*
S-GB-O-001 *Sample Screening Volatile Organics Prior to Preparation*

17. Tables, Diagrams, Flowcharts, Appendices, Addenda etc.

17.1 Not applicable

18. Revisions

Document Number	Reason for Change	Date
G3-GRO-7 Rev. 2	Reformatted SOP body to Pace analytical format	**12Apr2005**
S-GB-O-010-Rev.1	Updated cover page to new format Section 8 - Replaced instances of EnChem to Pace Analytical Services, Inc. – Green Bay Laboratory Section 12.1.5 - Updated Procedure section Section 12 and 13 - Replaced BS/BSD with LCS/LCSD throughout document as necessary	**27Nov2007**

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STANDARD OPERATING PROCEDURE

Microwave Extraction for the Determination of Polynuclear Aromatic Hydrocarbons and Base/Neutral/Acids in Solid Matrices

Reference Method(s):SW-846 Method 3546

SOP NUMBER:	S-GB-O-045-REV.01
EFFECTIVE DATE:	Date of Final Signature
SUPERSEDES:	S-GB-O-045-rev.0

APPROVAL

Nils K Melberg
Nils Melberg, Laboratory General Manager — Date: 03/25/08

Kate E. Grams
Kate Grams, Laboratory Quality Manager — Date: 3/25/08

Glen A. Coder
Glen Coder, Department Manager — Date: 3/25/08

ANNUAL REVIEW

SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE APPROVAL. SOP IS VALID FOR ONE YEAR FROM DATE OF LAST SIGNATURE.

Signature	Title	Date

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1. PURPOSE

The Standard Operating Procedure (SOP) is used to prepare solid samples, based on SW846 Method 3546, for analysis of semi-volatile compounds. Extracts prepared by this method are analyzed by Pace SOPs ALL-O-001 *Determination of Semivolatile Organics by GC/MS*, S-ALL-GB-O-001 *Determination of Semivolatile Organics by GC/MS – Green Bay Addendum,* S-GB-O-020, *Analysis of Polynuclear Aromatic Hydrocarbons in Soil by GC/MS – SIM*, and S-GB-O-044, *Determination of Low Level PAHs by GC/MS-SIM in Solid and Biological Matrices*.

2. SCOPE AND APPLICATION

2.1 This procedure is applicable to extraction and concentration of nonvolatile and semivolatile organics from solids. Extracts may be prepared by this method for analysis by several chromatographic methods including, but not limited to, SW-846 8270C.

2.2 This SOP provides procedures for extracting both low and high concentration samples.

2.3 Appropriate cleanup procedures that may be required for some sample extracts are described in separate SOPs.

2.4 Determinative methods used for extracts prepared by this SOP are described in separate SOPs.

2.5 This procedure is restricted to use by, or under the supervision of, analysts experienced in preparation of extracts for chromatographic analysis. Each analyst must demonstrate the capability to generate acceptable results with this method to be considered qualified to report sample results.

3. SUMMARY OF METHOD

3.1 An aliquot of the solid sample (30.0-g for low concentration samples and 2.0-g for high concentration samples) is extracted using the microwave extraction unit.

3.2 The extract is concentrated (if necessary) and exchanged into the solvent required for the cleanup or determinative method (if necessary).

4. INTERFERENCES

Interferences may be introduced into sample extracts by contaminants in solvents, reagents, glassware, and any other material that comes in contact with the sample or extract during extract preparation. These interferences must be closely monitored by analyzing Method Blank samples and taking corrective action as required.

5. SAFETY

5.1 The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable. Cautions are included for known extremely hazardous materials.

5.2 Each laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of Material Safety Data Sheets (MSDS) is made available to all personnel involved in the chemical analysis

5.3 MSDS sheets are located in the Quality Assurance Office and should be consulted prior to handling samples and standards.

5.4 Samples should be considered biological contact hazards. Use appropriate protective equipment (lab coat, gloves and lab glasses) and aseptic techniques when handling these samples. Wash hands with soap and water upon completion of the procedure and clean the work surface with a disinfectant.

6. DEFINITIONS

Refer to Section 10.0 of the most current version of the Pace Quality Manual for the terms used at Pace Analytical. When definitions are not consistent with NELAC defined terms, an explanation will be provided in this SOP.

7. RESPONSIBILITIES AND DISTRIBUTION

7.1 Personnel

7.1.1 All personnel involved with sample preparation and analysis are responsible for adherence to this SOP. A controlled copy will be available for review and consultation within the area methods manual.

7.1.2 Personnel are responsible for ensuring that any deviations to this SOP are reported to the laboratory manager.

7.2 Laboratory Manager

7.2.1 The laboratory manager is responsible for ensuring adherence to this SOP and will receive a controlled copy of this SOP.

7.2.2 The laboratory manager is responsible for performing a biennial review of the SOP and reporting any required revisions to the Quality Assurance Office.

7.3 Quality Assurance Office

7.3.1 The QA Office is responsible for performing a biennial review of the SOP in conjunction with the semivolatile department and revising as needed.

7.3.2 The QA Office is responsible for ensuring that all revisions to the SOP are implemented.

7.4 Revisions

7.4.1 This SOP will be reviewed on a biennial basis at a minimum, and any required revisions will be incorporated

8. SAMPLE COLLECTION, PRESERVATION AND HANDLING

8.1 Samples are to be collected in glass jars with Teflon lined lids, demonstrated to be free of contamination at or below the reporting limit.

8.2 Samples are to be chilled to 4 ± 2°C immediately after collection or to a specified temperature range governed by accredit ting authorities to preserve integrity. Samples that are hand delivered to the laboratory immediately after collection may be accepted if there is evidence, such as arrival on ice, that the chilling process has begun.

8.3 Shipments to the laboratory must be timely to avoid preparation holding time issues. Shipment to the laboratory may be accomplished by hand delivery, courier services or common carrier during normal business hours (8:00 am – 5:00 pm central time). Arrangements to accept samples outside normal business hours must be made with personnel prior to shipment.

8.4 Upon receipt and after processing requests for analysis, samples are to be refrigerated at 4 ± 2°C until preparation. After preparation the extracts are held at $<0^0$ C until analysis.

8.5 See Appendix A Table F for a summary.

8.6 Holding Times

8.6.1 Soil Samples – Samples must be extracted within 14 days of collection.

8.6.2 Extracts – Extracts must be analyzed within 40 days of preparation.

8.7 See Appendix A Table F for a summary.

9. EQUIPMENT AND SUPPLIES

See Appendix A Table B and Table C for a summary.

10. REAGENTS AND STANDARDS

10.1 Where the purity of reagents and standards are not specified analytical reagent grade will be used. A grade no less than those specified by the references will not be used.

10.2 Polynuclear Aromatic Hydrocarbon (PAH) Standards.

10.2.1 Surrogate standards - The surrogate standards are listed in Table 2:

Table 2

Nitrobenzene-$d_{(5)}$
2-Fluorobiphenyl
p-Terphenyl-$d_{(14)}$

10.2.1.1 This stock standard is obtained from Restek (Catalog # 31082), or equivalent, at a concentration of 5000 ppm.

10.2.1.2 B/N Surrogate Standard at 150 ug/ml:

10.2.1.2.1 To prepare the intermediate stock standard, 3000ul of a 5000 ug/ml B/N surrogate mix is added to a 100ml volumetric and brought to final volume with CH_2Cl_2.

10.2.1.2.2 Surrogate standards must be added to all blanks, spikes, and sample extracts.

Note: This solution is stored in a refrigerator at 4° C.

10.2.2 PAH spike standards – The PAH spike mix is listed in Table 3. (Note: Additional compounds may be analyzed on a project specific basis.)

Table 3

Compound
Naphthalene
2-Methylnaphthalene
1-Methylnaphthalene
Acenaphthylene
Acenaphthene
Fluorene
Phenanthrene
Anthracene
Fluoranthene
Pyrene
Benzo(a)anthracene
Chrysene
Benzo(b)fluoranthene
Benzo(k)fluoranthene
Benzo(a)pyrene
Indeno (1,2,3-cd)pyrene
Dibenz[a,h]anthracene
Benzo(g,h,i)perylene

10.2.2.1 The stock standard is obtained from Accustandard, PAH M-610-FL-R-5X, or equivalent, at a concentration of 500 ug/ml.

10.3 Base/Neutral/Acids (BNA) Standards.

10.3.1 Surrogate standards - The surrogate standards are listed in Table 4:

Table 4

2-Fluorophenol	Acid Surrogate
Phenol-$d_{(6),}$	Acid Surrogate
Nitrobenzene-$d_{(5)}$	B/N Surrogate
2-Fluorobiphenyl	B/N Surrogate
2,4,6-Tribromophenol	Acid Surrogate
p-Terphenyl-$d_{(14)}$	B/N Surrogate

10.3.1.1 The intermediate surrogate solution contains base/neutral and acid based compounds.

10.3.1.1.1 The B/N-based surrogate compounds are spiked at an on-column concentration of 50 ng.

10.3.1.1.2 The acid-based surrogate compounds are spiked on-column at a concentration of 75 ng.

10.3.1.1.3 Soils are spiked with 1 mL at a concentration of 75/50 ug/mL intermediate standard.

10.3.1.1.4 Surrogate standards must be added to all blanks, spikes, and sample extracts. Take into account all dilutions of sample extracts.

10.3.1.1.5 These stock standards are obtained from Restek (Catalog #'s 31082 and 31083) at concentrations of 5000 ug/mL and 7500 ug/mL respectively.

10.3.1.2 8270 Surrogate Standard, 75/50 ug/mL intermediate

10.3.1.2.1 5 mL of 5000 ug/mL B/N surrogate + 5 mL of 7500 ug/mL acid surrogate diluted to 500 mL in CH_2Cl_2.

Note: This solution is stored in a refrigerator at 4° C +/- 2.

10.3.2 Lab Control and Matrix spike standards - A LCS, MS and MSD are spiked with the entire compound list at an on-column concentration of 50 ng. 250 uL of a 200 ug/mL stock custom mix standard (Supelco # 20084376), along with 10 uL of a 5000 ug/mL N-nitrosodiphenylamine (Supelco Cat# 46702-U) stock solution are injected into each LCS, MS and MSD.

Note: This solution is stored in a refrigerator at 4° C +/- 2.

11. CALIBRATION

11.1 Analytical Balance Calibration

11.1.1 Annual Calibration - The balance must be calibrated at least annually by an outside agency and checked daily before each use using Class 1 or 2 weights. Refer to Pace SOP S-ALL-Q-013 *Support Equipment*.

11.2 Daily Calibration Check

11.2.1 Clean the balance and surrounding area prior to starting the daily calibration check.

11.2.2 Check the sight level on the balance. If it needs adjusting, level the balance.

11.2.3 The weight set ID indicated in the logbook is used as the primary set. If an alternate weight set ID is used, that ID must be recorded in the comment section of the balance calibration logbook for that day.

11.2.4 Tare the balance before weighing the NIST certified weights.

11.2.5 Use forceps or other means to lift each weight (Do not touch the weights with fingertips as the residue may artificially adjust the true value of the weights). Record the date of the calibration check, the true value of the weight, and the actual measured weight in the logbook. Repeat this procedure for the other certified weights. If calibration weights differ from the certified weights by more than specified in the balance calibration logbook, corrective action must be taken (see 11.3).

11.3 Corrective Action

11.3.1 Clean the balance and balance pan. Check the sight level on the balance and adjust if necessary. Re-tare and reweigh all the certified weights.

11.3.2 The internal calibration function (if available) of the balance may be used as a means of corrective action.

11.3.3 Utilize the internal calibration function and diagnostics. Refer to instrument manual.

11.3.4 Contact the QA office for assistance if the balance does not meet the calibration tolerances.

11.3.5 If the above action does not correct the problem, the balance should be taken out of service and appropriately labeled to avoid improper usage. A service technician should be contacted.

11.3.6 Record any corrective action. Initial and date all entries in the logbook.

11.4 Microwave calibration expressed as Power in Watts.

11.4.1 Use the following procedure to determine actual power output at any of the following levels: 400, 800 and 1600 Watts. Record all measurements in the instrument maintenance logbook.

11.4.2 Ensure that the solvent sensor assembly is disconnected prior to performing any power test on the MARS system.

11.4.3 Install the turntable in the microwave cavity.

11.4.4 With the main menu displayed, highlight "Load Method. " Press the "SELECT" key. The directory menu screen will appear.

11.4.5 Use the arrow keys to highlight the CEM Directory and again press the "SELECT" key and the CEM Menu screen will appear.

11.4.6 Use the arrow keys to highlight one of the power tests 400W, 800W or 1600W Power test and press the "SELECT" key to return to the main menu.

11.4.7 Place 1000 mL of ambient temperature (18-22 ºC) deionized water in a 1000-mL PTFE or polypropylene beaker.

11.4.8 Using a thermometer with 0.1 ºC gradations, measure and record the initial temperature, T_i. Ensure that the thermometer is immersed to its indicated immersion line prior to reading the temperature.

11.4.9 Remove the thermometer from the beaker. Carefully place the beaker in Vessel #1 position on the microwave turntable. Gently close the door to avoid spilling any of the water.

11.4.10 Press "START".

11.4.11 At the end of the programming time (2 minutes), remove the beaker from the microwave cavity. Stir the water thoroughly for 30 seconds, measure and record the peak temperature reading. This is the final temperature, T_f.

11.4.12 The microwave output is calculated as follows: Power in Watts = $47(T_f-T_i)$.

11.4.13 At the 400W power test the calculated power must be > 340Watts, at the 800W power test the calculated power must be $\geq$ 680 Watts and at the 1600W power test the calculated power must be $\geq$ 1360 Watts.

11.4.14 The microwave power test must be performed weekly at one of the setting. It is recommended to use the 1600W setting since this is the closest to the settings used for our extraction method.

12. PROCEDURE

12.1 Extraction – Low Concentration Samples

12.1.1 Inspect the 75-mL microwave extraction vessels to ensure they are clean and dry. Pre-rinse vessels with appropriate solvent and discard the rinsate as waste.

12.1.2 Weigh a 30.0-g aliquot of each sample into a vessel, removing twigs, rocks and other foreign material (refer to SOP S-ALL-Q-021, *Sub-Sampling (Sample Homogenization)*). Mix the sample with an equal volume of anhydrous sodium sulfate, on an as needed basis, until a free-flowing powder is obtained.

12.1.3 For each batch of 20 samples, or less, prepare two additional sample aliquots. One will serve as a MS and the second as a MSD. Also prepare 2 aliquots of reagent sand to serve as the Method Blank and LCS.

12.1.4 Spiking of Samples.

12.1.4.1 PAH Samples

12.1.4.1.1 Add 100uL of the150 ug/mL surrogate spike solution to each sample aliquot, LCS, MB, MS, and MSD. In addition, add 20uL of the PAH spike mix at 500ug/mL to the LCS, MS and MSD samples.

12.1.4.2 BNA Samples

12.1.4.2.1 Add 1 mL of the 75/50 ug/mL surrogate spike solution to each sample aliquot, LCS, MB, MS, and MSD. In addition, add 250 uL of the LCS/Matrix spike mix @ 2000ug/mL and 10 uL of N-nitrosodiphenylamine @ 5000 ug/mL to the LCS, MS and MSD samples.

12.1.5 Immediately add 25 mL of CH_2Cl_2 to each sample aliquot, add the vessel plug and screw on the vent cap. Tighten the cap by either using the capping station or hand tightening. Note: (1) When hand-tightening, finger tighten then turn approximately 30 degrees more. (2) When using the Capping station, turn on the capping station and insert the vessel with cap while holding onto the vessel. Keep the vessel in the station until the motor stops turning and remove. The Capping station has a preset torque and doesn't require adjusting. DO NOT re-torque vessels without completely loosening the covers first.

Note: Other solvent blends may be used based on project requirements. A MDL and IDC study must be performed if different solvent blends are used.

12.1.6 Insert each vessel into a high-pressure microwave sleeve. Make sure the sleeve is pushed up tight against the bottom of the vessel cap, otherwise the vessel may explode during the extraction process.

12.1.7 Add vessels to microwave carousel. Make sure vessels are evenly spaced around the carousel in order for the heating sensors to work properly. This only becomes an issue if you have less than a full circle of vessels on the carousel.

12.1.8 Turn on the microwave extractor and set the microwave extractor to method 3546 Large and press "START". This method is set as follows:

12.1.8.1 Power Setting: 1600 W at 100%

12.1.8.2 Ramp Rate: 10 minutes to a final temperature of 115 ºC.

12.1.8.3 Hold at 115 ºC for 10 minutes

Note: If less than 12 samples are extracted within the batch, use method 3546 Small. The method is set as follows:

Power Setting: 800 W at 100%

Ramp Rate: 10 minutes to a final temperature of 115 ºC.

Hold at 115 ºC for 10 minutes

12.1.9 Allow the vessels to cool to room temperature (~ 30 minutes). Empty the entire contents of the microwave vessel into a filtering funnel pre-assembled with a glass wool plug and sodium sulfate. The sample extract is collected in a 60 mL disposable vial set underneath the funnel. Rinse the microwave vessel with approximately 15 mL of CH_2Cl_2 to collect any remaining sample residue and pour into the filter funnel. Once the remaining sample residue is poured into the funnel, rinse the sodium sulfate with CH_2Cl_2 and place the pressure filter apparatus on top of the funnel to pressure filter the sample into the 60 mL collection vessel. After all sample extract has been pressure filtered, proceed to concentration. Samples can also be filtered gravimetrically.

12.2 Extraction – High Concentration Samples

12.2.1 The criterion is the same as Low Concentration sample extraction procedure, except 2g of sample volume is used instead of 30g.

12.3 Concentration

12.3.1 Water Bath Concentration

12.3.1.1 Add 1-2 boiling chips to each 60 mL disposable vial containing sample extract and attach a three-ball micro-Snyder column.

12.3.1.2 Place the sample on the water bath with the bottom of the 60 mL vial partially immersed in water. The water bath temperature should range between 75° to 85° C. After heating to temperature, the balls in the micro-Snyder column should actively chatter but not flood with solvent.

12.3.1.3 Remove the 60 mL vial from the water bath when the extract volume has concentrated to approximately 500 uL. After the unit has cooled, rinse the Snyder column with CH_2Cl_2 , collect solvent into the vial and remove the Snyder column. Transfer the sample aliquot into a 2mL autosampler vial marked and verified with 0.5, 1 and 1.5mL volume markings and adjust the final volume to 1mL.

12.3.2 If GPC cleanup is required as listed in section 12.4, the same concentration technique listed above should be followed but the sample aliquot volume should be taken to approximately 7mL, filtered with a glass syringe and accudisc filter and brought to a 10mL final volume. The sample is now ready to be cleaned by GPC.

12.4 Extract Cleanup and Concentration

12.4.1 GPC Cleanup of Extracts: Sample extracts may have contaminants removed using Gel Permeation Chromatography following the latest version of S-GB-O-032 *Gel Permeation Chromatography.* All QC samples must be subjected to the same cleanup criteria as the samples. GPC cleanup is performed on a project basis.

12.4.2 Once all samples and QC have been subjected to GPC cleanup, assemble a K-D concentrator apparatus by attaching a 10-mL concentrator tube to a 300 ml evaporative flask. Quantitatively transfer GPC'd extract into K-D concentrators with two or three rinses of methylene chloride. Add one or two boiling chips to concentrator apparatus and attach a three-ball macro-snyder column.

12.4.3 Place the K-D apparatus on a warm water bath (75° to 85° C) so that the concentrator tube is totally immersed in the warm water and the entire lower rounded surface of the flask is bathed with water. At the proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of the liquid reaches 3 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes.

12.4.4 Rinse the Snyder column and the evaporating flask with a small amount of methylene chloride. Remove Snyder column and evaporating flask.

12.4.5 Final concentration of the sample extract can be performed by either the Nitrogen Blowdown method or the Micro-snyder column method as follows:

12.4.6 Nitrogen Blowdown Concentration Method: Concentrate each sample to approximately 0.3 ml with nitrogen. Rinse the internal wall of the concentrator tube several times with methylene chloride during the nitrogen blowdown. DO NOT ALLOW THE EXTRACT TO BECOME DRY, OR NEARLY DRY AS THIS WILL RESULT IN LOSS OF ANALYTES. Adjust to a final volume of 0.5 ml using methylene chloride by rinsing down the walls of the concentrator tube. Transfer 0.5 ml of the extract to a prelabelled injection vial and cap with an injection cover.

12.4.7 Micro-Snyder Column Concentration Method: Add a clean boiling chip and attach a two-ball micro-Snyder column to the concentrator tube. Place the apparatus in the small water bath (80° to 85° C). At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the liquid reaches an apparent volume of 2 ml, remove the apparatus from the water bath and allow to drain and cool for at least 10 minutes. DO NOT ALLOW THE EXTRACT TO BECOME DRY, OR NEARLY DRY AS THIS WILL RESULT IN LOSS OF ANALYTES. Remove the Snyder column and rinse its lower joint with approximately 0.2 ml of methylene chloride into the concentrator tube. Use the Nitrogen Blowdown Concentration Method to further concentrate the extract to a final volume of 0.3 ml. Adjust to a final volume of 0.5 ml using methylene chloride by rinsing down the walls of the concentrator tube. Transfer 0.5 ml of the extract to a prelabelled injection vial and cap with an injection cover.

13. QUALITY CONTROL

13.1 All Quality Control measures shall be subjected to exactly the same preparation procedures as those used on actual samples.

13.2 Quality Control measures shall be assessed on an on going basis to determine the usability of the data. The controls measure contamination and statistical measures of accuracy and bias.

13.3 Method blanks shall be performed at a frequency of one per extraction batch, not to exceed 20 environmental samples. This is a negative control used to assess contamination during the preparation process.

13.4 Laboratory Control Spike (LCS) is performed at a frequency of one LCS per extraction batch, not to exceed 20 environmental samples. This is a positive control used to assess the manner in which the samples are prepared.

13.5 A matrix spike (MS) and a matrix spike duplicate (MSD) must be performed for every 20 samples when appropriate sample volume is present, otherwise a laboratory control spike duplicate will be performed. Matrix spikes are used to indicate matrix effects on the analysis of the analytes of interest. The sample used for the MS/D pair is either determined by the client or selected at random from client samples as sample volume allows.

13.6 Surrogate standards must be added to all samples, laboratory control spikes, matrix spikes, and method blanks prior to extraction. Surrogates are used to monitor the efficiency of the method on each sample and possible matrix related effects.

13.7 All quality control samples (MB, LCS, MS, MSD, and duplicate samples) must be analyzed by the same determinative methods as the samples in the batch. The acceptance criteria and corrective actions are described in the determinative method SOPs.

13.8 See Appendix A Table G for a summary.

14. METHOD PERFORMANCE

14.1 There are several requirements that must be met to insure that this procedure generates accurate and reliable data. A general outline of requirements has been summarized below. Further specifications may be found in the Laboratory Quality Manual.

14.1.1 The analyst must read and understand this procedure with written documentation maintained in his/her training file.

14.1.2 An initial demonstration of capability (IDC) must be performed per S-ALL-Q-020, *Orientation and Training Procedures*. A record of the IDC will be maintained in his/her QA file with written authorization from the Laboratory Manager and Quality Manager.

14.1.3 An annual method detection limit (MDL) study will be completed per S-ALL-Q-004, *Method Detection Limit Studies,* for this method and whenever there is a major change in personnel or equipment. The results of these studies are retained in the quality assurance office.

14.1.4 Periodic performance evaluation (PE) samples are analyzed per S-ALL-Q-010, *PE/PT Program,* to demonstrate continuing competence. All results are stored in the QA Office.

15. POLLUTION PREVENTION AND WASTE MANAGEMENT

15.1 The quantity of chemicals purchased is based on expected usage during its shelf life and disposal cost of unused material. Actual reagent preparation volumes reflect anticipated usage and reagent stability.

15.2 Excess reagents, samples and method process wastes are characterized and disposed of in an acceptable manner. For further information on waste management consult the current version of ALL-S-002, *Waste Handling.*

15.3 The laboratory Chemical Hygiene Plan/Health and Safety Plan contains additional information on pollution prevention.

16. REFERENCES

16.1 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, Method 3546, “Microwave Extraction”, Draft Update IVB, 11/2000.

16.2 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, Method 3500B, “Organic Extraction and Sample Preparation”, Update III, 12/1996.

16.3 Pace Analytical Services, Inc – Green Bay, SOP S-GB-O-020, Analysis of Polynuclear Aromatic Hydrocarbons in Soil by GC/MS – SIM.

16.4 Pace Analytical Services, Inc – Green Bay, SOP S-GB-O-044, Determination of Low Level PAHs by GC/MS-SIM in Solid and Biological Matrices.

