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REMEDIAL DESIGN WORK PLAN – APPENDIX B
QUALITY ASSURANCE PROJECT PLAN

HIMCO SITE
ELKHART, INDIANA

Prepared For:
Himco Site Trust

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Prepared by:
Conestoga-Rovers & Associates
651 Colby Drive
Waterloo, Ontario
Canada N2V 1C2

Office: 519•884•0510
Fax: 519•884•0525

QUALITY ASSURANCE PROJECT PLAN

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HIMCO SITE
ELKHART, INDIANA

REVISION NUMBER: 2

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PREPARED BY: CONESTOGA-ROVERS & ASSOCIATES

Approved By: _____ Date: _____
Project Manager - CRA
Alan Van Norman

Approved By: _____ Date: _____
QA Officer - CRA
Steven Day

Approved By: _____ Date: _____
Project Manager – TA-North Canton
Amy McCormick

Approved By: _____ Date: _____
Laboratory Director – TA-North Canton
Opal Davis-Johnson

Approved By: _____ Date: _____
Laboratory Director – TA–Knoxville
Tom Yoder

Approved By: _____ Date: _____
USEPA Remedial Project Manager
Rosauro del Rosario

Approved By: _____ Date: _____
USEPA Region 5 Quality Assurance Reviewer

Approved By: _____ Date: _____
IDEM Project Manager
Jessica Huxhold Fliss

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LIST OF ACRONYMS AND SHORT FORMS

CD	-	Consent Decree
CDA	-	Construction Debris Area
CRA	-	Conestoga-Rovers & Associates
DQOs	-	Data Quality Objectives
EDD	-	Electronic Data Deliverable
FSP	-	Field Sampling Plan
IDEM	-	Indiana Department of Environmental Management
LCS	-	Laboratory Control Sample
LCS/LCSD	-	Duplicate Laboratory Control Samples
LIMS	-	Laboratory Information Management System
MS/MSD	-	Matrix Spike/Matrix Spike Duplicate
NELAP	-	National Environmental Laboratory Accreditation Program
NMOC	-	Non-Methane Organic Compounds
PARCCS	-	Precision, Accuracy, Representativeness, Comparability, Completeness, Sensitivity
ROD	-	Record of Decision
QA	-	Quality Assurance
QA/QC	-	Quality Assurance/Quality Control
QAPP	-	Quality Assurance Project Plan
QC	-	Quality Control
RA	-	Remedial Action
RD	-	Remedial Design
RPD	-	Relative Percent Difference
RDA	-	Recommended Dietary Allowances
RPM	-	Remedial Project Manager
RSD	-	Relative Standard Deviation
SDG	-	Sample Delivery Group
Site	-	Himco Site, Elkhart, Indiana
SOP	-	Standard Operating Procedure
SOW	-	Statement of Work
SVOCs	-	Semi-volatile Organic Compounds
SW-846	-	"Test Methods for Evaluating Solid Waste, Physical/Chemical Methods", EPA SW-846, 3rd Edition with Updates I through IIIB
TAL	-	Contract Laboratory Program Target Analyte List
TA-North Canton	-	TestAmerica Laboratories, Inc. – North Canton, Ohio
TCL	-	Contract Laboratory Program Target Compound List
USEPA	-	United States Environmental Protection Agency
VOCs	-	Volatile Organic Compounds

1.0 INTRODUCTION

United States Environmental Protection Agency (USEPA) policy requires that all work performed by or on behalf of USEPA involving the collection of environmental data be implemented in accordance with a USEPA-approved Quality Assurance Project Plan (QAPP). The QAPP is a planning document that provides a "blueprint" for obtaining the type and quantity of data needed to support environmental decision making. The QAPP integrates all technical and quality aspects of a project and documents all quality assurance (QA), quality control (QC), and technical activities and procedures associated with planning, implementing, and assessing environmental data collection operations.

This QAPP has been prepared by Conestoga-Rovers & Associates (CRA) in accordance with the QAPP guidance documents "EPA Requirements for Quality Assurance Project Plans", EPA QA/R-5 (March 2001), "Guidance for Quality Assurance Project Plans", EPA QA/G-5 (December 2002), and "Region 5 Instructions on the Preparation of a Superfund Division Quality Assurance Project Plan, Revision 0", June 2000. As specified in these documents, there are four basic groups of elements that must be included in a QAPP. These four groups and associated elements are as follows:

- Group A - Project Management. The elements in this group include all aspects of project management, project objectives, and project history.
- Group B – Data Generation and Acquisition. The elements in this group include descriptions of the design and implementation of all measurement systems that will be used during the project.
- Group C – Assessment/Oversight. The elements in this group encompass the procedures used to ensure proper implementation of the QAPP.
- Group D – Data Validation and Usability. The elements in this group cover the QA activities that occur after the data collection phase of the project is completed.

The above four groups and associated elements are documented in this QAPP for the remedial design (RD) activities to be conducted at the Himco Site in Elkhart, Indiana (Site). This QAPP is Appendix B of "Remedial Design Work Plan, Himco Site, Elkhart, Indiana" (RD Work Plan).

2.0 PROJECT MANAGEMENT

The responsibilities of management, QA personnel, field personnel, and laboratory personnel are provided in the following subsections. Additionally, the organization of the project is presented to identify the lines of communication among the participants, and any special training/certification requirements for the project are identified.

2.1 MANAGEMENT RESPONSIBILITIES

The Himco Site Trust has selected CRA to be its technical consultant for the RD activities at the Site. USEPA has approved CRA to be the designated Supervising Contractor as defined in the Consent Decree (CD). As such, CRA is authorized to perform, direct, or supervise any work required for the RD. CRA's Project Manager has selected a project team consisting of CRA's technical personnel (engineering, hydrogeology, risk assessment, chemistry, and data management), QA personnel, and the analytical laboratory. CRA's Project Manager is ultimately responsible for ensuring that the project objectives are achieved. CRA's Project Manager and his specific responsibilities are as follows.

Alan Van Norman – Project Manager - CRA

- technical representation for Himco Site Trust;
- overview of field activities;
- overview of laboratory activities;
- advise on corrective actions;
- preparing and reviewing reports;
- coordination of CRA's technical group;
- overview of data tracking process; and
- final evidence file custodian.

The analytical laboratory's Project Manager is responsible for ensuring that the project objectives are achieved by the laboratory. The laboratory selected for this project is TestAmerica Laboratories, Inc. (formerly Severn Trent Laboratories, Inc.) of North Canton, Ohio (TA-North Canton). The laboratory is located at 4101 Shuffel Drive, NW in North Canton, Ohio 44720 (phone: 330-497-9396). TA-North Canton's Project

Manager is responsible for ensuring that the project objectives are achieved. TA-North Canton's Project Manager and her specific responsibilities are as follows:

Amy McCormick – Project Manager – TA-North Canton

- ensures all resources of the laboratory are available on an as-required basis;
- reviews completeness of final analytical reports; and
- approves final reports prior to submission to CRA.

The USEPA Region 5 Remedial Project Manager (RPM) is responsible for overview of this project. This individual also is responsible for submitting this QAPP and any subsequent revisions or amendments to the appropriate USEPA personnel for review and approval and for providing approval of the QAPP. Rosauro del Rosario is USEPA's RPM for the RD/RA at the Site.

The Indiana Department of Environmental Management (IDEM) Project Manager is responsible for reviewing and providing comments to USEPA on project plans for the RD/RA. Jessica Huxhold Fliss is IDEM's Project Manager for the Site.

2.2 QUALITY ASSURANCE RESPONSIBILITIES

Project team members with QA responsibilities include CRA's QA Officer and TA's QA Officer. The specific responsibilities of the project team QA officers are as follows:

Steve Day – Quality Assurance Officer – CRA

- overview and review field QA/QC procedures;
- review laboratory QA/QC procedures;
- oversee data validation and data assessment;
- coordinate internal field technical system audits;
- document field corrective actions, if necessary;
- advise on laboratory corrective action procedures;
- verify accuracy of field data transferred into spreadsheet format;
- verify accuracy of analytical database after data are imported;
- prepare and review QA reports; and
- QA representation of project activities.