16.5 Pace Analytical Services, Inc – Green Bay, SOP S-GB-O-032 *Gel Permeation Chromatography*.

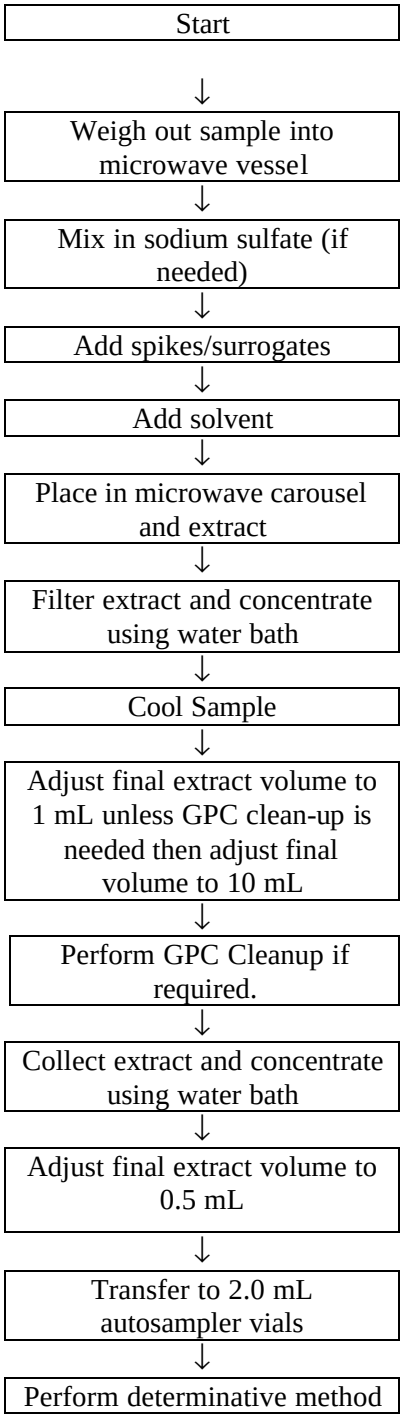
16.6 Pace Analytical Services, Inc – Green Bay, SOP ALL-O-001 *Determination of Semivolatile Organics by GC/MS.*

16.7 Pace Analytical Services, Inc – Green Bay, SOP S-All-GB-O-001 Determination of Semivolatile Organics by GC/MS – Green Bay Addendum.

16.8 Pace Analytical Services, Inc – Green Bay , SOP S-ALL-Q-021, *Sub-Sampling (Sample Homogenization)*

17. TABLES, DIAGRAMS, FLOWCHARTS, APPENDICES, ADDENDA ETC.

FLOWCHART



Appendix A

Tables

Table A **Required Safety Equipment**

Table B **Equipment**

Table C **Supplies**

Table D **Reagents**

Table E **Standards**

Table F **Sample Collection**

Table G **Quality Control**

Table A

REQUIRED SAFETY EQUIPMENT

Item:	Safety Apparel Description	Mandatory for Procedure	Optional
1	Safety Goggles or Glasses	x	
2	Lab Coat	x	
3	Gloves	x	
4	Face Shield		x

Table B
EQUIPMENT

Equipment	Manufacturer	Model(s)	Serial #	Date In Service
Microwave Extractor	CEM	907501	MD9414	July 2007
Heated Water Bath	Organimation	N-EVAP	N/A	March 1992
Pressure Filter Apparatus	N/A	N/A	N/A	July 2007

Table C
SUPPLIES

Supplies	Manufacturer*	Vendor*	Catalog #
2 mL autosampler vials	VWR	VWR	66020-953
Aluminum crimp seals	VWR	VWR	66010-847
Rubber pipette bulb	NJ Rubber	VWR	R5002-2
N-Dex Nitrile Glove Powder free (medium)	Best	Fisher Scientific	6005 PFM
N-Dex Nitrile Glove Powder free (large)	Best	Fisher Scientific	7005L
N-Dex Nitrile Glove (extra large)	Best	Fisher Scientific	7005XL
Labtone glassware detergent	VWR	VWR	21851-006
Tube and bottle brush	VWR	VWR	PK-5-17041-002
5.75” disposable pipets	Fisher Scientific	Fisher Scientific	13-678-20-A
Disposable culture tubes	VWR	VWR	60825-618
25 mL adjustable repipetor	VWR	VWR	40000-066
Lab notebooks	VWR	VWR	51280-108
600 mL beakers	Kimble	Fisher Scientific	13910-145
250 mL beakers	Kimble	Fisher Scientific	14005-250
150 mL beakers	Kimble	Fisher Scientific	02539J
60 degree powder funnel	Pyrex	VWR	30240-047
2.0 mL class A Volumetric Flask	Pyrex	Fisher Scientific	20-814-B
5.0 mL class A Volumetric Flask	Pyrex	Fisher Scientific	29623-300
25.0 mL class A Volumetric Flask	Pyrex	Fisher Scientific	10-210-A
50.0 mL class A Volumetric Flask	Pyrex	Fisher Scientific	10-210-B
9 oz Amber jars	QEC	QEC	2124-0009
33 ml stainless steel cells	Dionex	Dionex	049562
Cellulose filters	Dionex	Dionex	049458
60 mL collection vials	I-Chem	VWR	405531
250 mL K-D flasks	HGF	HGF	
25 mL Concentrator Tubes	HGF	HGF	
10 mL Concentrator Tubes	HGF	HGF	
Micro distilling columns	Kontes	VWR	569261-0324
Stainless Steel Spatula	VWR	VWR	
25 uL gastight syringe	Hamilton	Fisher Scientific	24559
50 uL gastight syringe	Hamilton	Fisher Scientific	111111
100 uL gastight syringe	Hamilton	Fisher Scientific	13-684-100
250 uL gastight syringe	Hamilton	Fisher Scientific	81100
500 uL gastight syringe	Hamilton	Fisher Scientific	81217
1000 uL gastight syringe	Hamilton	Fisher Scientific	1482425
Pyrex baking dish	Corning	---	6001078

*** Equivalent supplies may be used.**

Table D

REAGENTS

Reagent	Purity	Manufacturer	Vendor	Catalog #
Methylene Chloride	Pesticide Quality	Burdick & Jackson	Fisher Scientific	CS300-200
Acetone	Pesticide Quality	Burdick & Jackson	Fisher Scientific	010-4
Di-ionized Water	Type I ASTM	----	----	----
Ottawa Sand	-----	Fisher Scientific	Fisher Scientific	S23-3
Sodium sulfate (anhydrous; 10-60 mesh)	ASC grade	Fisher Scientific	Fisher Scientific	MK802406
Nitrogen	99.99%	Whatman	----	----

Table E
STANDARDS

Standard	Acronym	Concentration	Direction found in Section:	Alias
SV INTERNAL STANDARD	STOCK	4000 PPM	Reagents & Standards	INT. STD. STOCK
B/N SURROGATE MIX	STOCK	5000 PPM	Reagents & Standards	SURR. STOCK
PAH STANDARD MIX	STOCK	100 PPM	Reagents & Standards	CAL. STOCK
PAH STANDARD MIX	STOCK	500 PPM	Reagents & Standards	SPIKE STOCK
PAH INTERNAL STANDARD (SOIL)	INT. STD. INTER.	2000 PPM	Reagents & Standards	INT. STD. INTER.
B/N SURROGATE STANDARD	SURR. INTER.	150 PPM	Reagents & Standards	SURR SPIKE
SV ACID SURROGATE MIX	STOCK	7500 ug/mL	Reagents & Standards	SURR STOCK
BNA CUSTOM STANDARD MIX	STOCK	200 ug/mL	Reagents & Standards	SPIKE STOCK
N-NITROSODIPHENYLAMINE	STOCK	5000 ug/mL	Reagents & Standards	SPIKE STOCK

Table F
SAMPLE COLLECTION, PRESERVATION, SHIPMENT AND STORAGE

Matrix	Prep Method	Container(s)	Preservation	Shipment Conditions	Lab Storage Conditions
SOIL	SW 846 3545	Amber jar with teflon lined lid	None	On ice 4+/- 2° Celsius	Refrigerate 4+/- 2° Celsius

Table G
QUALITY CONTROL

Preparation Method ⇨ Quality Control Measure ⇩	**SW846 8270C**
Initial Calibration	Minimum of five levels; lowest level near but above MDL.
Method Blank	One per batch of samples, up to 20 enviromental samples, whichever is more frequent.
DFTPP Tune Check	One at the beginning of a 12 hour time clock or more frequent.
Calibration Verification Standard (CVS)	One at the beginning of a 12 hour time clock or more frequent.
Independent Calibration Verification	Indepenent source run immediately after the calibration curve.
Laboratory Control Spike	One LCS per batch of samples, up to 20 environmental samples, whichever is more frequent.
Matrix Spike and Duplicate	One pair per batch of samples, up to 20 environmental samples, whichever is more frequent.
Internal Standards	Added to every sample.
Method Validation	Annually
MDL	Annually
Surrogate Standards	Added to every sample.

18. REVISIONS

Document Number	Reason for Change	Date
S-GB-O-045-Rev. 0	First Issue	21Sept2007
S-GB-O-045-Rev.1	Added Base/Neutral/Acid Information to SOP Section 12.1.9 – Added filtering can be done gravimetrically.	24Mar2008

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STANDARD OPERATING PROCEDURE

Determination of Parent and Alkylated PAH Compounds in Solid and Liquid Matrices by Gas Chromatography/Mass Spectrometry (GC/MS):

Capillary Column Technique With Selective Ion Monitoring

SOP NUMBER:	S-MN-O-561-Rev.00
EFFECTIVE DATE:	25 March 2009
SUPERSEDES:	First Issue

APPROVAL

Laboratory General Manager — Date: 3/25/2009

Laboratory Quality Manager — Date: 3/25/09

ANNUAL REVIEW

SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE APPROVAL. SOP IS VALID FOR ONE YEAR FROM DATE OF LAST SIGNATURE.

Signature	Title	Date

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1. PURPOSE

1.1. The purpose of this Standard Operating Procedure (SOP) is to set forth the procedure used for the determination of parent and alkylated polyaromatic hydrocarbons in solids and liquids that are partitioned into an organic solvent that is compatible with gas chromatography/mass spectrometry.

2. SCOPE AND APPLICATION

2.1. This method is used to determine the concentration of semivolatile organic compounds in extracts prepared from all types of solid and liquid matrices.

3. SUMMARY OF METHOD

3.1. A measured amount of sample, approximately 1000 mL for liquids and 30 g for solids, is extracted with methylene chloride using an appropriate extraction technique. The methylene chloride extract is dried, concentrated to a volume of 1 mL, and analyzed by GC/MS. Qualitative identification of the analyte of interest in the extract is performed using the retention time and relative abundance of at least one characteristic mass. Quantitation is performed using the internal standard technique with a single characteristic mass in coordination with the calibration curve.

4. INTERFERENCES

4.1. Matrix interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in the ion current profiles. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks.

4.2. Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature of the environment being sampled.

4.3. An interference that is unique to selected ion monitoring techniques can arise from the presence of an interfering compound containing the quantitation mass ion. This event results in a positive interference to the reported value for the compound of interest. This interference is controlled to some degree by acquiring data for a confirmation ion. If the ion ratios between the quantitation ion and the confirmation ion are not within the specified limits, then interferences may be present.

5. SAFETY

5.1. The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable. Cautions are included for known extremely hazardous materials

5.2. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of Material Safety Data Sheets (MSDS) and a formal safety plan are available to all personnel involved in the chemical analysis.

5.3. MSDS are located in a centralized location and should be consulted prior to handling samples and standards.

6. DEFINITIONS

6.1. Definitions of terms found in this SOP are found in the glossary section of the Pace Analytical Services, Inc. Quality Manual.

7. SAMPLE COLLECTION, PRESERVATION AND HANDLING

7.1. CONTAINERS

7.1.1. Liquid samples should be collected in 1-liter amber glass bottles with Teflon-lined lid.

7.1.2. Solid samples should be collected in a 4 oz glass jar with Teflon-lined lid.

7.2. STORAGE

7.2.1. The samples must be refrigerated at 4°C ± 2°C from the time of collection until extraction. The extracts must also be kept refrigerated until analysis.

7.3. HOLDING TIME

7.3.1. The water samples must be extracted within 7 days from date of collection. Soil samples must be extracted within14 days of collection. The samples extracts must be analyzed within 40 days of sample extraction.

8. EQUIPMENT AND SUPPLIES

8.1. Hewlett-Packard gas chromatograph/mass spectrometer model 5973/ 6890 and Hewlett-Packard Autosampler model 7683A (or equivalent).

8.2. Column – DB-5MS, 30 m x 0.25 mm (ID) bonded-phase silicone coated fused silica capillary column, 0.5 um film thickness (or equivalent).

8.3. Data system.

8.3.1. Acquisition software (HP Chemstation B.02.04 or equivalent)

8.3.2. Processing software – Target version 4.14 or equivalent.

8.4. Recommended GC/MS operating conditions:

Dwell Time per ion:	25 to 100 µS
Temperature Program:	75˚C, hold for 1 minutes
	20˚C/min to 340˚C held for 0.5 minutes
Injection Temperature:	275˚C
Transfer Line Temperature:	300˚C
Sample Volume:	2 µL
Carrier Gas:	Helium

9. REAGENTS AND STANDARDS

9.1. All surrogate and matrix spike solutions are verified prior to use per the ALL–Q–025.

9.2. All calibrations are verified using a second source standard. The second source is evaluated as a CCV or a LCS and the response must be within the acceptance criteria outlined in the ALL-Q-025 SOP.

9.3. Standards are brought to their final volume with methylene chloride except for the MS/SS spikes which are diluted in acetone.

9.4. Alkylated Window Check Standard – used to assess and evaluate alkylated groups. This standard is analyzed to determine the window for the C2-Naphthalene, C3-Naphthalene, etc… (see Attachment I) this window is then used to integrate the corresponding areas associated with

C2-Naphthalene, C3-Naphthalene, etc in samples. The alkylated groups are quantitated against the parent compounds curve.

Compound	Concentration	Amount	Final Volume	Int. Concentration
Coal Tar	neat	100mg	5 mL	20000 µg/mL

Compound	Concentration	Amount	Final Volume	Final Concentration
Int. Solution	20000 µg/mL	1.0 ml	5 ml	4000 µg/mL

9.5. SURROGATES

9.5.1. SIM Intermediate Surrogate Stock

Compound	Concentration	Amount	Final Volume	Final Concentration
B/N Surrogate	5000 µg/mL	1.0 ml	10 ml	500 µg/mL

9.5.2. SIM Stock Standard (spiking solution)/Ical Stock Standard

Compound	Concentration	Amount	Final Volume	Final Concentration
SIM Custom Mix	250 µg/mL	0.200 mL	5 ml	10 µg/mL
SIM Intermediate SS	500 µg/mL	0.020 mL	5 ml	2 µg/mL

9.6. MATRIX SPIKES

9.6.1. Example for PAH

Compound	Concentration	Amount	Final Volume	Final Concentration
SIM Cust. Mix	250 µg/mL	0.800 ml	200 ml	1 µg/mL

9.7. INITIAL CALIBRATION STANDARDS

9.7.1. Initial Calibration Example for PAH

Level	Parent Concentration	Amount	Final Volume	Final Conc PAH	Final Conc. Surrogate
1	10 µg/mL	0.004 ml	1 ml	0.04 µg/mL	0.008µg/mL
2	10 µg/mL	0.030 ml	1 ml	0.3 µg/mL	0.06µg/mL
3	10 µg/mL	0.050 ml	1 ml	0.5 µg/mL	0.1µg/mL
4	10 µg/mL	0.100 ml	1 ml	1.0 µg/mL	0.2µg/mL
5	10 µg/mL	0.300 ml	1 ml	3.0 µg/mL	0.6µg/mL
6	10 µg/mL	0.500 ml	1 ml	5.0 µg/mL	1.0µg/mL
7	10 µg/mL	0.700 ml	1 ml	7.0 µg/mL	1.4µg/mL
8	10 µg/mL	1.0 ml	1 ml	10.0 µg/mL	2.0µg/mL

9.8. Tune Standard

Solution	Parent Concentration	Amount	Final Volume	Final Concentration
DFTPP	1000 µg/mL	0.05 mL	1 mL	50 µg/mL

9.9. SIM Internal Standard

Solution	Parent Concentration	Amount	Final Volume	Final Concentration
Internal Standard Mix	4000 µg/mL	0.625 mL	10 mL	250 µg/mL

10. CALIBRATION

10.1. DFTPP

10.1.1. Section 7.3.1.2 and Table 3 of SW846 method 8270C allows for the use of alternate tuning criteria (such as CLP or 525 criteria). The CLP Statement of Work (SOW) states that a tune is not required (applicable) for PAH. The tune standard (DFTPP) will be analyzed for diagnostic purposes, and the ratios used will be those listed in the CLP criteria-- even though it is not necessary to pass ratios, tailing, or breakdown. The 12 hour window to analyze samples starts at the injection time of the continuing calibration standard. The diagnostic criteria are listed in Section 10.1.3.

10.1.2. When evaluating peaks, SIM is closer to GC than full scan mass spectrometry. The ions are set in the method, and will not show interferences from ions that are not monitored. Because of this, the retention time is stressed more than spectral matches for peak identification. The purpose of a tune in full scan mode is to ensure that the mass spectrometer is in a correct ratio of ions to optimize method performance throughout the entire analytical run. Since SIM is more like a GC run, and the ions are set in separate windows across the analytical run, the tune is considered not applicable.

10.1.3. Diagnostics

The tune can still serve as a troubleshooting guide for the analyst to assess instrumentation issues such as column degradation.

10.1.3.1 If the instrument has trouble passing calibrations consistently, PCP is present, and DDT is not breaking down excessively, then the result of any calibration issues is more likely due to standard degradation and not the system itself.

10.1.3.2 Conversely, if the system has trouble consistently passing calibrations or recoveries are inconsistent from run to run, PCP is not present, and/or DDT is breaking down, the result is more than likely due to a system issue. This might indicate instrument maintenance should be performed; such as injection port maintenance, clipping/replacing the column, cleaning split lines, cleaning weldments, or replacing columns.

10.2. INITIAL CALIBRATION

10.2.1. The mass spectrometer is operated in the selected ion monitoring (SIM) mode using appropriate windows to include the quantitation and confirmation masses listed in Table 1.

10.2.2. Analytes are quantified using the internal standard with the closest retention time. If interferences are noted, the next most intense ion is used as the quantitation ion.

10.2.3. Prior to the analysis of samples, the GC/MS system must be initially calibrated at a minimum of five concentrations to determine the linearity of response utilizing calibration standards.

10.2.4. Calculate response factors (RFs) for each compound as outlined in Equation 1.

10.2.5. The average RF should be calculated for each compound, and the percent relative

standard deviation (%RSD) is calculated for each compound (as outlined in Equation 2). The %RSD must be ≤15% for each compound, or a different curve fit must be utilized. The correlation coefficient must be ≥0.995 if a linear regression is used. The COD must be ≥0.990 if a quadratic curve is used with a minimum of 6 levels.

10.2.6. The alkylated groups of analytes (C2-Naphthalene, C3-Naphthalene, etc) do not have commercial standards available for calibrations. Therefore, the windows for these groupings will be determined by the analysis of a coal tar standard (or equivalent) prior to sample analysis each day. These windows will be quantitated utilizing the parent compound for the group. The alkylated groups of analytes will utilize the curve and RF generated from Naphthalene to quantitate the windows. C1-Fluorenes, C2-Fluorenes, etc, will utilize the curve and RF generated from Fluorene to quantitate from, and so on.

10.3. INITIAL CALIBRATION VERIFICATION (ICV)

10.3.1. The ICV must be prepared from source materials independent of the calibration standards. It must contain all target compounds in the calibration (excluding the alkylated groups) and meet the acceptance criteria outlined in the ALL-Q-025 SOP.

10.3.2. SIM External Check (ICV)

10.3.2.1. SIM External Check Stock

Compound	Vendor	Concentration	Amount	Diluent Volume	Final Concentration
SIM Int. SS	Restek	500 µg/mL	.040 mL	1mL	20µg/mL
B/N Comp. Mix	Accustandard	2000µg/mL	.050 mL	1mL	100µg/mL
Comp. Mix #2	Accustandard	2000µg/mL	.050 mL	1mL	100µg/mL
Carbazole	Accustandard	2000µg/mL	.050 mL	1mL	100µg/mL
1-Methylnaphthalene	Accustandard	2000µg/mL	.050 mL	1mL	100µg/mL

10.3.2.2. SIM External Check

Compound	Concentration	Amount	Diluent	Final Concentration.
SIM Ext Check Stock.	100µg/mL	0.05mL	1mL	5µg/mL
Benzo(e)pyrene	50µg/mL	0.100mL	1mL	5µg/mL

10.4. CONTINUING CALIBRATION VERIFICATION (CCV)

10.4.1. A calibration standard containing each compound of interest must be analyzed every 12 hours. Compare the response factor data from the standards with the average response factor from the initial calibration for a specific instrument. Calculate the percent difference, as detailed in Equation 4.

10.4.2. The percent difference for each compound should be ≤20%, or 80-120%. A continuing calibration may be utilized above 120% when non-detect results are found in the associated samples. Continuing calibration criteria below 80% should not be utilized unless approval is given from the client and/or the data is qualified.

10.4.3. The internal standard responses and retention times in the calibration check standard must be evaluated immediately after or during data acquisition.

10.4.3.1. If the retention time for any internal standard changes by more than 30 seconds from the last check calibration, the analytical system must be inspected for malfunctions and corrections must be made.

10.4.3.2. If the EICP area for any of the internal standards changes by a factor of two, (-50% to +100%) from the last daily calibration standard check, the system must be inspected for malfunctions and corrections must be made.

11. PROCEDURE

11.1. SAMPLE PREPARATION

11.1.1. Samples are extracted and prepared in accordance with separate extraction procedures. See SOPs MN-O-506 and MN-O-540.

11.2. GC/MS ANALYSIS

11.2.1. The extract obtained from sample preparation should be spiked at 2.5 µg/mL with internal standard solution.

11.2.2. A typical days analysis would consist of a tune, continuing calibration, and window check, followed by QC and samples.

11.2.3. Analysis of the Alkylated Window Check needs to be evaluated prior to sample evaluation for the alkylated groupings. Each group has a specific ion used for monitoring as outlined in Table 1. The window check is processed and evaluated using Target. The windows for each group should be identified and used to evaluate the concurrent groups in the associated samples in the days run. The groups are set by assessing the ion group and drawing an integration that encompasses the retention time that corresponds to the window check standard. See Attachment 1 for example integrations and windows. Integration of these areas should be done on pattern recognition. Integrations for Alkylated PAH groups will require manual integrations.

11.2.4. If the response for any quantitated ion exceeds the initial calibration curve range of the GC/MS system, extract dilution must take place. Additional internal standard must be added to the diluted extract to maintain the required 2.5 µg/mL of each internal standard in the extract volume. The diluted extract must be reanalyzed.

11.2.5. Perform all qualitative and quantitative measurements as described in section 11.3 - Data Interpretation.

11.2.6. Samples can be analyzed upon successful completion of the initial calibration activities. When 12 hours have elapsed since the initial QC was completed, it is necessary to conduct a calibration check analysis.

11.2.7. Internal Standards Evaluation - Internal standard responses and retention times in all samples must be evaluated.

11.2.7.1. If the retention time for any internal standard changes by more than 30 seconds from the latest daily calibration standard, the analytical system must be inspected for malfunctions, with corrections made as required.

11.2.7.2. If the extracted ion current profile (EICP) area for any internal standard changes by more than a factor of two (-50% to 100%) from the latest daily

calibration standard, the MS system must be inspected for malfunctions and corrections made accordingly.

11.2.8. Each analytical run must also be checked for saturation (the level at which an individual compound will saturate the detection system). This a function of the overall system sensitivity and the mass spectral characteristics of that compound. The initial method calibration requires that the system should not be saturated for high response compounds. If any compound in any sample exceeds the analytical range, that sample must be diluted, the internal standard concentration readjusted, and the sample re-injected, as described in specific methods.

11.3. DATA INTERPRETATION

11.3.1. Qualitative Analysis – Target Analytes

11.3.1.1. The target compounds are identified by comparison of the sample mass spectrum to the mass spectrum of a standard of the suspected compound. Two criteria must be satisfied to verify the identifications: 1) elution of the sample component at the same GC relative retention time as the standard component, and 2) correspondence of the sample component and standard component mass spectra.

11.3.1.2. For establishing correspondence of the GC relative retention time (RRT), the sample component RRT must compare within ± 0.06 RRT units of the RRT of the standard component. For comparison purposes, the RRT should be evaluated against the standard analyzed prior to the sample. See Table 1 for internal standard assignment.

11.3.1.3. For comparison of standard and sample component mass spectra, mass spectra obtained on the GC/MS system used in the analysis are required. The ions from the reference mass spectrum are defined as the three ions of greatest relative intensity, or any ions over 30% relative intensity, if less than three such ions occur in the reference spectrum. The ions used are shown in Table 1.

11.3.1.4. The baseline to valley between isomers must be <25% of the sum of the two peak heights, or the result must be reported as isometric pairs.

11.3.1.4.1. All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100%) must be present in the sample spectrum.

11.3.1.4.2. The relative intensities of ions must agree within ±20% between the standard and sample spectra. In addition, the relative intensities of the ions should maximize within one scan of each other.

11.3.1.4.3. Ions greater than 10% in the sample spectrum must be considered and accounted for by the analyst making the comparison.

11.4. QUANTITATION

11.4.1. Target components identified shall be quantified by the internal standard method. The internal standard used shall be the one nearest the retention time to that of a given analyte.

11.4.1.1. The EICP area of characteristic ions of analytes listed in Table 1. The average response factor (RF) from the initial calibration is used to calculate the concentration in the sample.

11.4.1.2. Secondary ions may be used if interferences are present. The area of a secondary ion cannot be substituted for the area of a primary ion unless a response factor is calculated using the secondary ion.

11.4.2. Calculate the concentration in the sample using the average response factor from the initial calibration and Equation 5.

11.4.3. Calculate surrogate standard recovery on all samples, blanks and spikes. Determine if recovery is within limits and report on appropriate form. (See Equations 6 and 7) If recovery is not within internally generated limits, the following is required:

11.4.3.1. Check to be sure there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.

11.4.3.2. Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.

11.4.3.3. Re-extract and reanalyze the sample if the above steps do not solve the recovery problem, assuming there is sufficient sample volume remaining.

11.5. CALCULATIONS

11.5.1. Calculate response factors (RFs) for each compound as follows:

Equation 1

$$RF = \frac{A_x C_{is}}{A_{is} C_x}$$

Where: A_x = Area of the characteristic ion for the compound being measured.
A_{is} = Area of the characteristic ion for the specific internal standard.
C_{is} = Concentration of the specific internal standard (µg /mL).
C_x = Concentration of the compound being measured (µg /mL).

11.5.2. The percent relative standard deviation (%RSD) is calculated as follows:

Equation 2

$$\%RSD = \frac{SD}{\overline{RF}} x100$$

Where: $\overline{RF}$ = Mean of the Response Factors mentioned above.
SD = Standard Deviation of initial response (see Equation 3)

Equation 3

$$SD = \sqrt{\frac{\sum_{i=1}^{n}\left(RF_1 - \overline{RF}\right)^2}{n-1}}$$

Where: RF_1 = Each individual response factor
$\overline{RF}$ = Mean of the Response Factors mentioned above.
N = Number of response factors

11.5.3. The Percent Difference (%D) is calculated as follows:

Equation 4

$$\%Difference = \frac{\left(RF_i - RF_c\right)}{RF_i} x100$$

Where: Rfi = Average response factor from initial calibration
RF_c = Response factor from current verification check standard

11.5.4. The concentration of analyte in the sample is calculated as follows:

Equation 5

$$\text{Concentration (ug/L)} = \frac{(A_x)(I_s)(V_t)}{(A_{is})(\overline{RF}_i)(W_o)(V_i)}$$

$$\text{Concentration (ug/kg)} = \frac{(A_x)(I_s)(V_t)}{(A_{is})(\overline{RF}_i)(W_s)(V_i)\left(\frac{100-M}{100}\right)}$$

Where: A_x = Area of the characteristic ion for the compound to be measured
A_{is} = Area of the characteristic ion for the internal standard
I_s = Amount of internal standard injected in nanograms (ng)
W_o = Volume of sample extracted in liters
V_i = Volume of extract injected (µL)
V_t = Volume of total extract (mL)
$\overline{RF}$ = Average response factor from initial calibration
W_s = Weight for soil in kg
M = % Moisture

11.5.5. Calculate the Matrix Spike Percent Recovery as follows:

Equation 6

$$\%\,Recovery = \frac{SSR - SR}{SA} x100$$

Where: SSR= Spike Sample Results
SR = Sample Result
SA = Spike Added from spiking mix

11.5.6. The laboratory will calculate the relative percent difference between the matrix spike and matrix spike duplicate. The relative percent differences (RPD) for each component are calculated using the following equation:

Equation 7

$$RPD = \frac{|A - B|}{(A + B)/2} x100$$

Where: RPD = Relative Percent Difference
A = First Sample Value
B = Second Sample Value (duplicate)

12. QUALITY CONTROL

12.1. Method Blank

12.1.1. A method blank is an aliquot of a clean matrix that is carried through the entire analytical scheme (extraction, concentration, and analysis). The volume or weight used for the method blank must be approximately equal to the sample aliquots being processed.

12.1.2. Method blank analysis must be performed at the following frequency: once each batch, with every 20 samples of similar concentration and/or sample matrix, or whenever samples are extracted by the same procedure, whichever is more frequent. The method blank associated with a specific set or group of samples must be analyzed on each GC/MS system used to analyze that specific group or set of samples.

12.1.3. An acceptable method blank must contain results less than the reporting limit. If a laboratory method blank exceeds the criteria, the laboratory must consider the analytical system out of control, the source of the contamination must be investigated, and appropriate corrective measures must be taken and documented.

12.2. Laboratory Control Spike (LCS)

12.2.1. An LCS and an LCS duplicate shall be analyzed at a frequency of each analytical batch, or once per 20 samples, whichever is more frequent. An LCS consists of a control matrix spiked with all target analytes spiked and reported.

12.2.2. NOTE: An LCS duplicate is only required if insufficient sample is available to obtain a matrix spike and matrix spike duplicate.

12.2.3. LCS results are used to verify that the precision and bias of the analytical process are within control. The results of the LCS are compared to internally generated control limits established for both precision and bias to determine usability of the data. The results of analytes with recoveries outside the acceptance criteria are qualified on the final report.

12.2.3.1. If the analytes exceed the control limits, check calculation or standard preparation documentation to assure there are no errors; check internal standard and spiking solutions for degradation, contamination, etc.; also, check instrument performance. Reanalyze to confirm the initial results.

12.2.3.2. If no cause is determined, evaluate the associated samples for impact on the results. If the LCS is biased high and the associated samples are non-detect, report the data and qualify the LCS accordingly. If the LCS is biased low, all data associated is suspect for low bias.

12.2.3.3. Based on large analyte lists and poor performers, it may not be statistically possible to achieve passing recoveries for all analytes. Based on NELAC guidance, marginal exceedance limits are followed per Pace Analytical Services, Inc Quality Manual. Associated data is qualified accordingly based on the marginal exceedance table in the quality manual.

12.2.3.4. Re-extract and re-analyze the batch if the laboratory is unable to identify a definitive problem with the original extraction. If there is insufficient sample volume available for re-extraction, contact the PM to notify the client. The data may be reported with appropriate qualifiers if re-sampling may not occur.

12.3. Surrogate

12.3.1. Each sample (including MS/MSD, LCS/LCSD, and blanks) are spiked with surrogate compounds prior to extraction. The surrogate spiking compounds shown in Table 2 are used to fortify each sample or blank with the proper concentrations. Performance based criteria are generated from laboratory results.

12.3.2. Surrogate spike recovery must be evaluated for acceptance by determining whether the concentration (measured as percent recovery) falls inside the recovery limits established by the laboratory.

12.3.2.1. Reagent Blank Surrogate Recovery

12.3.2.1.1. When the surrogate recovery for any one surrogate compound is outside of the recovery limits for a reagent blank, the laboratory must take the following actions:

12.3.2.1.1.1. Check calculations to assure there are no errors; check internal standard and surrogate spiking solutions for degradation, contamination, etc.; also, check instrument performance.

12.3.2.1.1.2. Re-analyze the extract if the above fails to reveal the cause of the non-compliant surrogate recoveries.

12.3.2.1.1.3. If the measures listed in the preceding paragraphs fail to correct the problem, the analytical system

must be considered out of control. The problem MUST be corrected before continuing, unless approval to continue is obtained from the client. If the recovery is above criteria, results are non-detect, and it is determined that the system is within control, the data may be reported.

12.3.2.1.1.4. This may mean recalibrating the instrument but it may also mean more extensive action. The specific corrective action is left up to the GC/MS supervisor.

12.3.2.2. Sample Surrogate Recovery

12.3.2.2.1. When the surrogate recovery of any one surrogate compound is outside of the recovery limits for a sample, it is the responsibility of the laboratory to establish that the deviation is not due to laboratory problems.

12.3.2.2.2. The laboratory will document deviations outside acceptable quality control limits by taking the following actions:

12.3.2.2.2.1. Check calculations to assure there are no errors; check internal standard and surrogate spiking solutions for degradation, contamination, etc.; and, check instrument performance.

12.3.2.2.2.2. If there is obvious matrix interference, the data may be footnoted appropriately and reported.

12.3.2.2.2.3. If no obvious matrix interference is present, re-analyze the sample or extract. If reanalysis of the sample or extract solves the problem, then only the sample data from the analysis with surrogate spike recoveries within the method limits will be submitted.

12.3.2.2.2.4. Re-extract and re-analyze the sample if the laboratory is unable to identify a definitive problem with the original extraction.

12.3.2.2.2.5. Report the surrogate spike recovery data and the sample data from the original extraction.

12.3.2.2.2.6. All deviations that cannot be corrected by the points listed above will be narrated in a discrepancy report and the client notified.

12.4. Matrix Spike/Matrix Spike Duplicate (MS/MSD)

12.4.1. MS/MSD Frequency of Analysis - A matrix spike and matrix spike duplicate must be performed once each batch or with every twenty (20) samples of similar concentration and/or similar sample matrix, whichever is more frequent. (Note: If sample is not available, an LCS and an LCS duplicate should be analyzed.)

12.4.2. All target compounds (with the exception of the alkylated groups) are used to prepare

matrix spiking solutions. The analytical protocols require that a uniform amount of matrix spiking solution be added to the sample aliquots prior to extraction.

12.4.3. Samples requiring optional dilutions and chosen as the matrix spike/matrix spike duplicate samples, must be analyzed at the same dilution as the original unspiked sample.

12.4.4. Individual component recoveries of the matrix spike are calculated using Equation 6.

12.4.5. The reproducibility of RPD of the MS/MSD is calculated using Equation 7.

12.4.6. The matrix spike and matrix spike duplicate are not utilized to determine whether the batch is acceptable. Recoveries and RPDs outside the control limits are qualified on the final report.

13. METHOD PERFORMANCE

13.1. There are several requirements that must be met to ensure that this procedure generates accurate and reliable data. A general outline of requirements has been summarized below. Further specifications may be found in the Laboratory Quality Manual and specific Standard Operating Procedures.

13.1.1. The analyst must read and understand this procedure with written documentation maintained in his/her training file which is located in the QA Office.

13.1.2. An initial demonstration of capability (IDC) must be performed per SOP All-Q-020. A record of the IDC will be maintained in his/her file with written authorization from the Laboratory Manager and Quality Manager. Results are stored in the QA office.

13.1.3. An annual minimum detection limit (MDL) study following SOP ALL-Q-004 will be completed for this method and whenever there is a major change in personnel or equipment. Results are stored in the QA Office.

13.1.4. Periodic performance evaluation (PE) samples are analyzed periodically to demonstrate continuing competence per SOP All-Q-010. Results are stored in the Quality office.

14. POLLUTION PREVENTION AND WASTE MANAGEMENT

14.1. The quantity of chemicals purchased is based on expected usage during its shelf life and disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

14.2. The Environmental Protection Agency (USEPA) requires that laboratory waste management practice be consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are characterized and disposed of in an acceptable manner. For further information on waste management consult SOP ALL-S-002 *Waste Handling*.

15. REFERENCES

15.1. ASTM D7363 Determination of Parent and Alkyl Polycyclic Aromatics in Sediment Pore Water

15.2. NOAA Technical Memorandum NOS ORCA 130, March 1998

15.3. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition, Update I, Method 8000B

15.4. Contract Laboratory Program Statement of Work (SOW) for Multi-Media, Multi-Concentration Organics Analysis (SOM01.2)

16. TABLES, DIAGRAMS FLOWCHARTS, ATTACHMENTS, APPENDICES, ETC.

16.1. Table 1 – Analytes and Quantitation Limits

16.2. Table 2 – Surrogates Spiking Compounds

16.3. Table 3 – DFTPP

16.4. Attachment I – Alkylated Window Check Integration Examples

17. REVISIONS

Document	Change	Date
S-MN-O-561-rev.00	First Issue	25Feb2009

Table 1: Analytes/SIM Windows/Ions

Monitoring Ions*	Analyte Name	Approximate Retention Times (minutes)	Alkylated Quant Compound (curve used for quantitation)	SIM Group	Internal Std Reference
128, 127	Naphthalene	3.4		1	Naphthalene-d8
142, 141, 115	2-Methylnaphthalene	4.2		2	Naphthalene-d8
142, 141, 115	1-Methylnaphthalene	4.3		2	Naphthalene-d8
152, 151, 153	Acenaphthylene	5.3		3	Acenaphthene-d10
153, 154, 152	Acenaphthene	5.5		3	Acenaphthene-d10
166, 165	Fluorene	6.2		3	Acenaphthene-d10
178, 179	Phenanthrene	7.4		4	Phenanthrene-d10
178, 179	Anthracene	7.5		4	Phenanthrene-d10
202, 200, 101	Fluoranthene	8.9		5	Phenanthrene-d10
202, 200, 101	Pyrene	9.2		5	Chrysene-d12
228, 226, 113	Benzo(a)anthracene	10.8		6	Chrysene-d12
228, 226, 114	Chrysene	10.9		6	Chrysene-d12
252, 250, 126	Benzo(b)fluoranthene	12.1		7	Perylene-d12
252, 250, 126	Benzo(k)fluoranthene	12.1		7	Perylene-d12
252, 250, 125	Benzo(e)pyrene	12.4		7	Perylene-d12
252, 250, 126	Benzo(a)pyrene	12.5		7	Perylene-d12
276, 138, 137	Indeno(1,2,3-cd)pyrene	13.6		8	Perylene-d12
278, 139	Dibenz(a,h)anthracene	13.6		8	Perylene-d12
276, 138, 137	Benzo(g,h,i)perylene	13.8		8	Perylene-d12
142.1	C1-Naphthalene	3.8-4.4	2-Methylnaphthalene	2	Naphthalene-d8
156.1	C2-Naphthalene	4.3-5.2	Naphthalene	2	Naphthalene-d8
170.1	C3-Naphthalene	4.8-7.2	Naphthalene	3	Naphthalene-d8
184.1	C4-Naphthalene	5.5-8.0	Naphthalene	3,4,5	Naphthalene-d8
180.1	C1-Fluorene	5.5-9.0	Fluorene	3,4,5	Acenaphthene-d10
194.1	C2-Fluorene	5.5-10	Fluorene	3,4,5	Acenaphthene-d10
208.1	C3-Fluorene	6.7-10	Fluorene	4,5	Acenaphthene-d10
192.1	C1-Phenanthrene/Anthracene	7.0-8.8	Phenanthrene	4,5	Phenanthrene-d10
206.1	C2-Phenanthrene/Anthracene	7.5-9.5	Phenanthrene	4,5	Phenanthrene-d10
220.1	C3-Phenanthrene/Anthracene	8-10.4	Phenanthrene	5,6	Phenanthrene-d10
234.1	C4-Phenanthrene/Anthracene	9.4-10.5	Phenanthrene	5,6	Phenanthrene-d10
216.1	C1-Fluranthene/Pyrene	8.5-11	Fluoranthene	5,6	Phenanthrene-d10
242	C1-Benzo(a)anthracene/Chrysene	9.5-11.5	Benzo(a)anthracene	5,6	Chrysene-d12
256	C2-Benzo(a)anthracene/Chrysene	9.5-12.5	Benzo(a)anthracene	5,6,7	Chrysene-d12
270	C3-Benzo(a)anthracene/Chrysene	9.5-14	Benzo(a)anthracene	5,6,7,8	Chrysene-d12
284	C4-Benzo(a)anthracene/Chrysene	12-13.5	Benzo(a)anthracene	7,8	Chrysene-d12

***Bold** Ions indicate quant ions

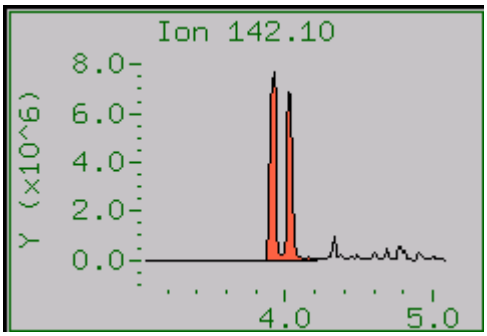
Table 2: Surrogate Spiking Compounds

Compound	Fraction	Extract conc. (µg/mL)
Nitrobenzene-d_5	BN	1.0
2-Fluorobiphenyl	BN	1.0
Terphenyl-d_{14}	BN	1.0

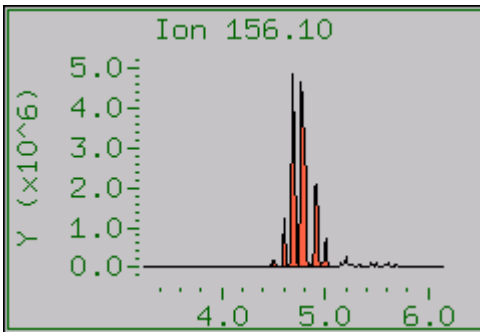
Table 3: Ion Abundance Criteria For DFTPP

Mass (M/z)	Relative Abundance Criteria	Purpose of Checkpoint
51	10-80% of the base peak	Low-mass sensitivity
68	< 2% of Mass 69	Low-mass resolution
70	< 2% of Mass 69	Low-mass resolution
127	10-80% of the base peak	Low-to mid-mass sensitivity
197	< 2% of Mass 198	Mid-mass resolution
198	Base peak or > 50% of Mass 442	Mid-mass resolution and sensitivity
199	5-9% of Mass 198	Mid-mass resolution and isotope ratio
275	10-60% of the base peak	Mid- to high-mass sensitivity
365	> 1% of the base peak	Baseline threshold
441	Present and < Mass 443	High-mass resolution
442	Base peak or > 50% of Mass 198	High-mass resolution and sensitivity
443	15-24% of Mass 442	High-mass resolution and isotope ratio

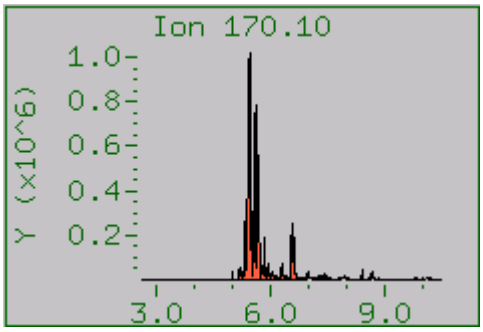
Attachment 1



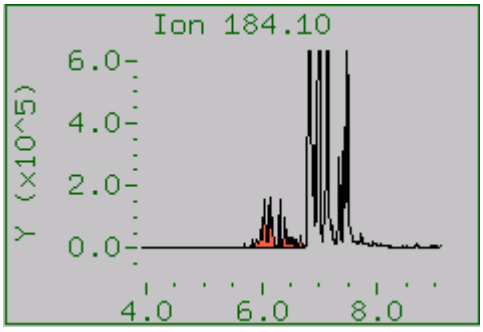
C1-Naphthalene



C2-Naphthalene



C3-Naphthalene



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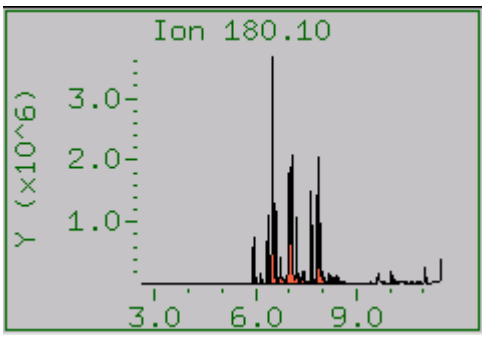
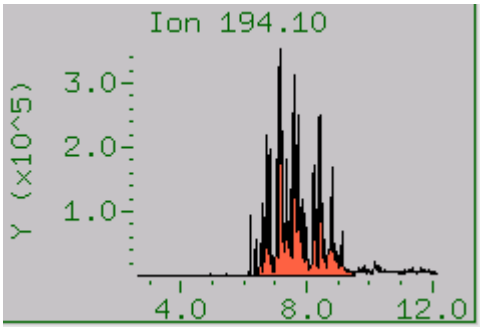
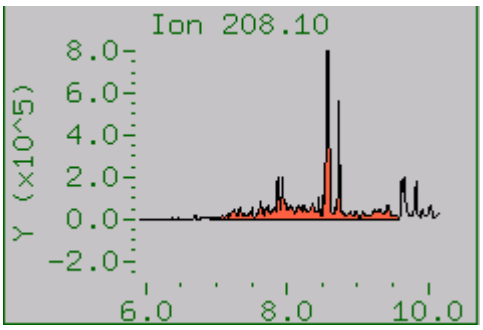


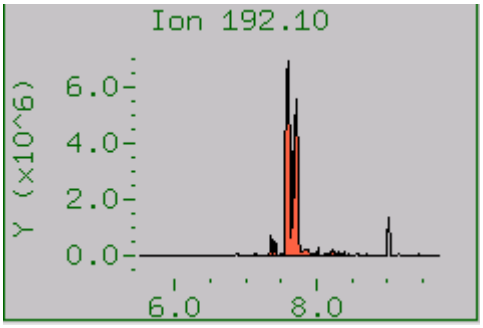
C1-Fluorene



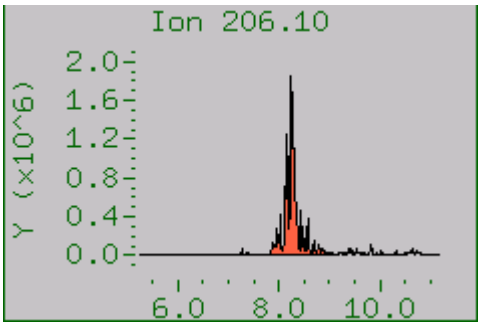
C2-Fluorene



C3-Fluorene



C1-Phenanthrene/Anthracene



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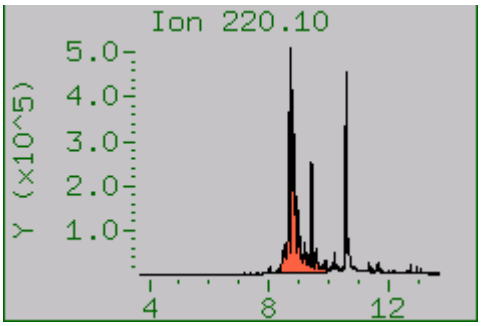

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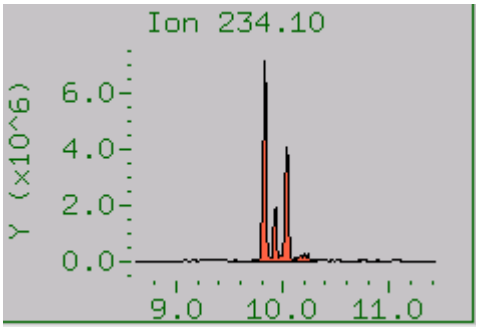
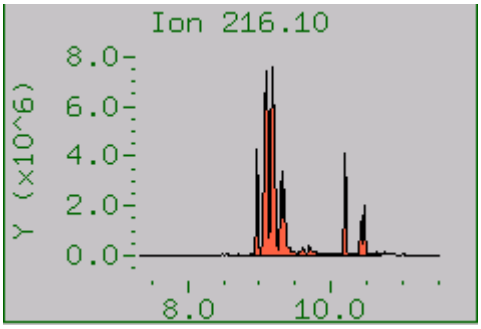
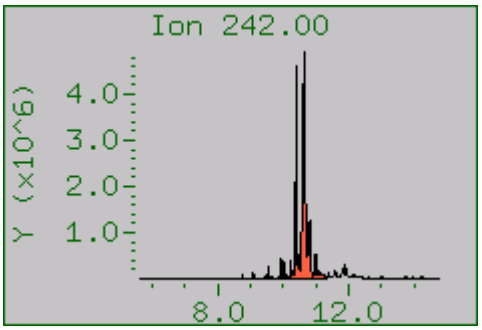


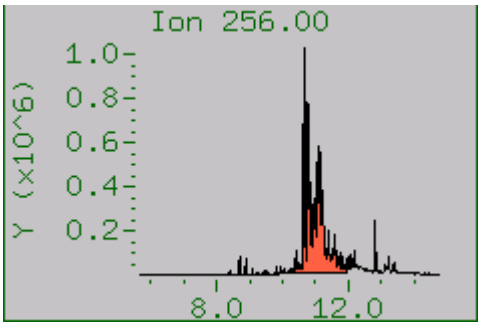
C4-Phenanthrene/Anthracene



C1-Fluoranthene/Pyrene



C1-Benz(a)anthracene/Chrysene



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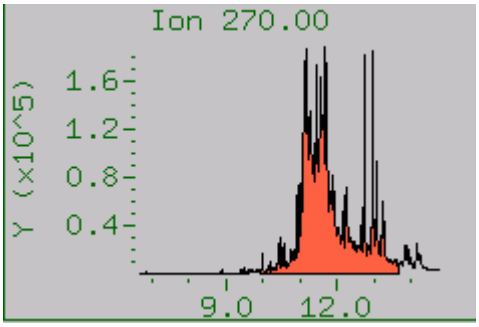
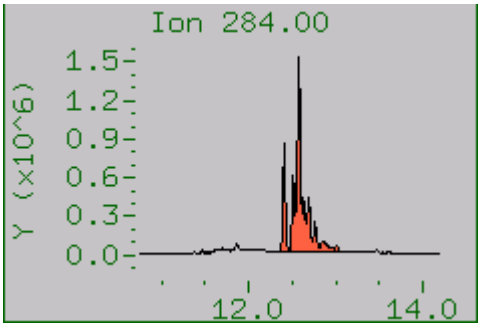


C3-Benz(a)anthracene/Chrysene



C4-Benz(a)anthracene/Chrysene

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STANDARD OPERATING PROCEDURE

Ammonia using Micro-Distillation and Analyzed by Lachat 8000 Flow Injection

Reference Method: EPA 350.1

SOP NUMBER:	S-GB-I-048-REV.01
EFFECTIVE DATE:	Date of Final Signature
SUPERSEDES:	S-GB-I-048-REV.00

APPROVAL

Nils Melberg, Laboratory General Manager — Date: 11/06/08

Kate Grams, Laboratory Quality Manager — Date: 12/29/08

Chad Rusch, Department Manager — Date: 11/5/08

ANNUAL REVIEW

SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE APPROVAL. SOP IS VALID FOR ONE YEAR FROM DATE OF LAST SIGNATURE.