Dorothy Leeson – Quality Assurance Officer – TA-North Canton

- coordinate and overview of internal laboratory systems audits;
- coordinate QA review of data deliverables;
- implement and document laboratory corrective actions, if required;
- technical representation of laboratory QA procedures and activities; and
- oversee preparation of laboratory standard operating procedures (SOPs).

The USEPA Region 5 Field Support Section (FSS) Quality Assurance Reviewer is responsible for reviewing and providing final approval of the QAPP.

2.3 FIELD RESPONSIBILITIES

CRA will conduct or oversee all field sampling and obtain field measurements related to sampling. Specific procedures for field sample collection and field measurements are provided in the Field Sampling Plan (FSP), which is Appendix A of the RD Work Plan.

2.4 LABORATORY RESPONSIBILITIES

TA-North Canton will perform the chemical analyses of all groundwater and soil samples collected during the pre-design investigations. Groundwater samples will be analyzed for USEPA's Target Compound List (TCL): volatile organic compounds (VOCs), TCL semi-volatile organic compounds (SVOCs), USEPA's Target Analyte List (TAL) metals, bromide, chloride, and sulfate. Soil samples collected from the Construction Debris Area will be analyzed for TCL SVOCs, TAL metals, and total cyanide. If soil samples are collected during the landfill cover investigation (described in Section 2.8.1), the samples will be analyzed for TCL VOCs.

Soil gas samples will be internally subcontracted to and analyzed by TestAmerica's Knoxville, Tennessee laboratory for VOCs, non-methane organic compounds (NMOC), nitrogen, hydrogen sulfide, and carbon monoxide. Soil gas samples will be sent to TA-North Canton for log-in and shipping to TA-Knoxville. Soil gas sample analyses and data will be tracked by TA-North Canton's Project Manager. All data deliverables will be issued by TA-North Canton.

A qualified geotechnical laboratory will be retained to analyze selected soil samples for the physico-chemical properties of grain size distribution, organic content, pH, and the geotechnical testing associated with the pre-design soil gas investigation.

Specific information regarding the sampling and analysis program are provided in Section 2.7 and Table 2.1 of this QAPP.

The specific responsibilities of project laboratory personnel are as follows:

Ray Risden – Operations Manager – TA-North Canton

- coordinate laboratory analyses;
- supervise in-house chain-of-custody;
- schedule sample analyses;
- oversee data review; and
- oversee preparation of analytical reports.

John McFadden – Sample Custodian – TA-North Canton

- receive and inspect the incoming sample containers;
- record the condition of incoming sample containers;
- sign appropriate documents;
- verify correctness of chain-of-custody documentation;
- notify Project Manager of any non-conformances identified during sample receipt and inspection;
- notify CRA of sample receipt;
- assign a unique identification number to each sample, and record client information and sample identification numbers in the sample receiving log;
- initiate transfer of the samples to appropriate laboratory sections; and
- control and monitor access/storage of samples and extracts.

2.5 PROJECT ORGANIZATION

The organization and lines of communication among the project participants identified in the preceding subsections are presented on Figure 2.1.

2.6 PROBLEM DEFINITION/BACKGROUND INFORMATION

The pre-design sampling and analysis program and the RD interim groundwater monitoring program are being conducted to obtain data required to design the remedial action (RA) specified in the CD and its Statement of Work (SOW). This QAPP addresses the sampling and analysis program required to obtain these data. Revisions to the sampling and analysis program described in this QAPP may be required based on the pre-design investigation data gathering activities to be conducted at the Site. Any revisions to this QAPP required to address modifications to the sampling and analysis program will be submitted to USEPA for review and approval prior to the work being conducted.

Site background and setting information, Site description, Site setting, regional and Site geology/hydrogeology, and previous data collection activities are provided in Section 2.0 of the RD Work Plan.

2.7 PROJECT/TASK DESCRIPTION

The RD scope of work is provided in Section 3.0 of the RD Work Plan. This scope of work includes certain pre-design investigations and the implementation of an interim groundwater monitoring program. The pre-design investigations are detailed in Section 4.0 of the RD Work Plan. An overview of the sampling and analysis program is summarized in Table 2.1. Sample matrices, target analytes, and targeted quantitation limits for the pre-design investigations and interim groundwater monitoring program are presented in Table 2.2. Project-required screening levels for VOCs in soil gas samples will be the criteria specified in Table 2 of Appendix VIII from "IDEM Draft Vapor Intrusion Pilot Program Guidance" (IDEM 2006). Project-required screening levels for VOCs, SVOCs, and metals in groundwater monitoring samples will be USEPA's primary drinking water maximum contaminant levels (PMCLs), secondary drinking water maximum contaminant levels (SMCLs), the recommended dietary allowances (RDA), and the targeted quantitation limits for select analytes (arsenic, vinyl chloride, and trichloroethene). Project-required screening levels for SVOCs, metals, and cyanide in soil samples collected from the Construction Debris Area (CDA). Project-required screening levels are included in Table 4.4 of the RD Work Plan.

2.7.1 PROJECT SCHEDULE

The project schedule is presented in Section 6.0 of the RD Work Plan. Though contingent on agency approval of the RD Work Plan, data collection activities are anticipated to commence in late summer of 2008.

2.8 QUALITY OBJECTIVES AND CRITERIA FOR MEASUREMENT DATA

The quality objectives and measurement performance criteria for data obtained for the RD investigations are presented in the following subsections.

2.8.1 DATA QUALITY OBJECTIVES

Data quality objectives (DQOs) are qualitative and quantitative statements derived from the outputs of each step of the DQO process. The DQO process is a series of planning steps based on the scientific method that is designed to ensure that the type, quantity, and quality of environmental data used in decision making are appropriate for the intended application.

There are seven steps in the DQO process that include:

1. Stating the problem;
2. Identifying the decision;
3. Identifying inputs to the decision;
4. Defining the boundaries of the study;
5. Developing a decision rule;
6. Specifying limits on decision errors; and
7. Optimizing the design for obtaining data.

The design of the anticipated sampling and analysis program provided in Table 2.1 was developed from information included in the SOW and Amended Record of Decision (ROD). The key components of the remedy for the Site are:

1. Landfill cover assessment and repair;

2. Landfill gas collection system;
3. Site security, maintenance, and institutional controls;
4. CDA remedy (excavation and removal of soil and debris or placement of soil cover over soil and debris);
5. Residential well abandonment and groundwater institutional controls;
6. Municipal water connections; and
7. Groundwater investigation and long-term monitoring.

The pre-design investigation tasks necessary to complete the RD that are addressed in this QAPP include:

1. Landfill/landfill cover investigation;
2. Landfill gas/soil gas investigation; and
3. Groundwater investigation and monitoring program development.

The DQO process has been developed using the pre-design investigation and interim groundwater monitoring program objectives in the Amended ROD and its SOW as problem statements. The resulting DQO statements are summarized in the following.

1. Problem	Visually delineate extent of waste and cover material around perimeter of landfill by test trenching.
2. Decision	Is the material observed in trenches waste or native material?
3. Inputs	Presumed landfill limits from 1996.
4. Boundaries	See Figure 4.1 of RD Work Plan.
5. Decision Rule	If material observed in trenches is waste, extend trench beyond presumed limits.
6. Error Limits	Ability to discriminate between waste and native material. Refer to RD Work Plan Section 4.2.1.
7. Design	Best professional judgment. Refer to RD Work Plan Sections 4.2.4 and 5.1.

1. Problem	Determine condition of existing landfill cover and detect VOCs in soil.
2. Decision	Is the existing soil cover capable of supporting vegetative growth and does the soil contain VOCs?
3. Inputs	Field VOC screening data, organic content, pH, nitrogen content, assimilable potassium and phosphorus, and grain size distribution data from sampling locations (Figure 4.2 of RD Work Plan).
4. Boundaries	See Figure 4.2 of RD Work Plan.
5. Decision Rule	If sampling data identifies areas of cover incapable of supporting vegetative growth, prepare soil balancing plan (i.e., areas for cut and fill) to replace/augment existing cover soil and if PID headspace screening data indicate VOCs are present at a concentration greater than 10 ppm above background, a sample will be collected for TCL VOC analysis (refer to RD Work Plan Sections 4.2.4 and 5.1).
6. Error Limits	Refer to QAPP Section 5.0 and SOPs.
7. Design	Best professional judgment. Refer to RD Work Plan Sections 4.2.4 and 5.1.