Signature	Title	Date

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1. Purpose

This Standard Operating Procedure (SOP) describes the analyses of Ammonia using Micro-Distillation and Analyzed by Lachat 8000 Flow Injection by EPA 350.1.

2. Scope and Application

2.1 This SOP is applicable to the analysis of Ammonia in drinking, ground, surface, and saline waters, domestic and industrial wastes, soils, and TCLP, SPLP, and ASTM extracts. The applicable range is MDL to the top standard in the curve. The current Pace Reporting Limit is 0.5 mg/L. The current MDL can be found in EpicPro.

2.2 This SOP utilizes the Lachat 8000 analyzer.

3. Summary of Method

3.1 The sample is buffered at a pH of 9.5 with a borate buffer in order to decrease hydrolysis of cyanates and organic nitrogen compounds, and is distilled into a solution of boric acid. Alkaline phenol and hydrochlorite react with ammonia to form indophenol blue that is proportional to the ammonia concentration measured at 630 nm. The blue color formed is intensified with sodium nitroprusside and measured on the auto-analyzer.

3.2 Wisconsin groundwater samples do not need to be distilled before analysis. All other samples must be distilled before analysis.

4. Interferences

4.1 Ammonia in the laboratory may become a contaminant in this test. Care should be taken that ammonium hydroxide, either as a reagent or as a cleaning substance is not in the same room as the instrument.

4.2 Calcium and magnesium ions may be present in concentrations sufficient to cause precipitation problems during analysis. A 5% EDTA solution is used to prevent the precipitation of calcium and magnesium ions in river water and industrial wastes.

4.3 Sample turbidity and color may interfere with this method. Turbidity must be removed by filtration prior to analysis. Sample color that absorbs in the photometric range used will also interfere.

4.4 Residual chlorine must be removed by pretreatment of the sample with sodium thiosulfate before distillation.

4.5 Cyanate, which may be encountered in certain industrial effluents, will hydrolyze to some extent even at pH of 9.5 at which distillation is carried out.

5. Safety

5.1 All samples, standards, and reagents should be treated as hazardous. Safety glasses, gloves, and lab coats are to be worn. The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined. However, each chemical compound should be treated as a potential health hazard. Exposure to these chemicals must be reduced to the lowest possible level by a safe technique. Special care should be taken when handling the high concentration acids and oxidizing reagents used for sample digestion.

5.2 The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of any chemical. A reference file of Material Safety Data Sheets (MSDS) and a formal safety plan are made available to all personnel involved in chemical analysis and should be consulted prior to handling samples and standards.

5.3 Excess reagents, samples and method process wastes are characterized and disposed of in an acceptable manner. For further information on waste management consult the current version of ALL-S-002, *Waste Handling.*

5.4 The laboratory Chemical Hygiene Plan/Health and Safety Plan contains additional information on pollution prevention.

6. Definitions

Definitions can be found in Section 10 of the most recent version of the Pace Analytical Services, Inc. Quality Manual.

7. Sample Collection, Preservation and Handling

Table 1. SAMPLE COLLECTION, PRESERVATION, HOLDTIME, SHIPMENT, AND STORAGE

Matrix	Prep Method	Container(s)	Preservation Hold Time	Shipment Conditions	Lab Storage Conditions
Aqueous	EPA 350.1	250 ml plastic containers	H_2SO_4 28 days	On ice 4+/- 2° Celsius	4°C
Solid	EPA 350.1	Plastic or glass containers	None 28 days	On ice 4+/- 2° Celsius	4°C

8. Reagents and Standards

Table 2. REAGENTS

Reagent	Alias	Concentration	Directions found in
Ammonium Chloride - Need from two sources		Neat	
Deionized Water	Carrier		
Sodium Hydroxide (NaOH)		Neat	
Sodium Borate ($Na_2B_4O_7$)		Neat	
Borate Buffer	Releasing Solution	0.55 M	Table 4
Sulfuric Acid		Concentrated	
Sulfuric Acid	Trapping Solution	0.016 M	Table 4
Phenol	88% liquefied phenol	88%	
Sodium Phenolate Solution	Reagent 1		Table 4
Sodium Hypochlorite	Chlorox Bleach	5.25%	
Sodium Hypochlorite Solution	Reagent 2		Table 4
Disodium Ethylenediamine Tetraacetate (Na_2EDTA)		Neat	
Buffer	Reagent 3		Table 4
Sodium Nitroprisside [$Na_2Fe(CN)_5NO.2H_20$]		Neat	
Sodium Nitroprusside Solution	Reagent 4		Table 4
Sodium Thiosulfate		Neat	
Sodium Thiosulfate Solution	Dechlorinating Agent		Table 4
Sodium Hydroxide Solution	3 N	3 N	Table 4
Sodium Hydroxide		Neat	

Table 3. STANDARDS

Standard	Concentration	Direction found in Section:	Alias
Ammonium Chloride	100 mg/L	Table 5	Stock Standard
Ammonium Chloride (1) Must be different Lot # than Stock	100 mg/L	Table 5	Second Source Stock Standard
Ammonium Chloride (2) Must be different Lot # than Stock	1200 mg/L	Table 5	Second Source Stock Standard
Level 1 Calibration Standard	20 mg/L	Table 5	Cal Std. 1
Level 2 Calibration Standard	8.0 mg/L	Table 5	Cal Std. 2
Level 3 Calibration Standard	4.0 mg/L	Table 5	Cal Std. 3
Level 4 Calibration Standard	2.0 mg/L	Table 5	Cal Std. 4
Level 5 Calibration Standard	1.0 mg/L	Table 5	Cal Std. 5
Level 6 Calibration Standard and RLVS Standard	0.50 mg/L	Table 5	Cal Std. 6
Level 7 Calibration Standard / CCB	0.00 mg/L	Table 5	Cal Std. 7
Initial Check Verification	10 mg/L	Table 5	ICV
Continuing Check Verification	10 mg/L	Table 5	CCV
Matrix Spike/Matrix Spike Duplicate	10 mg/L	Table 5	MS/MSD
Laboratory Control Spike/Laboratory Control Spike Duplicate	10 mg/L	Table 5	LCS/LCSD

Table 4. PREPARATION OF REAGENTS

Standard	Alias	Final Concentration	Directions	Final Volume
Borate Buffer	Releasing Solution	0.55 M	Weigh 5 g of neat sodium borate ($Na_2B_4O_7$) into 964 g DI water. Add 22 g sodium hydroxide (NaOH). Shelf life = 1 year.	1000 ml
Sulfuric Acid Solution	Trapping Solution	0.016 M	Add 0.40 mL of concentrated sulfuric acid ~ 900 ml DI water. Dilute to volume. Shelf life = 1 year.	1000 ml
Sodium Phenolate	Reagent 1		Dissolve 88 mL of 88% liquefied phenol into ~ 600 ml DI water. Slowly add 32 g sodium hydroxide while stirring. Dilute to volume. Prepare weekly.	1000 ml
Sodium Hypochlorite Solution	Reagent 2		Dilute 250 ml of 5.25% sodium hypochlorite to mark with DI wat er. MAKE FRESH DAILY.	500 ml
Buffer	Reagent 3		Dissolve 50.0 g disodium ethylenediamine tetraacetate and 5.5 g sodium hydroxide in ~ 900 ml DI water. Dilute to volume. Shelf life = 1 month.	1000 ml
Sodium Nitroprusside Solution	Reagent 4		Dissolve 3.5 g sodium nitroprusside in ~ 900 ml DI water. Dilute to volume. Shelf life = 1 month.	1000 ml
Sodium Thiosulfate Solution	Dechlorinating Agent		Dissolve 3.5 g sodium thiosulfate in ~ 900 ml DI water. Dilute to volume. Shelf life = 1 year.	1000 ml
Sodium Hydroxide Solution	3 N	3 N	Dissolve 120 g sodium hydroxide in ~ 900 ml DI water. Dilute to volume. Shelf life = 1 year.	1000 ml

Table 5. PREPARATION OF STANDARDS

Standard	Alias	Final Concentration	Directions	Final Volume
Primary Stock Standard	Stock Standard	100 mg/L	Weigh 0.382 g of neat ammonium chloride into ~500 ml DI water. Dilute to volume. Shelf life = 6 months.	1000 ml
Secondary Stock Standard (1)	Second Source Stock Standard	100 mg/L	Weigh 0.382 g of neat second source ammonium chbride into ~500 ml DI water. Dilute to volume. Shelf life = 6 months.	1000 ml
Secondary Stock Standard (2)	Second Source Stock Standard	1200 mg/L	Weigh 4.58 g of neat second source ammonium chloride into ~500 ml DI water. Dilute to volume shelf life = 6 months.	1000 ml
Level 1 Calibration Standard	Cal. Std. 1	20 mg/L	Pipette 20 ml of primary stock standard into 100 ml volumetric flask. Dilute to volume with DI water. Prepare monthly.	100 ml
Level 2 Calibration Standard	Cal. Std. 2	8.0 mg/L	Pipette 8.0 ml of primary stock standard into 100 ml volumetric flask. Dilute to volume with DI water. Prepare monthly.	100 ml
Level 3 Calibration Standard	Cal. Std. 3	4.0 mg/L	Pipette 4.0 ml of primary stock standard into 100 ml volumetric flask. Dilute to volume with DI water. Prepare monthly.	100 ml
Level 4 Calibration Standard	Cal. Std. 4	2.0 mg/L	Pipette 2.0 ml of primary stock standard into 100 ml volumetric flask. Dilute to volume with DI water. Prepare monthly.	100 ml
Level 5 Calibration Standard	Cal. Std. 5	1.0 mg/L	Pipette 1.0 ml of primary stock standard into 100 ml volumetric flask. Dilute to volume with DI water. Prepare monthly.	100 ml
Level 6 Calibration Standard and RLVS Standard	Cal. Std. 6	0.50 mg/L	Pipette 0.50 ml of primary stock standard into 100 ml volumetric flask. Dilute to volume with DI water. Prepare monthly.	100 ml
Level 7 Calibration Standard / CCB	Cal. Std. 7	0.0 mg/L	Pipette 0.0 ml of primary stock standard into 100 ml volumetric flask. Dilute to volume with DI water. Prepare monthly.	100 ml
Initial Check Verification	ICV	10 mg/L	Pipette 0.05 ml of secondary stock (2) standard into 6 ml ,distill and dilute to volume with DI water.	6 ml
Initial Check Blank	ICB	0.0 mg/L	Pipette 6ml of DI water distill and dilute to volume.	6 ml
Continuing Check Verification	CCV	10 mg/L	Pipette 10 ml of primary stock standard into 100 ml volumetric flask. Dilute to volume with DI water. Prepare monthly.	100 ml
Matrix Spike/ Matrix Spike Duplicate	MS/MSD	10 mg/L	Pipette 0.05 ml of secondary stock (2) standard into sample tubes. Add 6.0 ml of sample.	6 ml
Laboratory Control Spike/ Laboratory Control Spike Duplicate	LCS/LCSD	10 mg/L	Pipette 0.05 ml of secondary stock (2) standard into sample tubes. Add 6.0 ml of DI water.	6 ml

9. Equipment and Supplies

Table 6. EQUIPMENT

Equipment	Manufacturer	Model(s)/Catalog Number •
Lachat 8000	Lachat	Lachat
Micro-Distillation Unit	Lachat	Micro Distillation
Top loading Analytical Balance	Mettler	BA310P
1000 µL Pipette	Eppendorf	05-402-76 (Fisher Cat#)
500 µL Pipette	Eppendorf	05-402-72 (Fisher Cat#)
250 µL Pipette	Eppendorf	05-402-69 (Fisher Cat#)
50 uL Pipette	Labsystems	F87407
Bottle Top Dispenser (0.5 - 5.0mL)	Brinkman Dispensette	13-688-221 (Fisher Cat#)
Repipetors (0.5 - 5.0mL)	Barnstead/Thermolyne	13-687-33 (Fisher Cat#)
Vented Hood	Hamilton	
Spoonula (Lab Spoon)	FisherBrand or equivalent	14-375-10 (Fisher Cat#)
Super Colonna Tube Press	Lachat	
Burette – 20 ml	Kimax	03-700-22C
Ammonia Manifold	Lachat	10-107-06-1-B
Interference filter – 630 nm	Lachat	
13 cm x 0.022 i.d. sample loop	Lachat	
pH Meter	Orion	
Gloves – Heat Resistant		

- Or equivalent

Table 7. SUPPLIES

Supplies	Manufacturer	Catalog Number •
Distillation tubes	Lachat	A17117A
Culture Tubes 13X100	Fisher	71500 13100
Volumetric Flasks	Fisher	Various
Syringe – 20 mL	Bectin Dickenson	309661
Syringe Prefilter – 25 mm	Nalgene	F271-21
Potassium Iodine Starch Paper	Fisher Scientific	V260
Disposable Beakers	MG Scientific	B250-50-INV
Parafilm		
Pipettes – Transfer		
• Or equivalent		

10. Calibration and Standardization

10.1 Instrument Settings

Sample throughput:	80 samples/h, 45s/sample
Pump and Speed:	35
Cycle Period:	45
Peak Base Width:	24 s
% Width Tolerance:	100
Threshold:	10000
Inject to start of peak:	28 s
Chemistry:	Direct

10.2 Follow steps 11.2 –11.3.28 to run calibration procedure.

10.3 Calibration Criteria

Calibration Rep Handling:	Replace
Calibration Fit Type:	1st Order Polynomial
Weighting Method:	None
Force through zero:	No

10.3.1 The instrument must be calibrated every time it is set up.

10.3.2 The correlation coefficient must be at least 0.995.

10.3.3 The calibration curve must be a minimum of 5 standards plus a blank.

10.3.4 Place working standards in decreasing concentration.

11. Procedure

11.1 Sample Preparation

NOTE: Document all sample volumes, standards and reagents used in the distillation on the prep log.

11.1.1 Wisconsin groundwater samples are analyzed directly and do not need to be distilled or pH adjusted before analysis. All other samples must be distilled before analysis. All other water samples must be pH adjusted before distillation. If a Wisconsin groundwater sample contains turbidity, the sample is filtered before analysis via a syringe and 25 mm filter.

11.1.2 Check all samples for residual chlorine with potassium iodine-starch paper by placing several drop of sample on the paper with a disposable pipette. If the potassium iodine-starch paper turns purple or black, residual chlorine is present. Add as much sodium thiosulfate solution as necessary to remove all residual chlorine.

11.1.3 Place 30 mL of water sample into 50 mL disposable beakers labeled with sample numbers. Using a calibrated pH meter, adjust water sample to between pH 5 to 9 with 3 N NaOH before distillation. Note pH adjustment on prep log.

11.2 Distillation Procedure

This section of the SOP details the steps in distilling the samples before analysis. In the following procedure, **D** and **M** refer to the marks on the collector tube. **D** means "distillation" end, and **M** means "measuring" end.

11.2.1 Set the controller to 120°C, allow the heater to warm up. This will take about 40 minutes. The operating temperature of the distillation block needs to be verified annually.

11.2.2 Label tubes with the **M** end up, place as many tubes as you have samples into the collector tube rack. Fill the tubes with 1 ml of 0.016 M H_2SO_4 trapping solution, add Teflon liner and cap.

11.2.3 For liquid samples place 6 ml of prepared sample into each sample tube with a calibrated automatic pipette.

11.2.4 For soil samples weigh out 0.20 g of soil or sludge to the nearest 100th on a calibrated balance and dilute to 6 ml with deionized water tube with a calibrated automatic pipette into each sample tube. If the sample is high in organics use smaller sample size.

11.2.5 For liquid prepare one method blank by adding 6 mL of DI water to sample tube using a calibrated automatic pipette.

11.2.6 For soil samples, prepare one method blank by weighing out 0.20 g of washed sea sand to the nearest 100th on a calibrated balance and dilute to 6 ml with deionized water tube with a calibrated automatic pipette.

11.2.7 For liquid samples, prepare one LCS (and LCSD if needed) by adding 6.0 ml 0.016 M sulfuric acid solution and 0.05 ml of 1200 mg/L secondary spiking solution into sample tubes using a calibrated automatic pipette.

11.2.8 For soil samples, prepare one LCS (and LCSD if needed) by weighing out 0.20 g of washed sea sand to the nearest 100th on a calibrated balance. Bring to 6 ml volume with deionized water. Add 0.05 ml of 1200 mg/L secondary spiking solution using a calibrated automatic pipette into each sample tube.

11.2.9 For liquid samples, prepare one MS/MSD pair per 10 samples by adding 6.0 ml of sample and 0.05 ml of 1200 mg/L secondary spiking solution using a calibrated automatic pipette into each sample tube.

11.2.10 For soil samples, prepare one MS/MSD pair by weighing out 0.20 g of sample to the nearest 100th on a calibrated balance. Bring to 6 ml volume with deionized water. Add 0.05 ml of 1200 mg/L secondary spiking solution using a calibrated automatic pipette into each sample tube.

11.2.11 Add 1.0 ml of 0.55 M borate buffer solution to all samples.

11.2.12 Immediately push the **D** end of an Ammonia-1 collector tube over the open end of each sample tube to start the seal.

11.2.13 Place the assembly in the press, putting the sample tube through the hole in the white base. Before pressing, the user should grip the collector tube firmly at the breakaway point to keep the tube from shifting during the pressing procedure.

11.2.14 The pressing motion should be a smooth constant pressure, which is just enough to slide the sample tube inside the collector tube. A jerky, forced motion may cause added strain to the tube and could potentially crack it. Press down on the handle until the stop ring on the sample tube hits the **D** end of the collector tube.

11.2.15 Put on heat-resistant gloves. Push the sample tube and **D** end of each tube all the way into the preheated block so that the collector tube stop ring touches the block. Placing 21 tubes should take less than one minute.

11.2.16 Set the timer for 30 minutes.

11.2.17 When 30 minutes is up, remove the first tube, use heat-resistant gloves, from the block and immediately pull its sample tube using a downward twisting motion as opposed to a sideways motion. You must remove the sample tube within 4 seconds of removing it for the block or suck-back of the sample will occur. Dispose of the sample tube and the hot solution.

11.2.18 Invert each collector tube and place it into the collector tube rack, now with the **D** end up. It should take less than two minutes to pull and separate all 21 tubes.

11.2.19 Hold collector tube horizontally and rinse its walls with the distillate in order to homogenize it. Roll tube in order to collect all droplets from the walls of the tube. Return the tube to an upright position so the **D** end is up.

11.2.20 With the **D** end up, break the collector tube in half by pulling the **D** end hard toward yourself to break it, the twisting and tearing off the **D** end. Discard the **D** end.

11.2.21 In the **M** end of the tube dilute to the 6.0 ml mark with DI water. This results in the original sample volume, but now in 0.003 M sulfuric acid. Pour into cuvettes.

11.2.22 Parafilm and refrigerate distillates if ammonia determination is not done immediately.

11.3 Basic System Operation - Analytical

This portion of the SOP is designed to allow the user to set up and run a method, print a sample report, then shut down using the more basic software functions. For a more detailed explanation of the many other options, the user should refer to the Lachat Software Reference Manual. It is assumed that a method program has already been created for the chemistries you wish to run.

11.3.1 Create calibration curve standards, ICV/CCV standards and ICB/CCB samples as per Tables 5. A new calibration curve is prepared monthly and run each analytical day.

11.3.2 Turn on computer with ON/OFF button. Turn on printer. The power to the monitor, autosampler and reaction module is controlled with a multi-outlet noise filter and surge suppresser located behind the reaction module. Turn the red switch to “ON”.

11.3.3 Allow the autosampler to perform its startup routine and wait until the autosampler stops with the probe above the wash bath.

11.3.4 Log into the Network with your Login name and password. Windows program will be activated. Program Manager screen will appear. Click twice on Lachat Instruments. Click twice on the Omnion FIA icon on the Lachat Instruments window. The startup box will come up, and then click on **'OK'**. The autosampler probe will go into the wash bath and dilutor activity may be heard. The injection valves may turn to the Inject state if they were not already there.

11.3.5 To encourage GALP (Good Automated Laboratory Practice), Omnion requires that the operator "Log-in" every time with name and password. Enter your assigned name and password in the correct case in the spaces indicated and then click on the **'OK'** button.

11.3.6 After you have logged in, the Omnion FIA Main Menu will appear on the screen. The header should contain the serial number of the software key. No messages should be seen about the SS420 boards, or any serial port failures. Click on the Instrument button labeled 'FIA Instrument 1'.

11.3.7 Each valve allocated to this instrument will be cycled from Load to Inject and Load to Inject again. This is a test of the valves and if no messages are received about failing valves, then they are OK.

11.3.8 If a valve fails, a box will tell you which channel's valve failed. You can press OK and continue. You should arrange for service for the failing valve by calling Lachat Instruments.

11.3.9 After the injection valves are tested, an instrument window for FIA Instrument 1 will appear. Omnion will automatically open the last Method, Tray, DQM Plan and Data File used. Arrow up to 'File" and click. When window appears click on '**Open Method'**.

Under Open Method File Directories, click on **c:\omnion\methods** and then click on the method you will be running. A list of methods will appear. Highlight the appropriate one in the **File Name** box and click on **'OK'**.

11.3.10 The Method will open and the **Analyte Table** will appear. It will show the Analyte Name and which Channel it is run on. The concentration Units and concentration of the calibration standards will be listed. To the far right will be the timing periods, which the instrument uses to detect the peaks.

11.3.11 Click on **'File'** again and then **'Open Tray'**. The **'Open Tray File'** window will come up. Directories will be **c:\omnion\trays\method**. Click on the method you will be running. A list of previous trays for that particular method will appear. Click on a recent **tray file name and** the on **'OK'** to call it up. Edit this tray below the Calibration Standards with the sample numbers you will be running. Also edit any dilutions that will be required.

11.3.12 Click on **Save Tray As** and edit name of tray to reflect today's' date and letter to reflect which run: YYMMDDL. L is the sequence of the tray that day i.e., a=first tray, b=second tray and so on. Example: 960730a.

11.3.13 Click on **File** again and then on **Open DQM**. The Open DQM File window will come up. Directories will be **c:\omnion\DQM\method**. Click on the method you will be running and then on the method **DQM File Name**. Click on **OK** and the DQM (Data Quality Management) Plan will appear.

This DQM Plan supplements the tray table itself and acts as a standard operating procedure to be used when running this tray. Check the DQM to make sure it will apply to this tray, or edit it if necessary. If any changes were necessary then the DQM should be saved, and then replace the DQM in the tray, to make the changes permanent. If no changes were necessary, then minimize this window.

11.3.14 Click on the **Run Tray** button. The Tray Run Window will appear. Leave the **Method** and **Tray** spaces blank to run the currently loaded Method and tray. You must fill in the **Data File** space so that Omnion knows where to put the data it will generate. Click on **Catalog** after the **Data File** space to see a list of previous data files. Click on an old file name and then edit it to match today's tray name. Click on **OK**.

11.3.15 Follow Section 17.3 of Lachat QuikChem Method 10-107-06-1-A for proper manifold setup. Insert the proper manifold for the desired analysis to the proper channel specified in the Analyte Table. The load/inject valve for each channel has six connections with the following designations:

Port #	Function
1	Sample Loop Inlet
2	Carrier Stream Inlet (From Pump)
(Short section of plastic tubing remains port #2 at all times)	
3	Outlet to reaction manifold
4	Sample loop outlet
5	Sample loop waste line
6	Sample source line (from sampler, pump)

Each reaction manifold has a line with pump tubing attached labeled "carrier". Disconnect the pump tubing from this line and reconnect it to the section of line that comes from port #2. Connect the section of tubing coming from the reaction manifold to port #3.

11.3.16 Connect the outlet line from the manifold, located top right, to the bottom inlet of the flow cell.

11.3.17 Insert backpressure loop of 200 cm of 0.022" i.d. tubing, between top outlet of flow cell and the waste line.

11.3.18 Place waste line into phenol waste collection container.

11.3.19 Install proper 630 interference filter.

11.3.20 If required, allow heating unit to heat to correct temperature.

11.3.21 Install 13 cm x 0.022 i.d. sample loop in ports #1 and # 4.

11.3.22 Install the pump tubing onto pump cartridges. Check for wear on the pump tubing by rolling between thumb and fingers when stretched across a pump cartridge. Replace tubing if "flat" spots are felt.

11.3.23 Move tension levers to left to provide proper tension.

11.3.24 Check all connections for leakage and proper flow. Make sure waste lines are routed to proper container.

11.3.25 Properly label and fill calibration standard, CCV standard and CCB vials with proper solutions.

11.3.26 When ready, click on **RUN** on the Tray Run Window and the analysis will start. The symbol for the tray on the toolbar will turn to a **STOP** sign until analysis is complete.

11.3.27 If necessary to stop the run anytime, click on the **STOP** sign. A window will come down with the options to RESUME or ABORT TRAY.

11.3.28 After instrument has calibrated, click on the **Review Calibration** button on the toolbar. The graph of the calibration will be displayed along with the area of each standard. If the r-value of the calibration is 0.995 or better, print the calibration graph and allow the analysis to continue.

11.3.29 After analysis is completed the **STOP** sign in the Toolbar will be replaced with **Run Tray.** Click on File and the window will come down. Click on Export Data. Export data window will appear. Highlight whatever Data Items and Channel Dependent Data Items you want exported to EXCEL Save Export Data As window will appear. Directories should be r:\wetchem\data\lachat\test\year\month

Highlight the text file you have just run in the File Name box. Click on **OK** and data will be exported to EXCEL. Then go back and click on File again. When window comes down, click on Open Runtime Rpt. Open Runtime Report File window will appear. It should have current data, method and file name of analysis just completed, or if going back at a later date, then highlight the one that you want. Click on **OK** and the Runtime Report will appear on the screen. Click on File and then on Print/Export Runtime Rpt. Runtime Report window will appear.

Click on **OK** to print. On Print window choose the Print Range you want. **ALL** is normally highlighted. Click on **OK**.

11.3.30 Samples that have results greater than the highest standard in the calibration curve need to be diluted appropriately so the result falls within the calibration curve, and reanalyzed. Document all dilutions on prep log.

11.3.31 Document all standards and reagents used in analysis in raw data. Sign and Date raw data.

11.3.32 After analysis is complete, place reagent lines in D.I. water and rinse several minutes. Remove lines from water and pump air through the lines until dry.

11.3.33 Turn off pump, release tension levers on pump cartridges and remove pump tubing from cartridges.

11.3.34 Disconnect pump tubing to port #2 at the pump tubing connector, disconnect line to port #3 at port #3 connector and connect pump tubing from #2 to line from manifold.

11.3.35 Disconnect manifold outlet line from flow cell inlet connector.

11.3.36 Wrap pump tubing lightly around manifold panel and store in appropriate box, with sample loop and interference filter.

NOTE: Any daily or periodic maintenance must be recorded in the instrument daily logbook.

11.4 SHUTDOWN

11.4.1 Click on EXIT icon

11.4.2 Omnion FIA Data System Window appears. Click on **Logoff**.

11.4.3 Window listing **User** Name and question: **Logoff Current Session?** Click on **YES**.

11.4.4 Window for User Name and Password comes up. Click on **EXIT**.

11.4.5 Window comes up with: **Terminate Data System?** Click on **YES.**

11.4.6 Turn off computer, printer and switch on surge suppresser.

11.5 CALCULATIONS

The instrument provides calculated sample results in mg/L. Calculations are only necessary if a dilution was used.

Liquid Calculation

Raw Data Value (mg/L) x Dilution Factor = Ammonia (mg/L)

Soil Calculation

$$\frac{\text{Raw Data Value (mg/L) X 0.006 L X Dilution Factor}}{\text{(0.0002 Kg x \% solids in decimal form)}} = \text{Ammonia (mg/Kg)}$$

12. Quality Control

12.1 Refer to the most current version of the Pace Quality Manual Appendix I *Quality Control Calculations* and SOP GB-Q-009 *Common Laboratory Calculations and Statistical Evaluation of Data* for equations and calculation details.

12.2 **Initial Calibration Verification (ICV)**

12.2.1 The ICV is analyzed before samples.

12.2.2 The ICV is distilled with the batch.

12.2.3 Concentration must be within $\pm$ 10% of the true value. When measurements are outside the control limits, the analysis must be terminated, the problem corrected, and the calibration re-verified.

12.2.3.1 If the ICV is greater than the control limit and the samples are non-detects, the sample may be reported without a flag.

12.2.4 The lot number of the Ammonium Chloride Standard used to make the ICV must be different from that of the calibration curve standards.

12.3 **Continuing Calibration Verification (CCV)**

12.3.1 The CCV is analyzed after every 10 samples.

12.3.2 The CCV is not distilled with the batch.

12.3.3 Concentration must be within ± 10% of the true value. When measurements are outside the control limits, the analysis must be terminated, the problem corrected, and the calibration re-verified. If the reset CCV fails, recalibrate and reanalyze all samples back to the last acceptable CCV.

12.3.3.1 If the CCV is greater than the control limit and the samples are non-detects, the sample may be reported without a flag.

12.3.4 The lot number of the Ammonium Chloride Standard used to make the CCV must be different from that of the ICV.

12.4 **Initial Calibration Blank (ICB) and Continuing Calibration Blank (CCB)**

12.4.1 The ICB must be analyzed after the ICV and before samples. The CCB must be analyzed after the CCV and before samples.

12.4.2 The ICB is distilled and the CCB is not distilled with the batch.

12.4.3 The absolute value must be < PRL. When measurements are above the PRL, terminate analysis, correct the problem, and the calibration re-verified. If the reset of the I/CCB fails, recalibrate and reanalyze all analytical samples analyzed since the last compliant calibration blank.

12.4.3.1 If the sample concentration is greater than ten times the concentration in the ICB or CCB, the samples do not need to be reanalyzed.

12.5 **Reporting Limit Verification Standard (RLVS)** – A standard prepared at the concentration of the Pace Reporting Limit. It is analyzed after the calibration, recovery 60-140% of true value. If outside the limits, reanalyze once. If still outside the limits, recalibrate.

12.6 **Method Blank (MB)**

12.6.1 A MB is carried through all prep procedures and analyzed with a frequency of 5% or one per batch of up to 20 environmental samples. Must be distilled with batch.

12.6.2 The absolute value must be < PRL.

12.6.2.1 When measurements are above the PRL, terminate analysis, correct the problem, verify the calibration, and reanalyze all analytical samples analyzed since the last compliant calibration blank.

12.6.2.2 If the analyte is detected in the method blank, method blank criteria is evaluated and flagged with appropriate (B) qualifier to the MDL when MDL reporting is required: qualify with appropriate "B" qualifier sample results less than 20 times the absolute value detected in the blank. Additionally, method blank acceptance may be based on project specific criteria or determined from analyte concentrations in the sample and are evaluated on a sample-by-sample basis. Other criteria may apply, such as regulatory limit and the analyte concentration in the samples.

12.7 **Laboratory Control Sample (LCS)**

12.7.1 The LCS is carried through all preparation procedures with frequency of 5% or one per batch of up to 20 environmental samples. A Laboratory Control Spike Duplicate (LCSD) must be analyzed if there is insufficient sample volume to perform a matrix spike/matrix spike duplicate or if the client requests one. Must be distilled with batch.

12.7.2 Concentration must be within ± 10% of the true value for waters. For soils, the concentration must be within calculated in –house limits or default limits of ± 20%.

12.7.2.1 When measurements are outside the control limits, check for errors in calculations, standards preparation and spiking. If an error or problem is found and can be corrected by amending the calculations and the results falls within the limits, accept the data and report without a qualifier flag.

12.7.2.2 If no errors are found and sufficient sample is available, re-prepare the LCS (and/or LCSD) and all associated samples. If the recovery is within the limits in the analysis, accept the second set of data. If the recovery is still out side the limits after re-analysis, contact the PM to determine the resolution. If the client does not require additional work, report the data, applying an appropriate flag to the samples associated with the non-compliant LCS.

12.7.2.3 If sufficient sample volume is not available, report the sample data with appropriate (L) qualifier on each of the samples associated with the non-compliant LCS (and/or LCSD). Contact the project manager regarding the occurrence.

12.7.3 When an LCSD is performed, the precision between the LCS and LCSD must a be =/< 20% RPD.

12.7.3.1 When measurements are outside the control limits, check for errors in calculations, standards preparation and spiking. If an error or problem is found and can be corrected by amending the calculations and the results falls within the limits, accept the data and report without a qualifier flag.

12.7.3.2 If no calculation errors are found when measurements are outside the control limits, flag the parent sample with appropriate "R" data qualifier.

12.7.4 The lot number of the Ammonium Chloride Standard used to make the CCV must be different from that of the LCS.

12.8 **Matrix Spike (MS) and Matrix Spike Duplicate (MSD)**

12.8.1 One pair per up to 10 environmental samples or 10% frequency whichever is more frequent. Must be distilled with batch.

12.8.2 Both QC samples must be calculated for accuracy and precision.

12.8.3 Concentration must be within ± 10% of the true value for waters. For soils, the concentration must be within calculated in –house limits or default limits of ± 20%.

12.8.3.1 When measurements are outside the control limits, check for errors in calculations, standards preparation and spiking. If an error or problem is found and can be corrected by amending the calculations and the results falls within the limits, accept the data and report without a qualifier flag.

12.8.3.2 If the four times the concentration of the spike is less than the level of the parent, accuracy need not be calculated.

12.8.3.3 If no calculation errors are found when measurements are outside the control limits, flag the parent sample with appropriate "M" data qualifier.

12.8.4 The precision between the MS and MSD must a be =/< 20% RPD.

12.8.4.1 When measurements are outside the control limits, check for errors in calculations, standards preparation and spiking. If an error or problem is found and can be corrected by amending the calculations and the results falls within the limits, accept the data and report without a qualifier flag.

12.8.4.2 If no calculation errors are found when measurements are outside the control limits, flag the parent sample with appropriate "R" data qualifier.

12.8.5 The parent sample used for MS/MSD pair is either determined by the client or selected at random from client samples as sample volume allows. No field, filter, trip or equipment blanks can be used for MS/MSD.

12.8.6 The lot number of the Ammonium Chloride used to make the CCV is different for the MS/MSD.

12.9 The appropriate leach blank must be distilled and analyzed along with the appropriate samples as leached on the same leach date. The absolute value must be < PRL. When measurements are above the PRL, terminate analysis, investigate and correct the problem, verify the calibration, and reanalyze all analytical samples analyzed.

12.10 When preparation of a sample exceeds 28 days past the time of collection, notify the project manager before proceeding. If a sample is run past 28 days after collection, flag with appropriate "H" data qualifier.

12.11 If a sample was diluted due to matrix effects and the result is a non-detect, the result must be qualified with appropriate "D" data qualifier.

13. Method Performance

13.1 There are several requirements that must be met to insure that this procedure generates accurate and reliable data. A general outline of requirements has been summarized below. Further specifications may be found in the Laboratory Quality Manual and specific Standard Operating Procedures.

13.1.1 The analyst must read and understand this procedure with written documentation maintained in his/her training file.

13.1.2 An initial demonstration of capability (IDC) must be performed per S-ALL-Q-020, *Orientation and Training Procedure*s. A record of the IDC will be maintained in his/her QA file with written authorization from the Laboratory Manager and Quality Manager.

13.1.3 An annual method detection limit (MDL) study will be completed per S-ALL-Q-004, *Method Detection Limit Studies*, for this method and whenever there is a major change in personnel or equipment. The results of these studies are retained in the quality assurance office.

13.1.4 Periodic performance evaluation (PE) samples are analyzed per S-ALL-Q-010, *PE/PT Program*, to demonstrate continuing competence. All results are stored in the QA office.

14. Pollution Prevention and Waste Management

14.1 Pollution prevention encompasses any technique or procedure that reduces or eliminates the quantity or toxicity of waste at the point of generation.

14.2 The quantity of chemicals purchased is based on expected usage during its shelf life and disposal cost of unused material. Actual reagent preparation volumes reflect anticipated usage and reagent stability.

14.3 Excess reagents, samples and method process wastes are characterized and disposed of in an acceptable manner. For further information on waste management consult the current version of ALL-S-002, *Waste Handling.*

14.4 The laboratory Chemical Hygiene Plan/Health and Safety Plan contains additional information on pollution prevention.

15. References

15.1 Quikchem Method 10-107-06-1-A, Lachat Instruments, March 29, 1988

15.2 Micro Dist Method Ammonia-1: Phenate Method, Lachat Instruments, April 27, 2000

15.3 EPA 600 R-93-100, Revised August 1993, Method 350.1, Determination of Nitrogen Ammonia by Semi-Automated Colorimetry – Revision 2.0.

15.4 Standard Methods for the Examination of Water and Wastewater, 18th Edition, p. 4-77, Methods 4500 NH3 B and H (1992)

16. Tables, Diagrams, Flowcharts, Appendices, Addenda etc.

16.1 Table A: **QUALITY CONTOL**

16.2 Table B: **ANALYST/TECHNICIAN DATA ASSESSMENT**

16.3 Flowchart

16.4 NH3 bench sheet example

16.5 NH3 prep sheet example

17. Revisions

Revision Number	Reason for Change	Date
S-GB-I-048-Rev.0	Updated to current Pace format First Issue.	17Feb2007
S-GB-I-048-Rev.01	Updated signature page. Deleted Section 7. Renumbered document. Section 12 - Updated data qualifiers Section 13 – Updated SOP references. Section 14 – Updated SOP reference Table B – Updated qualifiers	01Aug2008

Table A. QUALITY CONTROL

Preparation Method ⇨ Quality Control Measure ⇩	**EPA 350.1**
Method Blank	One per batch of samples, up to 20 environmental samples, whichever is more frequent. Must be distilled with batch.
Laboratory Control Spike and Duplicate	One per batch of samples, up to 20 environmental samples, whichever is more frequent. A LCSD is required if MS/MSD is not performed. Must be distilled with batch.
Matrix Spike / Matrix Spike Duplicate	One pair per batch of samples, up to 10 environmental samples, whichever is more frequent. Must be distilled with batch.
Initial Calibration	Minimum of 5 standards plus blank. Must be performed every time before samples are analyzed.
RLVS Standard	After the calibration
Calibration Verification (ICV/CCV)	ICV – analyzed after calibration but before samples. **The ICV is distilled with batch.** CCV – analyzed after every 10 samples. **The CCV is not distilled with batch.**
Calibration Blank (ICB/CCB)	ICB – analyzed after ICV. **The ICB is not distilled with batch.** CCB – analyzed after every CCV pair. **The CCB is not distilled with batch.**
Leach Blank	The appropriate leach blank must be distilled and analyzed along with the appropriate samples as leached on the same leach date.

Table B. ANALYST/TECHNICIAN DATA ASSESSMENT

Analytical Method Acceptance Criteria⇨ Data Assessment Measure ⇩	**EPA 350.1 If these conditions are not achieved Þ**
Method Blank and Leach Blanks	• 1
Accuracy & Precision Matrix Spike Samples	• 2
Accuracy & Precision Laboratory Control Spikes	• 3
Initial Calibration	• 4
RLVS standard	• 5
Initial / Continuing Calibration Verification	• 6
Initial / Continuing Calibration Blank	• 7

1. In the absence of project specific requirements, sample detects less than 20 times the method blank contamination level is reported with the appropriate "B" data qualifier. Sample detects greater than 20 times the method blank contamination are reported without qualification.

2. In the absence of project specific or method requirements, in-house generated limits will be used. If the concentration of the spike is less than 25% of the concentration of the parent, dilute parent to a level that the subsequent spike concentration will be greater than 25% the parent and so the parent concentration is above the EQL. Rerun the parent, MS, and MSD at this new dilution. If the MS and/or MSD fails at the diluted concentration, appropriately "M" flag the parent sample. If the parent, MS, or MSD is greater than the top standard in the curve, dilute and reanalyze the parent, MS, and MSD following the above guidance. If the concentration of the spike is greater than 25% of the concentration of the parent, appropriately "M" flag the parent sample if either the MS and/or MSD fails. If the MS and MSD fails precision control limits flag the parent with the appropriate "R" (precision) data qualifier.

3. If sample volume does not allow re-analysis the entire prep/analytical batch of samples shall be flagged with the appropriate "L" (accuracy) and appropriate "R" (precision) qualifier to reflect the deficiencies.

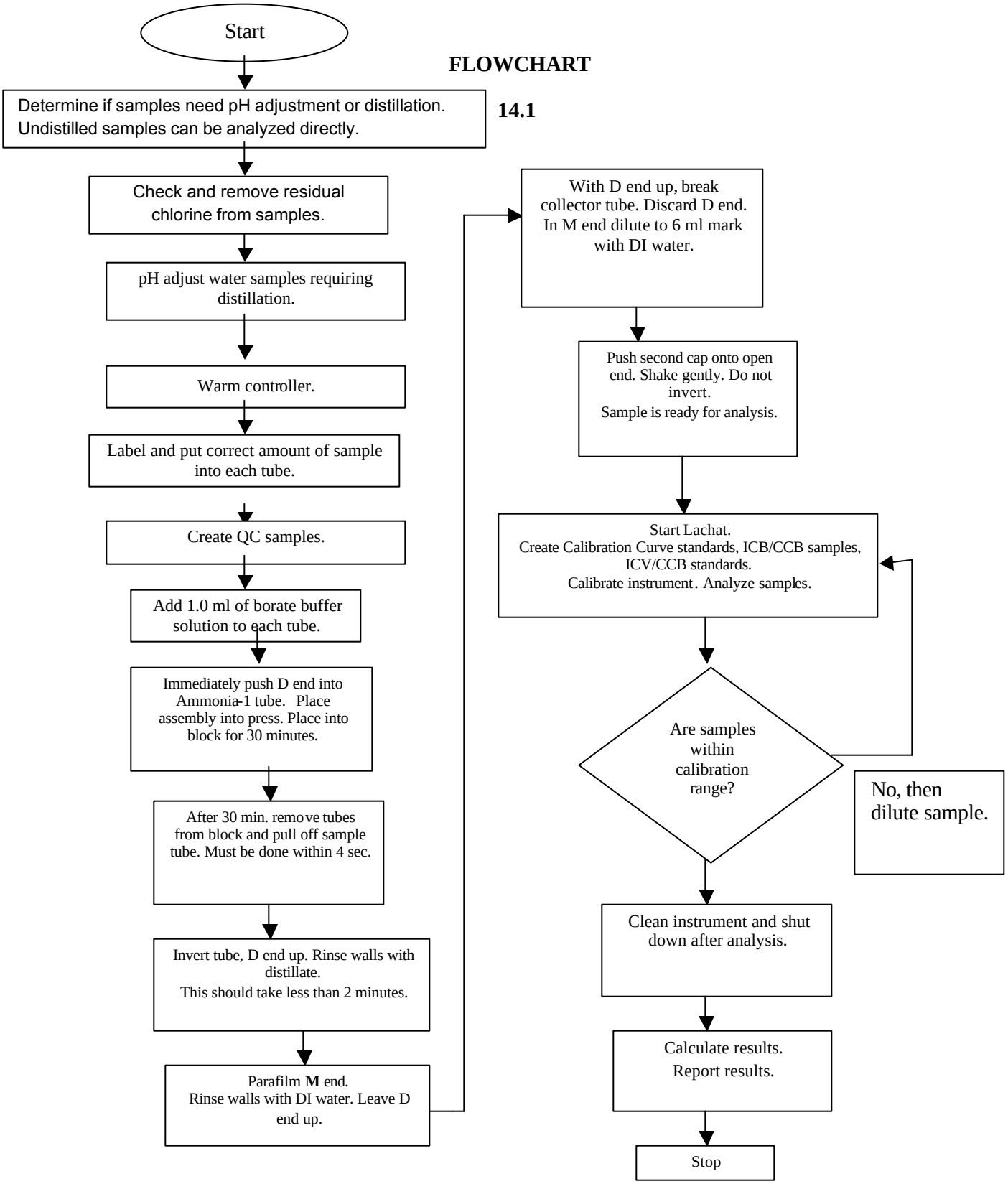
4. If correlation coefficient is less than 0.995 perform maintenance and recalibrate.

5. It is analyzed after the calibration, recovery 60-140% of true value. If outside the limits, reanalyze once. If still outside the limits, recalibrate.

6. If ICV/CCV is outside the control limits reanalyze the ICV/CCV to verify the instrument is outof control. If the 2nd analysis is outside control limits, perform maintenance and recalibrate. Samples that bracket the out of control standards must be reanalyzed. If the ICV/CCV recovers greater than the control limit and the samples bracketing the out of control ICV/CCV are non-detects, the results may be reported without a flag.

7. If ICB/CCB is outside the control limits reanalyze the ICB/CCB to verify the instrument is out of control. If the 2nd analysis is outside control limits, perform maintenance and recalibrate. Samples that bracket the out of control standards must be reanalyzed. Samples that are > 10X the concentration in the CCB the samples do not have to be reanalyzed.

FLOWCHART


Start
Determine if samples need pH adjustment or distillation. Undistilled samples can be analyzed directly.
14.1
Check and remove residual chlorine from samples.
pH adjust water samples requiring distillation.
Warm controller.
Label and put correct amount of sample into each tube.
Create QC samples.
Add 1.0 ml of borate buffer solution to each tube.
Immediately push D end into Ammonia-1 tube. Place assembly into press. Place into block for 30 minutes.
After 30 min. remove tubes from block and pull off sample tube. Must be done within 4 sec.
Invert tube, D end up. Rinse walls with distillate.
This should take less than 2 minutes.
Parafilm **M** end.
Rinse walls with DI water. Leave D end up.
With D end up, break collector tube. Discard D end. In M end dilute to 6 ml mark with DI water.
Push second cap onto open end. Shake gently. Do not invert.
Sample is ready for analysis.
Start Lachat.
Create Calibration Curve standards, ICB/CCB samples, ICV/CCB standards.
Calibrate instrument. Analyze samples.
Are samples within calibration range?
No, then dilute sample.
Clean instrument and shut down after analysis.
Calculate results.
Report results.
Stop

NH3 bench sheet example

Pace Analytical Services, Inc.

Analytical Review Report
Date Printed: 02/17/07
Approved By:
Analysis Date: 10/6/2006
Analyst: DAW
Approved Date:
Method: EPA 350.1
Data File: 100606.TXT
Worksheet#: 35214
Workbook Name: NH3100606

Lab Number	P/F	Dil	Raw Amt	TV	Matrix	%Rec	LCL	UCL	RPD	Max RPD	Units	Parameter
ICV 10	Pass	1	10.1822	10.0	W	101.8	90	110.0			mg/L	Nitrogen, Ammonia
ICB	Pass	1	0.09601		W		0.2	0.5			mg/L	Nitrogen, Ammonia
WCG2045-020MB	Pass	1	0.07602		S			+/-0.5			mg/L	Nitrogen, Ammonia
WCG2045-020MBLCS	Pass	1	10.3028	10.0	S	103.0	77	121.0			mg/L	Nitrogen, Ammonia
876514-001		1	4.06501		S						mg/L	Nitrogen, Ammonia
876402-001		1	5.27563		S						mg/L	Nitrogen, Ammonia
876450-001MS	Pass	1	15.6983	10.0	S	104.2	75	123.0			mg/L	Nitrogen, Ammonia
876450-001MSD	Pass	1	15.5405	10.0	S	102.6	75	123.0	1.0	20	mg/L	Nitrogen, Ammonia
WCG2045-021MB	Pass	1	0.10047		W			+/-0.5			mg/L	Nitrogen, Ammonia
WCG2045-021MBLCS	Pass	1	9.54773	10.0	W	95.5	90	110.0			mg/L	Nitrogen, Ammonia
CCV 10	Pass	1	10.0522	10.0	W	100.5	90	110.0			mg/L	Nitrogen, Ammonia
CCB	Pass	1	0.0452		W		0.2	0.5			mg/L	Nitrogen, Ammonia
876278-001		1	0.12084		W						mg/L	Nitrogen, Ammonia
876289-001		1	0.1325		W						mg/L	Nitrogen, Ammonia
876290-001		1	0.11449		W						mg/L	Nitrogen, Ammonia
876293-001		1	0.18982		W						mg/L	Nitrogen, Ammonia
876294-001		1	9.2027		W						mg/L	Nitrogen, Ammonia
876294-002		1	9.30663		W						mg/L	Nitrogen, Ammonia
876299-001		1	0.32287		W						mg/L	Nitrogen, Ammonia
ZZZZZZ	Over	1	46.0281		W						mg/L	Nitrogen, Ammonia
ZZZZZZ	Over	1	20.8733		W						mg/L	Nitrogen, Ammonia
ZZZZZZ	Over	1	21.3029		W						mg/L	Nitrogen, Ammonia
CCV 10	Pass	1	10.0272	10.0	W	100.3	90	110.0			mg/L	Nitrogen, Ammonia
CCB	Pass	1	0.0452		W		0.2	0.5			mg/L	Nitrogen, Ammonia
ZZZZZZ	Over	1	28.4855	10.0	W	81.8	90	110.0			mg/L	Nitrogen, Ammonia
ZZZZZZ	Over	1	28.3421	10.0	W	79.4	90	110.0	4.0	20	mg/L	Nitrogen, Ammonia
876364-001		1	1.21251		W						mg/L	Nitrogen, Ammonia
876367-001		1	14.0614		W						mg/L	Nitrogen, Ammonia
876423-001		1	11.1972		W						mg/L	Nitrogen, Ammonia
876424-002		1	6.29894		W						mg/L	Nitrogen, Ammonia
876491-001		1	14.2204		W						mg/L	Nitrogen, Ammonia
876536-001		1	10.1958		W						mg/L	Nitrogen, Ammonia
876536-001		1	4.21061		W						mg/L	Nitrogen, Ammonia
876553-002		1	2.02726		W						mg/L	Nitrogen, Ammonia
CCV 10	Pass	1	10.2416	10.0	W	102.4	90	110.0			mg/L	Nitrogen, Ammonia
CCB	Pass	1	0.0452		W		0.2	0.5			mg/L	Nitrogen, Ammonia
876554-001		1	5.68244		W						mg/L	Nitrogen, Ammonia
876556-002		1	2.8152		W						mg/L	Nitrogen, Ammonia
876556-002MS	Pass	1	13.4415	10.0	W	106.3	90	110.0			mg/L	Nitrogen, Ammonia
876556-002MSD	Pass	1	13.3068	10.0	W	105.0	90	110.0	1.0	20	mg/L	Nitrogen, Ammonia
876557-001		10	7.11301		W						mg/L	Nitrogen, Ammonia
876343-001		2	11.5281		W						mg/L	Nitrogen, Ammonia
876343-002		2	11.6901		W						mg/L	Nitrogen, Ammonia

NH3 prep sheet example

Pace Analytical Services, Inc. Distillation Log

Ammonia - distilled
EPA 350.1

Prep WS#: 2466514654
Prep Date: 10/12/06
Run Date: 10/18/06
Analyst: DAW

Balance (Weigh): 1134450 - 1.02219

	Matrix	Sample #	Pre-Dilution	Initial Vol/ Final Vol	Spike Log Number		Matrix	Sample #	Pre-Dilution	Initial Vol/ Final Vol	Spike Log Number
1	W	ICV 10		6ml/6ml	1934-27-22	31	W	876554-001		6ml/6ml	
2	W	CB		6ml/6ml		32	W	876556-003		6ml/6ml	
3	S	[illegible]		0.2g/6ml		33	W	876556-003MS		6ml/6ml	1934-27-29
4	S	[illegible]		0.2g/6ml	1934-27-23	34	W	876556-003MSD		6ml/6ml	1934-27-30
5	S	876554-001		0.1g/2ml		35					
6	S	876400-001		0.1g/2ml		36					
7	S	876400-001MS		0.1g/6ml	1934-27-24	37					
8	S	876400-001MSD		0.1g/6ml	1934-27-25	38					
9	W	[illegible]		6ml/6ml		39					
10	W	[illegible]		6ml/6ml	1934-27-26	40					
11	W	876700-001		6ml/6ml		41					
12	W	876589-001		6ml/6ml		42					
13	W	876590-001		6ml/6ml		43					
14	W	876603-001		6ml/6ml		44					
15	W	876604-001		6ml/6ml		45					
16	W	876604-002		6ml/6ml		46					
17	W	876606-001		6ml/6ml		47					
18	W	876607-001		10ml/6ml		48					
19	W	876641-001		5ml/6ml		49					
20	W	876644-002		6ml/6ml		50					
21	W	876645-[illegible]		6ml/6ml	1934-27-27	51					
22	W	876646-002MSD		6ml/6ml	1934-27-28	52					
23	W	876654-001		5ml/6ml		53					
24	W	876657-001		5ml/6ml		54					
25	W	876658-001		6ml/6ml		55					
26	W	876659-002		6ml/6ml		56					
27	W	876661-001		5ml/6ml		57					
28	W	876666-001		6ml/6ml		58					
29	W	876668-001		6ml/6ml		59					
30	W	876669-002		6ml/6ml		60					

There could be three kinds of dilutions in this run: pre, prep, or analytical. Pre-dilutions are done before the sample is analyzed. Prep-dilutions are done during the prep step. Analytical-dilutions are done on the instrument. The Pre-dilutions are noted on the prep log. The Prep-dilutions are noted in the Initial/Final Volumes on the Prep Log. On the raw data, the dilution noted is the Pre-dilution X the Analytical-dilution. The raw data dilution does not include the Prep-dilution.

Comments: _____

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STANDARD OPERATING PROCEDURE

Sulfide

Reference Method(s): Standard Methods, 18th Edition, Method 4500-S^2 E.
SW-846, Methods 9030B and 9034.

SOP NUMBER:	KS-I-027-rev.5
EFFECTIVE DATE:	Date of Final Signature
SUPERSEDES:	KS-I-027-rev.4

APPROVALS

David N. Neal, Laboratory General Manager — Date 5/3/07

Charles E. Girgin, Laboratory Quality Manager — Date 8/8/07

Kathleen White, Inorganic Manager — Date 5/1/07

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1. Purpose

The purpose of this SOP is to provide a laboratory specific procedure for determining sulfide in water and soil samples meeting the requirements specified in Standard Methods 4500-S^2 E and SW-846 9034.

2. Scope and Application

2.1 This SOP includes the measurement of sulfide in drinking, surface, and saline waters, domestic, industrial wastes and soils. The Practical Reporting Limit (PRL) for sulfide in water is 0.2 mg/L by Standard Methods 4500-S^2 E , 0.5 mg/L by SW-846 9034 and 5 mg/kg in soils by method 9034.

2.2 The method is suitable for all concentration ranges of sulfide however, appropriate aliquots should be used to avoid a titration volume >25 mL.

2.3 Acid insoluble sulfides are not measured by the use of this test. (Copper sulfide is the only common sulfide in this class).

2.4 The method is not applicable for sulfide in samples that contain a significant amount of oils, greases, and petroleum products.

3. Summary of Method

Excess iodine is added to a sample that may or may not have been treated with zinc acetate to produce zinc sulfide. The iodine oxidizes the sulfide to sulfur under acidic conditions. The excess iodine is backtitrated with sodium thiosulfate.

4. Interferences

4.1 Reduced sulfur compounds, such as sulfite, thiosulfate and hydrosulfite, which decompose in acid and may yield erratic results. Also, volatile iodine-consuming substances will give high results.

4.2 Samples must be taken with a minimum of aeration. Sulfide may be volatilized by aeration and any oxygen inadvertently added to the sample may convert the sulfide to an unmeasurable form.

5. Safety

5.1 The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable. Cautions are included for known extremely hazardous materials.

5.2 Each laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of Material Safety Data Sheets (MSDS) is made available to all personnel involved in the chemical analysis. The preparation of a formal safety plan is located in the Safety Coordinator's office.

5.3 MSDS sheets are located in the Quality Assurance Office and should be consulted prior to handling samples and standards.

5.4 Samples should be considered biological contact hazards. Use appropriate protective equipment (lab coat, gloves and lab glasses) and aseptic techniques when handling these samples. Wash hands with soap and water upon completion of the procedure and clean the work surface with a disinfectant.

6. Definitions

6.1 Accuracy – The degree of agreement between a measured value and the true or expected value.

6.2 Aliquot – A measured portion of a sample taken for analysis.

6.3 Analyte – The specific entity an analysis seeks to determine.

6.4 Batch – A grouping of no more than twenty samples of similar matrix which are prepared and/or analyzed together with the same method and the same lots of reagents within the same time frame, as designated by the method.

6.5 Blank – A blank is a sample designed to detect and/or monitor the contribution of analyte and non-analyte contamination, instrumental background and sample processing to the measurement system.

6.6 Calibration – The process of establishing the relationship between instrument response and know, traceable quantities of analytes of interest.

6.7 Calibration Check – Verification of the ratio of instrument response to analyte amount. A calibration check is performed by analyzing a solution containing the analyte in an appropriate solvent. Calibration check solutions are made from a stock solution different from the stock used to prepare standards.

6.8 Continuing Calibration – The process of analyzing standards periodically to verify the maintenance of calibration of the analytical system.

6.9 Detection Limit – The minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero, expressed either as a method detection limit or instrument detection limit.

6.10 Dry Weight – The weight of a sample based on percent solids. The weight after drying in an oven at a specified temperature.

6.11 Duplicate Analysis – A second measurement made on the same sample extract or digestate to assist in the evaluation of precision of analysis.

6.12 Duplicate Sample – A second aliquot of the same sample that is treated the same as the original sample in order to determine the precision of the method.

6.13 Environmental Sample – An environmental sample or field sample is a representative sample of any material (aqueous, non-aqueous, or multimedia) collected from any source for which determination of composition or contamination is requested or required.

Environmental samples can generally be classified as follows:

6.13.1 Surface and Ground Water

6.13.2 Drinking Water – Delivered (treated or untreated) water designated as potable water.

6.13.3 Water/Wastewater – Raw source waters for public drinking water supplies, ground waters, municipal influents/effluents, and industrial influents/effluents.

6.13.4 Sludge – Municipal sludges and industrial sludges.

6.13.5 Soil – Predominately inorganic matter ranging in classification from sands to clays.

6.13.6 Waste – Aqueous and non-aqueous liquid wastes, chemical solids, and industrial liquid and solid wastes.

6.14 EPIC (Pro) – LIMS developed by Pace Analytical (Environmental Project Information Control)

6.15 Holding Time – The elapsed time from the date/time of sample collection by the field personnel until the date/time of its processing/analysis. Holding time requirements are dictated by the method or QAPP.

6.16 Homogeneity – The degree to which a property or substance is evenly distributed throughout a material.

6.17 Initial Calibration – The process of analyzing standards prepared at specified concentrations, to define the quantitative response, linearity and dynamic range of the instrument to the analytes of interest. Initial calibration is performed whenever the results of a continuing calibration do not conform to the requirements of the method in use or at a frequency specified in the method.

6.18 Laboratory Control Sample – A control sample of known composition spiked with a known concentration of analytes of interest. Aqueous and solid laboratory control samples are analyzed using the same preparation, reagents, and analytical methods employed for field samples.

6.19 LIMS – Laboratory Information Management System.

6.20 Lot – A quantity of bulk material of similar composition processed or manufactured at the same time.

6.21 Matrix – The predominant material of which the sample to be analyzed is composed.

6.22 Matrix Spike – Aliquot of sample fortified (spiked) with known quantities of specified target compounds or analytes and subjected to the entire sample preparation and analysis procedure in order to assess the appropriateness of the method for the sample matrix by measuring recovery.

6.23 Matrix Spike Duplicate – A second aliquot of the sample that is treated the same as the original matrix spike sample. The relative percent difference between the matrix spike

and matrix spike duplicate is calculated and used to assess analytical precision.

6.24 Method Blank – An analytical control consisting of a blank matrix containing all reagents, internal standards and surrogate standards that are carried through the entire analytical procedure. The method blank is used to define the level of laboratory background and contamination, and to demonstrate that this level does not exceed acceptance limits. Acceptable levels of contamination are defined by project specific data quality objectives.

6.25 Method Detection Limit (MDL)– The minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero. Method Detection Limits are determined using replicate spike samples prepared by the lab and taken through all preparation and analysis steps of the method. The method detection limit is calculated using the appropriate Student's t-parameter times the standard deviation of a series of spiked samples.

6.26 Precision – The measurement of agreement of a set of replicate results among themselves without any prior information as to the true result. Precision is assessed by means of duplicate/replicate sample analysis.

6.27 PQL – The practical quantitation limit (PQL) is the lowest level that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operating conditions.

6.28 Quality Assurance – A system of policies and procedures whose purpose is to ensure, confirm and document that the product or service rendered fulfills the requirements of Pace Analytical and it client. Quality Assurance includes quality planning, quality control, quality assessment (auditing), quality reporting and corrective action.

6.29 Reagent Grade – Analytical reagent (AR) grade, ACS reagent grade, and reagent grade are synonymous terms for reagents which conform to the current specifications of the Committee on Analytical Reagents of the American Chemical Society.

6.30 Replicate Samples – Samples collected at the same time, from the same place, for the same analysis, as the original sample in order to determine precision between samples.

6.31 Reporting Limit (RL) – The level at which method, permit, regulatory and client specific objectives are met. The reporting limit may never be lower than the statistically determined MDL, but may be higher based on any of the above considerations. Reporting limits are corrected for sample amounts, including the dry weight of solids, unless otherwise specified. Reporting limits are generally two times the MDL.

6.32 Standard – A substance or material, the properties of which are known with sufficient accuracy, to permit its use to evaluate the same property in a sample.

6.33 Standard Curve – A standard curve is a graph which plots concentrations of a known analyte standard versus the instrument response to that analyte.

6.34 Standard Operating Procedure –A procedure adopted for repetitive use when performing specific measurement or sampling operation. It may be an industry accepted standard method or one developed by the user.

6.35 Traceability – The ability to trace the source and accuracy of a material (i.e. standard) to a recognized primary reference source such as the National Institute of Standards and Technology (NIST) or USEPA.

6.36 Validation – The process by which a sample, measurement, method or piece of data is deemed useful for a specified purpose as based upon the DQOs established for quality control measurements such as accuracy, precision, representativeness, and completeness.

7. Responsibilities and Distribution

7.1 General Manager

7.1.1 The General Manager has the overall responsibility for ensuring that SOPs are prepared and implemented for all activities appropriate to the region involving the collection and reporting of analytical data.

7.1.2 The General Manager and Laboratory Quality Manager have final review and approval authority for all SOPs prepared within the region.

7.2 Quality Manager (QM)

7.2.1 The QM will maintain a master file of all SOPs applicable to the operations departments and will schedule an annual review at a minimum with the appropriate department manager/supervisor.

7.2.2 The QM will assign a unique number to each SOP prepared prior to approval and distribution.

7.2.3 The QM will distribute SOPs to applicable personnel and maintain an accurate accounting of such distribution to ensure that the SOPs, in the hands of the users, are current and complete.

7.3 Department Manager/Supervisor

7.3.1 The Department Manager/Supervisor is responsible for ensuring all staff members are reading, following, and adequately trained in the use of SOPs

7.3.2 The department manager/supervisor coordinates the preparation and revision of all SOPs within the department.

7.3.3 The department manager/supervisor provides initial approval of all SOPs within the department.

7.3.4 The department manager/supervisor will make recommendations for SOP revision to the QM via written memo.

7.4 Individual Staff

7.4.1 Individual staff members are responsible for adherence to the specific policies and procedures contained in the applicable SOPs.

7.4.2 Individual staff members will only use a signed, controlled copy of the SOP. Each

person may make recommendations to the supervisor for revising SOPs as the need arises.

8. Sample Collection, Preservation, and Handling

Water samples should be collected in contaminant-free, 500 mL polyethylene plastic bottles containing of 1 mL 22% zinc acetate solution and 1 mL 50% NaOH solution and stored at 4°C immediately after collection. Soil samples are collected in 4-ounce wide-mouth jars and stored at 4 °C immediately after collection. Analysis must be performed within 7 days of collection.

9. Equipment and Supplies

9.1 Ordinary Laboratory glassware

9.2 25-mL buret

9.3 250-mL beakers

10. Reagents and Standards

Chemical Name	Grade	Preferred Vendor	Cat. #	Other
Hydrochloric acid (HCl)	ACS	Fisher	A508-212	
Starch indicator solution	ACS	Fisher	SS408-4	
Sodium thiosulfate solution, ($Na_2S_2O_{3)}$ 0.025 N	ACS	Fisher	LC25020-4	
Standard iodine solution, 0.025 N	ACS	Fisher	LC15620-2	

10.1 Hydrochloric acid, 6 N: Dilute 500 mL of concentrated HCl to 1 liter.

11. Calibration

11.1 Iodine solution Standardization

11.1.1 Measure approximately 100 mL of deionized water and add to a 250 mL beaker.

11.1.2 Add 5 mL of 6 N HCl to each flask, mix, and add a stir bar.

11.1.3 Pipet 10.0 mL of the iodine solution into the flask

11.1.4 Add, dropwise, enough starch solution until the blue color remains.

11.1.5 Backtitrate with the sodium thiosulfate solution until the blue color disappears. Record the amount of sodium thiosulfate was added.

11.1.6 Calculate the thiosulfate normality as follows:

$$\text{Thiosulfate solution, N} = \frac{A \times 0.025}{B}$$

where:

A = volume of iodine solution, mL
B = volume of thiosulfate solution, mL

12. Procedure

12.1 Analysis

12.1.1 Method Blank (MB): Prepare the MB by measuring 200 mL of deionized water or 10 g of glass beads plus about 200 mL deionized water and place into a 250-mL beaker.

12.1.2 Laboratory Control Sample (LCS): Prepare the LCS by measuring 200 mL of deionized water or 10 g of glass beads plus about 200 mL deionized water and place into a 250-mL beaker. Add 0.2 mL of the 1000 mg/L reference solution. The final concentration of the LCS is 2 mg/L or 40 mg/kg.

12.1.3 Matrix Spike (MS): Prepare the (MS) by measuring 200 mL of deionized water or 10 g of glass beads plus about 200 mL deionized water and place into a 250-mL beaker. Add 0.2 mL of the 1000 mg/L reference solution. The final concentration of the LCS is 2 mg/L or 40 mg/kg.

12.1.4 Client Samples: Measure 200 mL of the water or 10 g of the soil sample plus about 200 mL deionized water and place into a 250-mL beaker. Less sample size may be used if the expected sulfide content is high and will require more than 25 mL of titrant to reach an end point.

12.1.5 Add 5 mL of 6 N HCl to each flask, mix, and add a stir bar. NOTE: The stirring should not be fast enough to create a vortex.

12.1.6 To start the titration pipet 10.0 mL of the iodine solution into the flask. If the iodine color disappears add more iodine solution, in 10 mL increments, until the iodine color remains. Record the amount of total iodine solution was added.

12.1.7 Add, dropwise, enough starch solution until the blue color remains.

12.1.8 Backtitrate with the sodium thiosulfate solution until the blue color disappears. Record the amount of sodium thiosulfate was added.

12.2 EPIC Posting

12.2.1 This is a one-step acode.

12.2.2 Post the sample Initial Volume/Weight in mL or g, default is 200 mL/10 g, and the Final Volume in mL, default is 200 mL. For waters and soils always post 200 mL.

12.2.3 Post the sample final analyzed value in mg/L from using the formula below.

12.3 Manual Calculation

12.3.1 Water

$$\text{Sulfide, as mg/L} = \frac{[(A \times B) - (C \times D)] \times 16{,}000}{\text{mL of sample}}$$

12.3.2 Soil

$$\text{Sulfide, as mg/kg} = \frac{[(A \times B) - (C \times D)] \times 16{,}000}{\text{g of sample}}$$

where:

A = mL of iodine solution
B = normality of iodine solution
C = mL of sodium thiosulfate solution
D = normality of the thiosulfate solution

13. Quality Control

13.1 The Method Blank must not contain a positive result above the PRL. If the Method Blank contains a positive result above the PRL, acceptance of that blank requires supervisory approval.

13.2 LCS recovery acceptance limits are established on an annual basis by the QAO and distributed to each lab. If the recovery is not within those limits see the Supervisor immediately for further action.

13.3 Duplicate (Dup) assays should be performed for all analyses where appropriate. The Duplicate Relative Percent Difference (RPD) acceptance limit is established on an annual basis by the QAO and distributed to each lab. If the RPD is greater than the limit see the Supervisor immediately for further action.

13.4 MS and/or MSD assays should be performed for all analyses where appropriate. The recovery acceptance limits are established on an annual basis by the QAO and distributed to each lab. If the recoveries are not within those limits see the Supervisor immediately for further action.

13.5 MS/MSD assays should be performed for all analyses where appropriate. The MS/MSD Relative Percent Difference (RPD) acceptance limits are established on an annual basis by the QAO and distributed to each lab. If the RPD is greater than the limit see the Supervisor immediately for further action.

14. Method Performance and Deviations

14.1 There are several requirements that must be met to insure that this procedure generates accurate and reliable data. A general outline of requirements has been summarized below. Further specifications may be found in the Laboratory Quality Manual.

14.1.1 The analyst must read and understand this procedure with written documentation maintained in his/her training file.

14.1.2 An initial demonstration of capability (IDC) must be performed. A record of the IDC will be maintained in his/her file with written authorization from the Laboratory Manager and Quality Assurance Officer. Note to reviewer: include spike concentration and documentation procedures.

14.1.3 An annual minimum detection limit (MDL) study will be completed for this method and whenever there is a major change in personnel or equipment. MDL studies will be conducted in accordance with 40 CFR part 136, Appendix B, rev.1.11.

14.1.3.1 The concentration for the MDL standard will be 2 to 5 times the expected MDL.

14.1.3.2 The calculated MDL can not be less than 1/10 of the spike concentration, i.e. if you analyzed your MDL study at a concentration of 10 ug/L, then the calculated MDL could not be less than 1 ug/L. If it is lower than 1/10, the study needs to be repeated at a lower spike concentration.

14.1.4 Periodic performance evaluation (PE) samples are analyzed to demonstrate continuing competence.

14.1.5 This SOP procedure is modified to add the sample without injecting it under the surface of the iodine and HCl mixture.

15. Pollution Prevention and Waste Management

15.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

15.2 The quantity of chemicals purchased should be based on expected usage during its shelf life and disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

15.3 For information about pollution prevention that may be applicable to laboratories and research institutions, consult “Less is Better: Laboratory Chemical Society’s Department

of Government Regulations and Science Policy, 115 16th Street NW, Washington, DC 20036, (202) 872-4477.

15.4 The Environmental Protection Agency (USEPA) requires that laboratory waste management practice be conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes should be characterized and disposed of in an acceptable manner. The agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods, and bench operations, complying with the letter and spirit of any water discharge permit and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management consult the KS QAO.

16. References

16.1 Standard Methods for the Examination of Water and Wastewater, 18th Edition, Method 4500-S^{2-} E.

16.2 Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW846), 3rd Edition, Methods 9030B and 9034.

16.3 Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020 Revised March 1983, Method 376.1.

17. Tables, Diagrams, Flowcharts, Attachments, Appendices, Etc.

Not applicable

18. Revisions

Document Number	Changes	Date
KS-I-027-rev.4	Grammatical/Removal of outdated information.	September 13, 2005
KS-I-027-rev.5	**SOP** – Removed most references to Method 376.1. **Cover Page -** Revised method references. **Section 1** – Revised method references. **Section 2.1** – Revised method references. **Section 17.1** – Revised edition number.	April 18, 2007

Attachment 3

TriMatrix Laboratories, Inc.
Quality Assurance Manual and Standard Operating Procedures

Table of Contents

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1	24	GR-05-128	Available Cyanide by Flow Injection Ligand Exchange and Amperometry Reference Method: OIA - 1677

TriMatrix Laboratories, Inc.

UNCONTROLLED COPY

STANDARD OPERATING PROCEDURE

Available Cyanide by Flow Injection, Ligand Exchange and Amperometry

EPA Method OIA-1677

APPROVALS:

Area Supervisor: Heather L. Brady (Heather L. Brady) Date: 1-31-09

QA Officer: (Tom C. Boocher) Date: 1-26-09

Operations Manager: (Jeff P. Glaser) Date: 2/4/09

Procedure Number: GR-05-128
Revision Number: 0.1

Date Initiated: 1/21/04
Effective Date: 2/24/09

Date Revised: 1/24/09
Pages Revised: All

By: Jodi L. Blouw
Total Number of Pages: 24

If signed below, the last annual review required no procedural revision.

Date Reviewed	Reviewed by	Review Expires

1.0 SCOPE AND APPLICATION

1.1 This procedure measures available cyanide in water and wastewater by flow injection and ligand exchange with amperometric detection.

1.2 The applicable range is 0.002 mg/L to 0.05 mg/L available cyanide. The range may be extended by sample dilution.

2.0 PRINCIPLE METHOD REFERENCES

2.1 USEPA Method OIA-1677, *"Available Cyanide by Flow Injection, Ligand Exchange, and Amperometry"*, August 1999, EPA-821-R-99-013

3.0 SUMMARY OF PROCEDURE

3.1 Two samples are collected from each sample site. Initial sample pre-treatment occurs in the field. One sample is treated with lead carbonate, filtered to remove any precipitated lead sulfide, and preserved with sodium hydroxide. The second is simply preserved with sodium hydroxide. In the laboratory both samples are treated with ligand exchange reagents to release cyanide from cyano-metal compounds. Thermodynamically stable complexes are formed through the ligand exchange in cyano compounds containing zinc, copper, cadmium, mercury, nickel, and silver.

3.2 Sample acidification and introduction to the detector is by a flow injection system. Cyanide ion is detected amperometrically with a silver working electrode, silver/silver chloride reference electrode, and platinum/stainless steel counter electrode, at an applied potential of zero volts. The current generated is proportional to cyanide concentration in the sample.

4.0 PARAMETER OR COMPOUND LIST

4.1 Available Cyanide

5.0 REFERENCED SOPs

5.1 TriMatrix SOP GR-15-102, *Laboratory Waste Disposal,* latest revision

5.2 TriMatrix SOP GR-10-125, *Method Detection Limit (MDL)*, latest revision.

6.0 INTERFERENCES AND CORRECTIVE PROCEDURES

6.1 Treatment for all potential interferences occurs during sample collection. Samples containing water soluble aldehydes must be treated by adding ethylenediamine solution. Samples containing oxidizing agents must

be treated with ascorbic acid. All samples are treated for potential of sulfide interferences using lead carbonate. Refer to Section 8.0 for sample collection procedures.

7.0 SAFETY PRECAUTIONS

7.1 Analysts must comply with all instructions for health and safety as outlined in the TriMatrix Laboratory Safety Manual and Chemical Hygiene Plan.

7.2 The toxicity or carcinogenicity of chemicals used in this procedure has not been precisely determined. Each chemical must be treated as a potential health hazard. Exposure to chemicals must be reduced to the lowest possible level. A laboratory coat, approved safety glasses, and disposable gloves must be worn in the laboratory and during every step of the procedure.

7.3 Cyanide ion, hydrocyanic acid, all cyanide salts and most metal-cyanide complexes are extremely dangerous. As a contact poison, cyanide need not be ingested to produce toxic effects. Cyanide solutions produce hydrogen cyanide gas when acidified. Work with cyanide standards, reagents and samples must be performed in a well-ventilated hood by properly trained analysts.

8.0 SAMPLE SIZE, COLLECTION, PRESERVATION AND HANDLING PROCEDURES

8.1 Two samples will be collected at each sample point. One sample will be treated with lead carbonate and sodium hydroxide, and the second with only sodium hydroxide. See flowchart, Attachment 23.1.

IMPORTANT: To avoid analyte loss it is required that all sample treatments occur within 15 minutes of sample collection.

CAUTION: All containers labeled as Sodium Hydroxide and Lead Carbonate/Sodium Hydroxide contain 1.3 mL of 10N sodium hydroxide. This solution is very caustic. Avoid skin contact. Handle with care.

CAUTION: All containers labeled as Lead Carbonate contain 0.25 g of solid lead carbonate. Avoid inhalation and skin contact.

8.2 Collect a lead carbonate/sodium hydroxide treated sample. If the sample contains particulates, begin with Section 8.2.1. If the sample is particulate free, begin with Section 8.2.2.

8.2.1 Sample Contains Particulate Matter

8.2.1.1 If the sample contains particulate matter that would be removed upon filtration, the sample must be filtered prior to the lead carbonate pre-treatment to avoid the loss of any cyanides associated with the particulate matter. Using a powder funnel and a sheet of filter paper, filter the sample into the bottle labeled Lead Carbonate. Filter enough sample volume to fill the bottle up to its neck. Place the used filter paper into the bottle labeled Lead Carbonate/Sodium Hydroxide. Cap the Lead Carbonate bottle and gently swirl to mix the sample and the lead carbonate. The

lead carbonate will not completely dissolve into solution. The sulfide will react with the lead carbonate and precipitate out as lead sulfide. The sample must now be filtered through a membrane filter to prevent the loss of any cyanide through reaction with the precipitated lead sulfide. Using a new membrane filter apparatus and a hand vacuum pump, filter the sample. Transfer the filtrate into the Lead Carbonate/Sodium Hydroxide bottle containing the used filter paper. Do not pre-rinse the container or fill to overflowing, as a loss of the particulate matter and sodium hydroxide will result. Proceed to Section 8.3.

8.2.2 Sample Particulate Free

8.2.2.1 With a minimum of aeration, fill the 250 mL bottle labeled Lead Carbonate up to the neck with sample. Cap and gently swirl to mix the sample and the lead carbonate. The lead carbonate will not completely dissolve into solution. The sulfide will react with the lead carbonate and precipitate out as lead sulfide. The sample must now be filtered through a membrane filter to prevent the loss of any cyanide through reaction with the precipitated lead sulfide. Using a new membrane filter apparatus and the hand pump, filter the sample. Transfer the filtrate collected into the bottle labeled Lead Carbonate/Sodium Hydroxide. Do not pre-rinse the container or fill to overflowing to avoid the loss of the sodium hydroxide.

8.3 Collecting a Sodium Hydroxide Pre-Treated Sample

8.3.1 With a minimum of aeration fill the 250 mL bottle labeled Sodium Hydroxide with sample. Do not pre-rinse the container or fill to overflowing to avoid the loss of the sodium hydroxide.

8.4 A form titled "Available Cyanide Sample Treatment Record" has been provided to document all field pre-treatment activities (Attachment 23.2). It must be completed and returned with the samples.

8.5 Place all collected samples in the cooler. Surround the samples with ice. To avoid data qualification all samples must be received at a temperature of between 0 and 6° C. Seal all paperwork in the resealable bag. Replace the membrane filter pump in its resealable bag. Place the sealed bags containing the paperwork and the pump in the cooler. Place all plastic powder funnels and unopened membrane filters in the cooler. Seal the cooler and return it to TriMatrix.

8.6 All analyses must occur within 14 days from sample collection.

8.7 If samples are known or suspected to contain water soluble aldehydes, treat at the time of collection with 5 mL of 3.5% ethylenediamine solution per 250 mL sample collected.

8.8 If samples are known or suspected to contain chlorine, hypochlorite, or sulfite, treat at the time of collection with 0.15 g ascorbic acid per 250 mL sample collected.

9.0 INSTRUMENTATION, APPARATUS, AND MATERIALS

9.1 Flow Injection Analysis System – OI Analytical CNSolution FS 3100 with Amperometric Detector System

9.1.1 Data acquisition System with WinFLOW™ Software

9.1.2 Available Cyanide, Method OIA-1677 Cartridge

9.2 Volumetric flasks, Class A

9.3 Volumetric pipets, Class A

9.4 Analytical balance, readable to 0.1 mg

9.5 Plastic sample cups

9.6 Lead acetate test paper

10.0 ROUTINE PREVENTIVE MAINTENANCE

10.1 Peristaltic pump lines must be replaced as necessary.

11.0 CHEMICALS AND REAGENTS

11.1 Reagent water – Millipore ASTM Type II

11.2 Sodium Hydroxide, ACS grade

11.3 Hydrochloric Acid (approximately 37%) – ACS grade

11.4 Potassium Cyanide, ACS grade, primary source

11.6 Potassium Cyanide, ACS grade, secondary source

11.5 Mercury (II) Cyanide, ≥99% purity – Aldrich Catalog #208140 or equivalent

11.7 Silver Nitrate – ACS grade

11.8 Ascorbic Acid - Crystals

11.9 Ligand Exchange Reagent A (OI part #A001416) – Shelf life of 1 year from date received, 6 months from date opened, whichever occurs first. Store at 1-6° C.

11.10 Ligand Exchange Reagent B (OI part #A001417) – Shelf life of 1 year from date received, 6 months from date opened, whichever occurs first. Store at 1-6° C.

11.11 Potassium Chromate (K_2CrO_4) indicator solution (5% w/v) – Fisher Scientific (Cat #SP152-500) or equivalent.

11.12 Sodium hydroxide (1.0M) – Dissolve 40.0 g of sodium hydroxide pellets in approximately 500 mL of reagent water, in 1 L volumetric flask. Dilute to 1 L with reagent water. Store in an amber bottle at room temperature. Expiration is six months from the date made.

11.14 Carrier and Acid Reagent (0.1M Hydrochloric Acid) – Dilute 8.0 mL concentrated HCl to 1 L with reagent water. Expiration is six months from the date made.

11.15 Acceptor reagent (0.1M sodium hydroxide) – Dilute 100 mL of 1M NaOH to 1 L with reagent water. Expiration is six months from the date made.

11.16 Dilution Solution (0.01M) – In a 2L volumetric flask add 20 mL of 1M NaOH solution to 1L of reagent water. Dilute to volume with reagent water. Expiration is six months from the date made.

11.17 Rhodanine Indicator (0.2 mg/mL in acetone)–Weigh 20 mg of 5-[p-(dimethylamino)benzylidene]rhodanine (J.T. Baker, Cat #J431-02) into a 100 mL volumetric flask. Dilute to the mark with acetone. Expiration is six months from the date made.

11.18 Ethylenediamine solution – In a 100 mL volumetric flask, dilute 3.5 mL pharmaceutical grade anhydrous ethylenediamine with reagent water. Expiration is six months from the date made.

11.19 Acetate Buffer Solution, pH = 4.0: Dissolve 7.3 g anhydrous sodium acetate in a 50 mL volumetric flask filled with approximately 20 mL reagent water. Add 24 g glacial acetic acid and dilute to volume with reagent water. May be stored in an inert plastic bottle at room temperature up to 6 months.

11.20 Sodium Chloride (NaCl) standard (0.0192N) – Dissolve 1.125 g ACS grade NaCl (dried at 140° C) in reagent water and dilute to 1000 mL in a volumetric flask. Expiration is six months from the date made.

11.21 Silver Nitrate ($AgNO_3$) solution (0.0192N) – Weigh 3.27 g of $AgNO_3$ into a 1 L volumetric flask and bring to the mark with reagent water. Store in an amber glass container. Expiration is six months from the date made.

11.21.1 Standardize prior to every use, against 0.0192N NaCl using the argentometric method with K_2CrO_4 indicator:

$$Cl^- + AgNO_3 \xrightarrow{K_2CrO_4} AgCl(s) + NO_3$$

$$2Ag^+ + CrO_4{}^{2} \longrightarrow Ag_2CrO_4$$

11.9.1.1 Pipet 10.0 mL of NaCl standard into a beaker then add approximately 100 mL of reagent water. Add 1.0 mL of K_2CrO_4 indicator solution. Titrate with $AgNO_3$ solution to a pinkish yellow end point.

11.9.1.2 The $AgNO_3$ normality correction factor is calculated as follows:

$$\frac{A}{B} = C$$

where:
A = NaCl volume used, in mL
B = $AgNO_3$ titrated, in mL
C = normality correction factor

11.22 All reagent preparation must be recorded with a unique identification number in the LIMS system, or the appropriate paginated reagent logbook. Refer to Attachment 23.1 for a reagent logbook example.

12.0 STANDARDS PREPARATION

12.1 Cyanide Stock Solution (1000 mg/L):

12.1.1 Dissolve approximately 1 g sodium hydroxide in approximately 400 mL reagent water in a 500 mL volumetric flask (0.05M).

12.1.2 Add approximately 1.25 g potassium cyanide. Bring up to volume with reagent water and mix well.

12.1.3 Prepare a second stock solution from a separate source to use as a second source calibration verification standard (SCV).

12.1.4 Store refrigerated in amber glass. Expiration is six months from the date made.

12.2 Cyanide stock standardization:

12.2.1 Pipet 25.0 mL of the 1000 mg/L cyanide stock solution into a beaker filled with approximately 100 mL dilution solution.

12.2.2 Add 0.5 mL of rhodanine indicator.

12.2.3 Titrate with standardized $AgNO_3$ solution to the first color change. The solution will change from canary yellow to an endpoint color of salmon hue.

12.2.4 Add 0.5 mL of rhodanine indicator to 100 mL of dilution solution and titrate.

12.2.5 The standardized cyanide stock concentration is determined by the following equation (use the result in calculating the subsequent dilution concentrations and working standards):

$$mg/L\ CN^- = \frac{(A - B) \times C \times 1000}{mL\ CN^-\ used}$$

where:
A = $AgNO_3$ titrated for the stock solution, in mL
B = $AgNO_3$ titrated for the dilution solution blank, in mL
C = $AgNO_3$ normality correction factor from Section 11.9.1.2

12.2.6 Repeat the standardization routine on the SCV.

12.2.7 Perform standardization weekly to verify concentration.

12.3 Cyanide, 10 mg/L level – Pipet 10.0 mL of cyanide stock (1000 mg/L level) into a 1L volumetric flask partially filled with dilution solution. Bring up to volume with dilution solution. Store refrigerated in amber glass. Prepare fresh daily.

12.4 Second Source Cyanide Standard, 10 mg/L level – Pipet 10.0 mL of second source cyanide stock (1000 mg/L level) into a 1L volumetric flask partially filled with dilution solution. Bring up to volume with dilution solution. Store refrigerated in amber glass. Prepare fresh daily.

12.5 Cyanide 1.0 mg/L level – Pipet 10.0 mL cyanide solution (10 mg/L level) into a 100 mL volumetric flask partially filled with dilution solution. Bring up to volume with dilution solution. Store refrigerated in amber glass. Prepare fresh daily.

12.6 Calibration standards – Prepare fresh daily using dilution solution and 100 mL volumetric flasks.

Calibration Standards Concentration	Add	Final Volume
0 mg/L	-	100 mL
0.002 mg/L	10 mL of 0.02 mg/L	100 mL
0.005 mg/L	10 mL of 0.05 mg/L	100 mL
0.01 mg/L	1.0 mL of 1.0 mg/L	100 mL
0.02 mg/L	2.0 mL of 1.0 mg/L	100 mL
0.05 mg/L	5.0 mL of 1.0 mg/L	100 mL

12.7 Quality Control Standards

12.7.1 Mercury(II) Cyanide Stock Solution (1000 mg/L cyanide) – Weigh 0.486 g of mercury (II) cyanide into a 100 mL volumetric flask partially filled with dilution solution. Swirl to mix. Bring up to volume with dilution solution. Store refrigerated in amber glass. Expiration is 60 days from the date made.

12.7.2 Blank Spike (BS) Working Standard (100 mg/L cyanide) – Pipet 10 mL 1000 mg/L mercury(II) cyanide into a 100 mL volumetric flask partially filled with dilution solution. Swirl to mix. Bring up to volume with dilution solution. Store refrigerated in amber glass. Expiration is 60 days from the date made.

12.7.3 Blank Spike Spiking Standard (0.01 mg/L). Pipet 20 uL of the 100 mg/L mercury(II) cyanide solution into a 200 mL volumetric flask partially filled with dilution solution. Swirl to mix.

Bring up to volume with dilution solution. Store refrigerated in amber glass. Expiration is 60 days from the date made.

12.6.4 Second Source Verification Standard (0.01 mg/L). Pipet 100 uL of the 10 mg/L second source cyanide standard solution into a 100 mL volumetric flask partially filled with dilution solution. Swirl to mix. Bring up to volume with dilution solution. Store refrigerated in amber glass. Expiration is 60 days from the date made.

12.7 All working standards must be labeled with the following information:

12.7.1 Initials of preparer

12.7.2 Preparation date

12.7.3 Concentration

12.7.4 Parameter name

12.7.5 Expiration date

12.7.6 Stock standard ID

12.7.7 Preservative

12.8 All prepared standards must be recorded in an appropriate paginated standard logbook, with a unique identification number. Refer to Attachment 23.4 for a standards log example.

13.0 SAMPLE PREPARATION

13.1 Test the sample labeled "Lead Carbonate/Sodium Hydroxide" for the presence of sulfides with lead acetate paper.

13.1.1 Dip a lead acetate test strip into the acetate buffer solution prepared in Section 11.19. Dip the wetted strip in the sample. A positive sulfide test is indicated by a black color appearing on the paper.

13.1.2 If the lead acetate strip determines that sulfide is present in the lead carbonate treated sample, report this information with the sample result using an analysis narrative. Do not attempt to treat the sample with additional lead carbonate.

13.2 Verify, and if necessary adjust, the pH of both treated samples to approximately 12 before analysis.

13.3 To 50 mL of sample or standard at a pH of approximately 12, using a disposable eye dropper add 1 drop of ligand-exchange reagent A and 1 drop of ligand exchange reagent B. Mix thoroughly.

13.4 All analyses must be completed within 2 hours of the addition of the ligand reagents.

14.0 CALIBRATION PROCEDURES

14.1 Set up the flow injection analysis system and establish initial operating conditions for available cyanide analysis.

14.2 Ensure reagents are flowing smoothly through the system and no air bubbles are present in the flow cell.

14.3 Load and inject a 10 mg/L potassium cyanide standard.

14.4 Continue to inject 10 mg/L standards until three successive peak heights or areas average less than 2% RSD. An average of less than 2% RSD indicates electrode stabilization.

14.5 When the electrode has stabilized, inject the highest concentration calibration standard until three successive peak heights or areas average within 2% RSD, indicating stabilization at the top of the calibration range.

14.6 Inject the initial calibration standards from low to high. The instrument automatically regresses a calibration curve. The correlation coefficient for the calibration must be 0.995 or greater.

14.7 Inject the 0.01 SCV standard. The standard must recover between 90-110% of the true value for the initial calibration curve to be considered valid.

15.0 ANALYTICAL PROCEDURE

15.1 Transfer samples treated with ligand exchange reagents to sample cups and load in the autosampler. Samples must be analyzed within 2 hours of adding ligand exchange reagents.

15.2 Initiate the autosampler to inject samples.

15.3 Dilute and rerun samples with concentrations above the highest concentration of the calibration curve. All dilutions must be made using dilution solution and a fresh aliquot of sample that does not contain the ligand reagents.

16.0 CALCULATIONS AND DATA HANDLING

16.1 The instrument regresses all data against the calibration curve. Results are printed out in mg/L.

16.2 Compare the results of the lead carbonate treated sample to the sodium hydroxide only treated sample. Report the lower of the two results.

17.0 DATA REPORTING AND DELIVERABLES

17.1 Include the following with benchsheets, for each batch archived:

17.1.1 Calibration curve printout

17.1.2 Raw data printout

17.1.3 Run sequence sheet

17.2 The instrument logbook must be filled in for each batch handed in, with the following information:

17.2.1 Date analyzed

17.2.2 Analyst initials

17.2.3 Method name and number

17.2.4 Calibration standards used

17.2.5 Client name and sample numbers analyzed

17.3 The following must be recorded for each batch analyzed:

17.3.1 Reported concentration, SCV, CCV, CCB, MPB, BS, SPK, and MSD.

17.3.2 Instrument number, date run, supervisor, stock standard number, wavelength, cell path

17.3.3 Working standard concentration values, observed values, working ID numbers

17.4 Attached are examples of a calibration curve (Attachment 23.5), raw data (Attachment 23.7), an instrument logbook (Attachment 23.8), a preparation batch report (Attachment 23.9) and an analysis sequence report (Attachment 23.10).

18.0 QUALITY ASSURANCE

18.1 Before sample testing, each lot of lead acetate paper must be tested for sensitivity, when received.

18.1.1 Prepare a 10 mg/L solution of sulfide in water. Test the solution with a lead acetate strip from any untested lot and any new lot.

18.1.2 If a test strip detects sulfides in the 10 mg/L solution, the lot passes and may be used for sample testing. If a lot fails, it must be rejected. Return to purchasing for reimbursement through the vender.

18.1.3 Record all lead acetate paper testing and results in the laboratory reagent logbook beside the lot entry.

18.2 Quality control is required for each analytical batch of no more than 20 samples. A blank (MPB), blank spike (BS) and matrix spikes (MS/MSD) must accompany 20 or fewer samples. For analysis of more than 20 samples, two or more batches must be initiated with separate quality control.

18.3 Verify calibration before and after each analytical batch, bracketing up to 10 analyses.

18.3.1 Continuing Calibration Verification (CCV) is the 0.01 mg/L calibration standard analyzed as a sample. Acceptance limits for recovery are 86-118%. If recovery is not within the acceptance range, the instrument must be recalibrated and the sample batch re-analyzed with an acceptable calibration curve.

18.3.2 A Continuing Calibration Blank (CCB) must be analyzed after every CCV. The CCB is an analysis of the dilution solution spiked with the ligand reagents processed as a sample. Results must be less than the established reporting limit. If a CCB is greater than the reporting limit, contamination must be addressed and samples from the bracketed batch re-analyzed.

18.4 Once per batch an Method Preparation Blank (MPB) is required. An MPB is also dilution solution spiked with the ligand reagents. Results must be less than the reporting limit. If a MPB is greater than the reporting limit, contamination must be addressed and samples from the batch re-analyzed.

18.5 A Blank Spike (BS) is the 0.01 mg/L mercury(II) cyanide standard analyzed as a sample with each analytical batch. Acceptance limits for recovery are 82-132%. If recovery is not within the acceptance range, cyanide standards must be remade and the sample batch re-analyzed with an acceptable calibration curve.

18.6 One sample per matrix per batch of 20 must be spiked for a matrix spike and matrix spike duplicate.

18.6.3 Samples must be spiked with the 100 mg/L mercury(II) cyanide standard.

18.6.4 Acceptance limits for matrix spike recovery are 82-130%. If recovery is not within the acceptance range and BS recovery is acceptable, all samples in the batch from the same matrix or discharge must flagged when reported as unacceptable for regulatory reporting. The relative percent difference (RPD) for the average of the matrix spike and matrix spike duplicate results must be <11%.

19.0 DEMONSTRATIONS OF CAPABILITY/METHOD VALIDATION

19.1 Before actual sample analysis, each analyst must demonstrate an ability to generate acceptable accuracy and precision by running an Initial Demonstration of Capability (IDC). If multiple instruments are used for the same analysis, an IDC is required for each instrument, to document acceptable accuracy and precision from all equipment used.

19.1.1 Initial Demonstration of Capability

19.1.1.1 Pipet 20 uL of 100 mg/L mercury(II) cyanide solution into a 200 mL volumetric flask and dilute to volume with reagent water. The BS cyanide concentration is

0.01 mg/L. Take four aliquots of the BS solution and process in accordance with every step in the procedure, to obtain four results. Calculate average percent recovery and standard deviation of the average obtained. Average percent recovery must be within 92-122%. Standard deviation of the average must be ≤ 5.1%.

19.1.1.2 If these criteria are not met, locate and correct the source of the problem and repeat the test. Repeated failure however, will confirm a general problem with the procedure or technique being used. If this occurs, locate the source of the problem and correct the procedure or technique, then repeat the test. Samples may not be analyzed by any analyst on any instrument until a successful demonstration of capability has been completed. Copies of the successful demonstration of capability spreadsheet used to calculate IDC results and raw data must be given to the Quality Assurance Department.

19.1.2 Continuing Demonstration of Capability (CDC)

19.1.2.1 A CDC must be performed annually by all analysts using this procedure. A CDC may be accomplished by repeating the above using another set of four BS aliquots, by processing four consecutive BS results obtained during sample analysis or by submitting an acceptable PT study result on the appropriate paperwork. Alternatively, the last four of seven results obtained from an MDL study may be used as an IDC, if run exclusively by the analyst being tested. ONLY the last four of seven results may be used. Each of these choices must be run exclusively by the analyst being tested.

19.2 A Method Detection Limit (MDL) Study is required annually in accordance with TriMatrix SOP GR-10-125.

20.0 POLLUTION PREVENTION

20.1 Maintain an inventory of all chemicals used in the laboratory to monitor their use.

20.2 Never dispose of laboratory chemicals without first referencing appropriate written instructions of disposal for that particular material.

20.3 Conserve the use of chemicals where applicable.

20.4 Comply with all environmental laws associated with chemicals in the laboratory.

21.0 WASTE MANAGEMENT

21.1 Consult the appropriate Material Safety Data Sheet (MSDS) when disposing of chemicals. The laboratory intranet library contains an MSDS for all chemicals used in the library and can be accessed from any computer in the laboratory.

21.2 To minimize the environmental impact and costs associated with chemical disposal, order and use only the minimum amount of material required.

21.3 Follow all instructions in TriMatrix SOP GR-15-102 for laboratory waste disposal requirements.

22.0 REFERENCES

22.1 USEPA Method OIA-1677, *"Available Cyanide by Flow Injection, Ligand Exchange, and Amperometry"*, August 1999, EPA-821-R-99-013

23.0 ATTACHMENTS

23.1 Sample Collection Flowchart

23.2 Sample Treatment Record Example

23.3 Reagent Log Example

23.4 Standard Log Example

23.5 Calibration Curve Example

23.6 Chromatogram Example

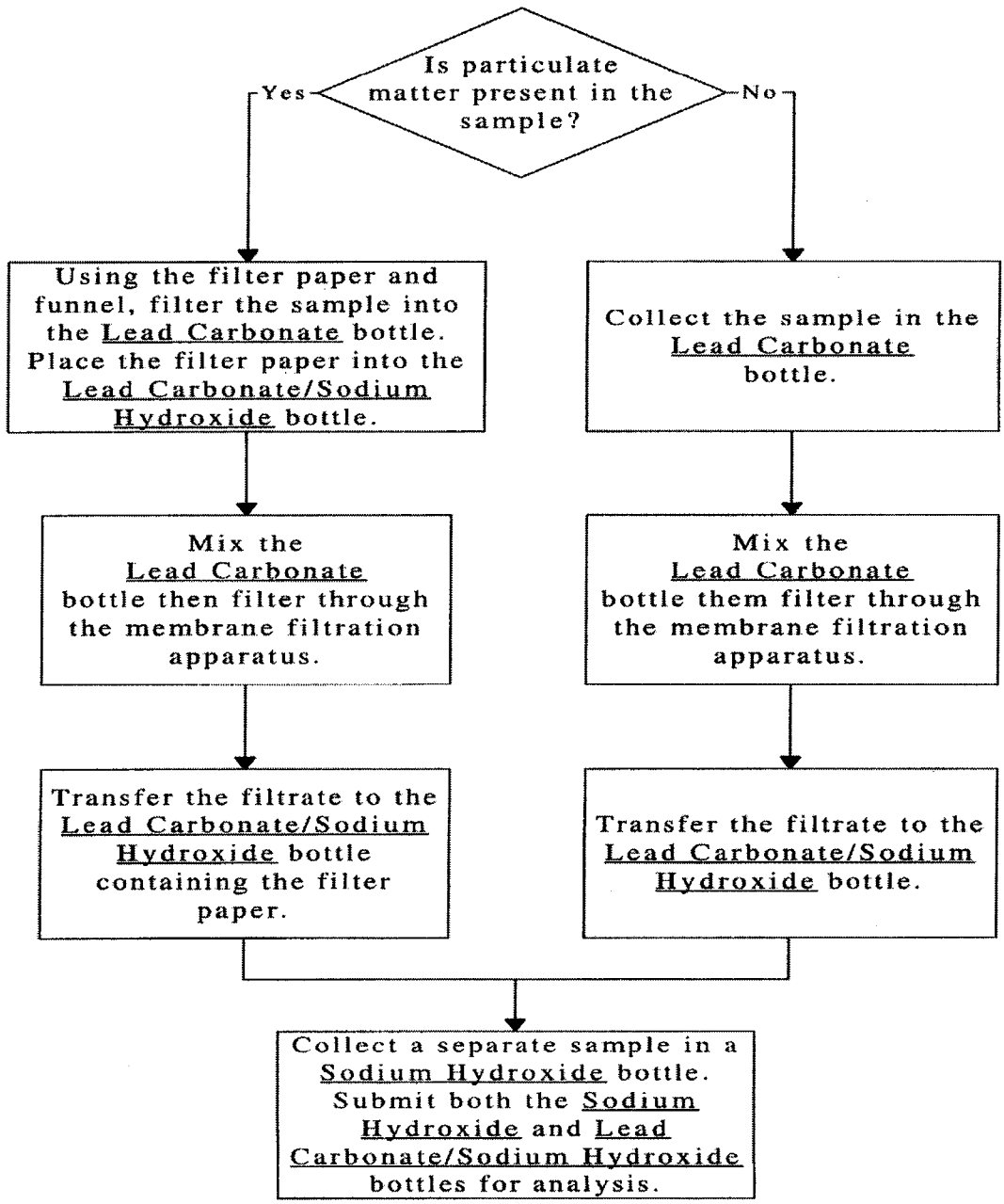
23.7 Raw Data Hardcopy Example

23.8 Instrument Logbook Example

23.9 Preparation Batch Report Example

23.10 Analysis Sequence Report Example

Attachment 23.1
Sample Collection Flowchart



Approved By: _____ 1-26-09 **Approved By:** Heather L. Brady
QA Officer **Area Supervisor**

Attachment 23.2
Sample Treatment Record Example

TriMatrix Laboratories, Inc.

Available Cyanide Sample Treatment Record

Sampled By: _____ **Company:** _____ **Date:** _____

	Sample ID	Time Collected	Did Sample Contain Particulate Matter and Require Filtration?	Sample Combined with Lead Carbonate	Filtrate Combined with Sodium Hydroxide	Time Treatment Completed	Treatment Completed within 15 minutes of Collection?	Preserved Sample Collected
1)			Yes / No	Yes / No	Yes / No		Yes / No	Yes / No
2)			Yes / No	Yes / No	Yes / No		Yes / No	Yes / No
3)			Yes / No	Yes / No	Yes / No		Yes / No	Yes / No
4)			Yes / No	Yes / No	Yes / No		Yes / No	Yes / No
5)			Yes / No	Yes / No	Yes / No		Yes / No	Yes / No
6)			Yes / No	Yes / No	Yes / No		Yes / No	Yes / No
7)			Yes / No	Yes / No	Yes / No		Yes / No	Yes / No
8)			Yes / No	Yes / No	Yes / No		Yes / No	Yes / No
9)			Yes / No	Yes / No	Yes / No		Yes / No	Yes / No
10)			Yes / No	Yes / No	Yes / No		Yes / No	Yes / No
11)			Yes / No	Yes / No	Yes / No		Yes / No	Yes / No
12)			Yes / No	Yes / No	Yes / No		Yes / No	Yes / No
13)			Yes / No	Yes / No	Yes / No		Yes / No	Yes / No
14)			Yes / No	Yes / No	Yes / No		Yes / No	Yes / No
15)			Yes / No	Yes / No	Yes / No		Yes / No	Yes / No
16)			Yes / No	Yes / No	Yes / No		Yes / No	Yes / No
17)			Yes / No	Yes / No	Yes / No		Yes / No	Yes / No
18)			Yes / No	Yes / No	Yes / No		Yes / No	Yes / No
19)			Yes / No	Yes / No	Yes / No		Yes / No	Yes / No

BP Available Cyanide Sample Field Treatment revision: 0.0

Approved By: _____ 1-26-09 **QA Officer** **Approved By:** Heather L. Brady **Area Supervisor**

Attachment 23.3
Reagent Log Example

Analytical Standard Record
TriMatrix Laboratories, Inc.
7080674

Description:	5-(4-(Dimethylamino)benzylidene)rhodani	Expires:	Mar-31-12
Standard Type:	Reagent	Prepared:	Mar-31-07
Solvent:	Solvent Lot #02112ch	Prepared By:	** Vendor **
Final Volume (mls):	10	Department:	Inorganic - Wet Chemistry
Vials:	1	Last Edit:	Aug-20-07 11:37 by RGJ

Aldrich part# 114588-10g
Lot#: 02112ch
Received 8/20/07

Analyte	CAS Number	Concentration	Units
			NA

Reviewed By _____ Date _____

Page 1 of 1

Approved By: _____ 1-26-09 **QA Officer**

Approved By: Heather L. Brady **Area Supervisor**

Attachment 23.4
Standard Log Example

Analytical Standard Record
TriMatrix Laboratories, Inc.
7020703

Description:	Mercury (II) Cyanide, 99%	Expires:	Feb-26-12
Standard Type:	Reagent	Prepared:	Aug-31-05
Solvent:	Solvent Lot #09512KD	Prepared By:	** Vendor **
Final Volume (mls):	5	Department:	Inorganic - Wet Chemistry
Vials:	1	Last Edit:	Feb-28-07 10:45 by TCB

Aldrich part# 208140-5G
Lot: 09512KD
Received 2/26/07

Analyte	CAS Number	Concentration	Units
			NA

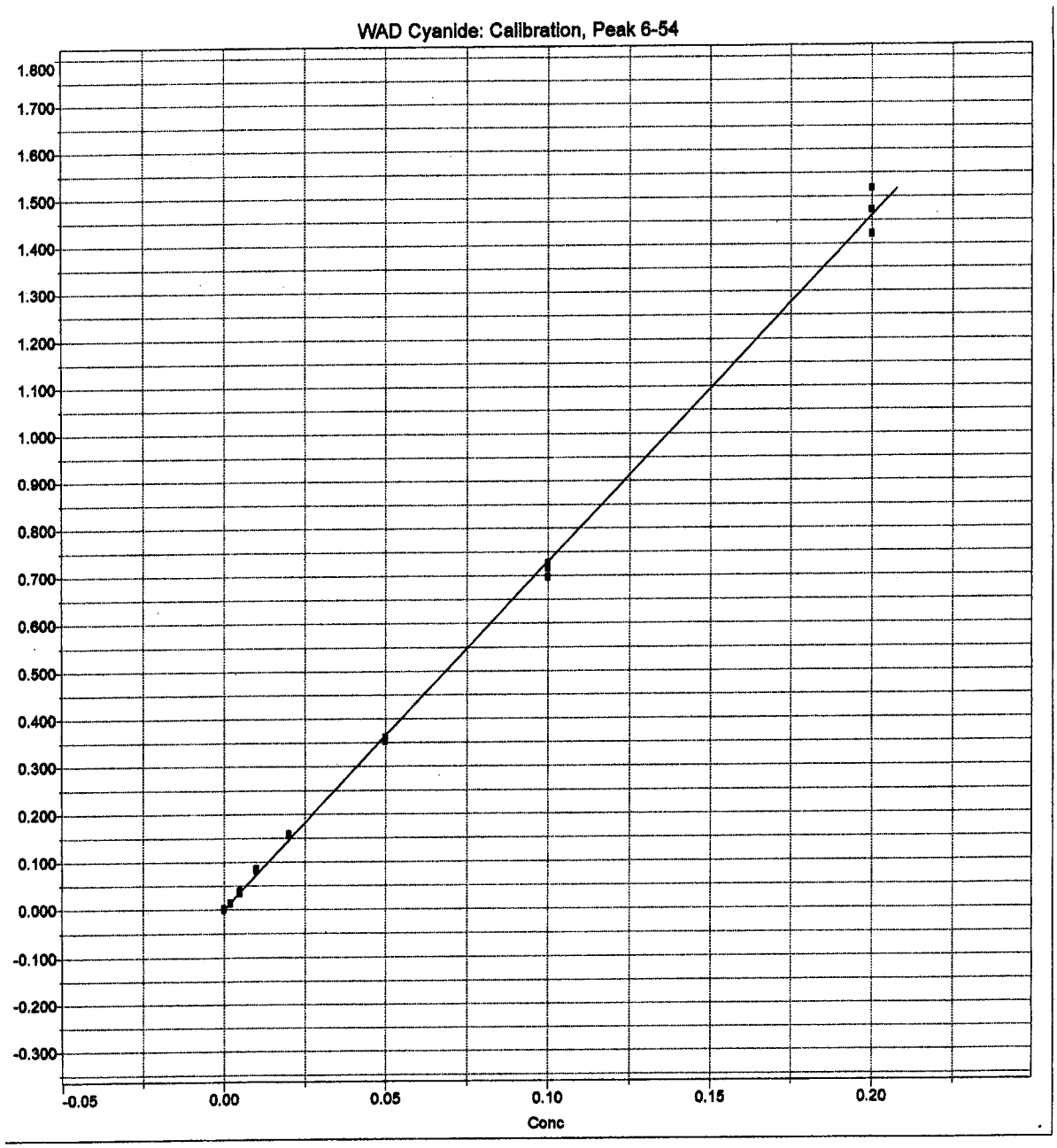
Reviewed By Date

Page 1 of 1

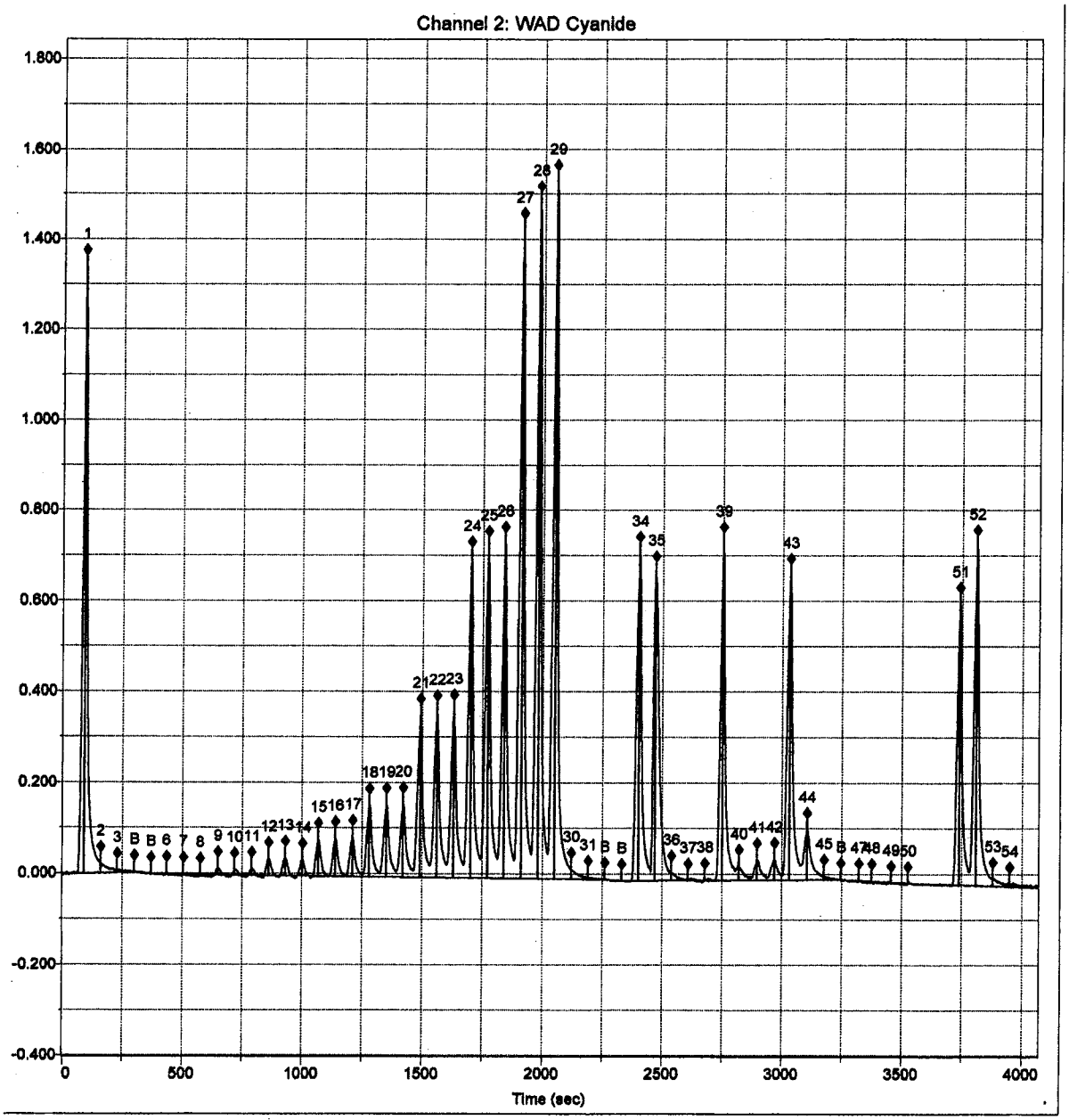
Approved By: 1-26-09 **QA Officer**

Approved By: Heather L. Brady **Area Supervisor**

Attachment 23.5
Calibration Curve Example



Attachment 23.6
Chromatogram Example



Approved By: m 1-26-09 QA Officer

Approved By: Heather L. Brady Area Supervisor

Attachment 23.7
Raw Data Hardcopy Example

File name: C:\FLOW_4\101603A.RST
Date: October 16, 2003
Operator: JLB

* Name	Conc	Height
* Cal 0.00 ppm	0.000000	181.043198
* Cal 0.00 ppm	0.000000	-4.012906
* Cal 0.00 ppm	0.000000	-104.101845
* Cal 0.002 ppm	0.002000	1373.030762
* Cal 0.002 ppm	0.002000	1102.777588
* Cal 0.002 ppm	0.002000	1292.374512
* Cal 0.005 ppm	0.005000	3497.617920
* Cal 0.005 ppm	0.005000	3854.768555
* Cal 0.005 ppm	0.005000	3296.115723
* Cal 0.01 ppm	0.010000	7906.530273
* Cal 0.01 ppm	0.010000	8109.208008
* Cal 0.01 ppm	0.010000	8508.294922
* Cal 0.02 ppm	0.020000	15473.135742
* Cal 0.02 ppm	0.020000	15494.695312
* Cal 0.02 ppm	0.020000	15692.991211
* Cal 0.05 ppm	0.050000	35231.214844
* Cal 0.05 ppm	0.050000	35697.085938
* Cal 0.05 ppm	0.050000	35915.371094
* Cal 0.10 ppm	0.100000	69614.828125
* Cal 0.10 ppm	0.100000	71547.507812
* Cal 0.10 ppm	0.100000	72476.671875
* Cal 0.20 ppm	0.200000	142001.921875
* Cal 0.20 ppm	0.200000	147023.343750
* Cal 0.20 ppm	0.200000	151688.500000

Calib Coef:
y=bx+a
a: (intercept) -1.9817e+0
b: 7.2986e+0

Corr Coef: 0.999363

Carryover: 1.52%

No Drift Peaks

File name: C:\FLOW_4\101603A.RST
Date: October 16, 2003
Operator: JLB

PeakCup		Name	Type	Dil		Wt	Height	Calc. (ppm)	Flags
1	8	Sync	SYN	1		1	133936	0.183537	LO
2	0	Carryover	CO	1		1	2042	0.002825	LO
3	0	Carryover	CO	1		1	520	0.000739	LO
B	0	Baseline	RB	1		1	0	0.000027	BL
B	0	Baseline	RB	1		1	0	0.000027	BL
6	1	Cal 0.00 ppm	C	1		1	181	0.000275	LO OL
7	1	Cal 0.00 ppm	C	1		1	-4	0.000022	LO
8	1	Cal 0.00 ppm	C	1		1	-104	-0.000115	LO
9	2	Cal 0.002 ppm	C	1		1	1373	0.001908	LO
10	2	Cal 0.002 ppm	C	1		1	1103	0.001538	LO OL
11	2	Cal 0.002 ppm	C	1		1	1292	0.001798	LO
12	3	Cal 0.005 ppm	C	1		1	3498	0.004819	LO
13	3	Cal 0.005 ppm	C	1		1	3855	0.005309	LO OL
14	3	Cal 0.005 ppm	C	1		1	3296	0.004543	LO
15	4	Cal 0.01 ppm	C	1		1	7907	0.010860	LO
16	4	Cal 0.01 ppm	C	1		1	8109	0.011138	LO
17	4	Cal 0.01 ppm	C	1		1	8508	0.011685	LO OL
18	5	Cal 0.02 ppm	C	1		1	15473	0.021227	LO
19	5	Cal 0.02 ppm	C	1		1	15495	0.021257	LO
20	5	Cal 0.02 ppm	C	1		1	15693	0.021529	LO
21	6	Cal 0.05 ppm	C	1		1	35231	0.048298	LO
22	6	Cal 0.05 ppm	C	1		1	35697	0.048937	LO
23	6	Cal 0.05 ppm	C	1		1	35915	0.049236	LO
24	7	Cal 0.10 ppm	C	1		1	69615	0.095406	LO OL
25	7	Cal 0.10 ppm	C	1		1	71548	0.098056	LO
26	7	Cal 0.10 ppm	C	1		1	72477	0.099329	LO
27	8	Cal 0.20 ppm	C	1		1	142002	0.194588	LO OL
28	8	Cal 0.20 ppm	C	1		1	147023	0.201468	LO
29	8	Cal 0.20 ppm	C	1		1	151688	0.207860	LO
30	0	Blank	BLN	1		1	-287	-0.000366	LO
31	0	Blank	BLN	1		1	310	0.000452	LO
B	0	Read Baseline	RB	1		1	0	0.000027	BL
B	0	Read Baseline	RB	1		1	0	0.000027	BL
34	7	CCV	CCV	1		1	71916	0.098561	LO F ICV
35	7	CCV	CCV	1		1	66489	0.091126	LO F
36	1	CCB	BLN	1		1	668	0.000943	LO ICB
37	1	CCB	BLN	1		1	-26	-0.000008	LO
38	1	blk	BLN	1		1	43	0.000086	LO BLK
39	9	lcs	U	1		1	73968	0.101373	LO LCS
40	2	crdl	U	1		1	1919	0.002657	LO CRDL
41	10	345650	U	1		1	4398	0.006053	LO 345650
42	11	345650 dup	U	1		1	4417	0.006079	LO 345650 dup
43	12	345650 spk	U	1		1	66863	0.091638	LO 345650 spk
44	13	346300	U	1		1	10030	0.013769	LO 346300
45	0	blank	BLN	1		1	638	0.000901	LO
B	0	read baseline	RB	1		1	0	0.000027	BL
47	7	ccv	CCV	1		1	175	0.000267	LO F sample cup was empty
48	7	ccv	CCV	1		1	156	0.000241	LO F
49	1	ccb	BLN	1		1	-135	-0.000157	LO
50	1	ccb	BLN	1		1	-43	-0.000032	LO
51	7	ccv	CCV	1		1	61660	0.084536	LO F
52	7	ccv	CCV	1		1	73498	0.100729	LO F CCV

Attachment 23.8
Instrument Logbook Example

TriMatrix Laboratories, Inc.

Instrument Number 299 Run Logbook

Date	Analyst	Method Name or Number	Concentration of Calibration Standards Used							Units	Client Names and Sample Numbers
			No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	No. 7		
			Calibration Requirements				Calibration Results				
			Calibration Requirements				Calibration Results				
			Calibration Requirements				Calibration Results				
			Calibration Requirements				Calibration Results				
			Calibration Requirements				Calibration Results				
			Calibration Requirements				Calibration Results				
			Calibration Requirements				Calibration Results				

file: instlogbook page: 1 of 50 revision: 0.0

Attachment 23.9
Preparation Batch Report Example

TriMatrix Laboratories, Inc.

PREPARATION BATCH 0709922 Page 1 of 1

Printed: 10/4/2007 12:07:40PM

Inorganic - Wet Chemistry, Waste Water, Method-Specific Preparation

(No Surrogate)

Batch Comments: (none)

Work Order	Analysis	Work Order	Analysis	Work Order	Analysis
0708448	Cyanide, Available OIA-16	0708454	Cyanide, Available OIA-16		

Lab Number	*Contain*	*Prepared*	*By*	*Initial (mL)*	*Final (mL)*	*uL Surrogate*	*Source ID*	*Spike ID*	*uL Spike*	*Client / QC Type*	*Extraction Comments*
0709922-BLK1		Aug-27-07 08:10	VAS	50	50					BLANK	
0709922-BLK2		Aug-27-07 08:10	VAS	50	50					BLANK	
0709922-BS1		Aug-27-07 08:10	VAS	50	50			7080841	50	LCS	
0709922-BS2		Aug-27-07 08:10	VAS	50	50			7080841	50	LCS	
0709922-MS1		Aug-27-07 08:10	VAS	50	50		0708448-01	7080841	50	MATRIX SPIKE	
0709922-MSD1		Aug-27-07 08:10	VAS	50	50		0708448-01	7080841	50	MATRIX SPIKE DUP	
0708448-01	A	Aug-27-07 08:10	VAS	50	50					[redacted]	
0708454-01	B	Aug-27-07 08:10	VAS	50	50					[redacted]	2 ug/L
0708454-02	B	Aug-27-07 08:10	VAS	50	50					[redacted]	2 ug/L
0708454-03	B	Aug-27-07 08:10	VAS	50	50					[redacted]	2 ug/L
0708454-06	B	Aug-27-07 08:10	VAS	50	50					[redacted]	2 ug/L
0708454-07	B	Aug-27-07 08:10	VAS	50	50					[redacted]	2 ug/L
0708454-08	B	Aug-27-07 08:10	VAS	50	50					[redacted]	2 ug/L
0708454-09	B	Aug-27-07 08:10	VAS	50	50					[redacted]	2 ug/L
0708454-10	B	Aug-27-07 08:10	VAS	50	50					[redacted]	2 ug/L
0708454-11	A	Aug-27-07 08:10	VAS	50	50					[redacted]	2 ug/L

Comments:	Analyst Initials:

bch_TriMatrix.rpt

Approved By: [signature] 1-26-09 **QA Officer**

Approved By: Heather L. Brady **Area Supervisor**

Attachment 23.10
Analysis Sequence Report Example

TriMatrix Laboratories, Inc. ANALYSIS SEQUENCE **7090721** Page 1 of 2 Printed: 10/4/2007 12:13:04PM

Inorganic - Wet Chemistry, Waste Water, Aug-27-07

Instrument = 299, Calibration = 7I07007

Sequence Analyses:
Cyanide, Available OIA-1677

Lab Number	*Analysis*	*Contain*	*STD ID*	*ISTD ID*	*Client / QC Type*	*Extraction Comments*
7090721-CAL1	QC		7080832		CAL STANDARD	
7090721-CAL2	QC		7080839		CAL STANDARD	
7090721-CAL3	QC		7080838		CAL STANDARD	
7090721-CAL4	QC		7080837		CAL STANDARD	
7090721-CAL5	QC		7080836		CAL STANDARD	
7090721-CAL6	QC		7080835		CAL STANDARD	
7090721-ICV1	QC		7080836		INITIAL CAL CHECK	
7090721-ICB1	QC		7080832		INITIAL CAL BLANK	
0709922-BLK1	QC				BLANK	
0709922-BS1	QC				LCS	
7090721-SCV1	QC		7080842		SECONDARY CAL CHECK	
7090721-CRL1	QC		7080839		MRL CHECK	
7090721-CCV1	QC		7080836		CALIBRATION CHECK	
7090721-CCB1	QC		7080832		CALIBRATION BLANK	
0708448-01	Cyanide, Available OIA-1677	A			[redacted]	
0709922-MS1	QC				MATRIX SPIKE	
0709922-MSD1	QC				MATRIX SPIKE DUP	
0708454-01	Cyanide, Available OIA-1677	B			[redacted]	2 ug/L
0708454-02	Cyanide, Available OIA-1677	B			[redacted]	2 ug/L
0708454-03	Cyanide, Available OIA-1677	B			[redacted]	2 ug/L
7090721-CCV2	QC		7080836		CALIBRATION CHECK	
7090721-CCB2	QC		7080832		CALIBRATION BLANK	
0708454-06	Cyanide, Available OIA-1677	B			[redacted]	2 ug/L
0708454-07	Cyanide, Available OIA-1677	B			[redacted]	2 ug/L
0708454-08	Cyanide, Available OIA-1677	B			[redacted]	2 ug/L

Comments:

Analyst Initials:

seq_TriMatrix.rpt

Approved By: _____ 1-26-09 **QA Officer**

Approved By: Heather L. Brady **Area Supervisor**