1. Problem	Detect SVOCs, metals, and cyanide in soil in CDA.
2. Decision	Should debris be covered in place or removed?
3. Inputs	Historical data from soil samples collected from 10 test trenches investigated during second phase of RI (see Figure 1.2 of RD Work Plan, data from soil samples collected from five test pits (refer to RD Work Plan Section 4.2.3; see RD Work Plan Figure 4.3), and USEPA Region 9 Preliminary Remediation Goals (PRGs).
4. Boundaries	See Figure 4.3 of RD Work Plan.
5. Decision Rule	If detections > PRGs and inconsistent with historical data, removal may be required.
6. Error Limits	Able to quantify at PRGs. Refer to QAPP Section 5.0 and SOPs.
7. Design	Best professional judgment. Refer to RD Work Plan Sections 4.2.4, and 5.1.

1. Problem	Determine the presence and potential migration of landfill gas (LFG) and VOCs in soil gas.
2. Decision	Are Site-related contaminants being released from the subsurface vapor migration pathway at unacceptable concentrations? Will hydrogen sulfide and methane migrate beyond the landfill boundary at some point in the future?
3. Inputs	Historical LFG and soil gas VOC data. Data from the installation and sampling of soil gas probes (refer to RD Work Plan Sections 4.3.3 and 4.3.4; see RD Work Plan Figure 4.4).
4. Boundaries	See RD Work Plan Figure 4.4.
5. Decision Rule	If Site-related contaminants (including hydrogen sulfide and methane) are being released from the subsurface along the eastern boundary of the Site at concentrations above the Remedial Action Objectives (RAOs) for LFG and soil gas (see RD Work Plan Sections 4.3.5 and 4.3.6), a Phase II LFG/Soil Gas Investigation will be required.
6. Error Limits	Able to quantify at RAOs. Refer to QAPP Section 5.0 and SOPs.
7. Design	Best professional judgment. Refer to RD Work Plan Sections 4.3.7, and 5.1.

1. Problem	Investigate groundwater east and southeast of the Site and establish groundwater monitoring program.
2. Decision	Is groundwater contamination adequately delineated at the Site (refer to RD Work Plan Section 4.4)?
3. Inputs	Historical groundwater data from existing monitoring well network (see RD Work Plan Figure 4.7), current groundwater quality data from a baseline groundwater sampling event (refer to RD Work Plan Section 4.4.3 and QAPP Table 2.1), VOC and indicator parameter data from phased vertical aquifer sampling events (refer to RD Work Plan Section 4.4.4 and QAPP Table 2.1), groundwater data from new monitoring wells and an interim groundwater monitoring program (refer to RD Work Plan Sections 4.4.5, 4.4.6, and 4.4.7; see RD Work Plan Figure 4.8; refer to QAPP Table 2.1).
4. Boundaries	See Work Plan Figures 1.2, 4.7, and 4.8.
5. Decision Rule	If contaminants exceed groundwater screening criteria in perimeter monitoring wells located east, south, and southeast of the Site, in buffer zone monitoring wells located east of the Site, installation of additional monitoring wells is required.

6. Error Limits	Able to quantify at groundwater screening criteria (refer to RD Work Plan Section 4.4.7 and Table 4.2; QAPP Section 5.0, Table 2.1, and SOPs).
7. Design	Best professional judgment. Refer to RD Work Plan Sections 4.4.7, and 5.1.

The planning team for the project consists of CRA's Project Manager and her technical team. The decision makers are CRA's Project Manager, USEPA's RPM, and IDEM's Project Manager. The DQO process ensures that the data collection program will be conducted in a resource-efficient and timely manner.

2.8.2 MEASUREMENT PERFORMANCE CRITERIA

The measurement performance criteria for precision, accuracy, representativeness, completeness, comparability, and sensitivity (PARCCS) are provided in the following subsections.

2.8.2.1 FIELD PRECISION CRITERIA

Precision of the field sample collection procedures will be assessed by the data from analysis of field duplicate samples. Field duplicate samples will be collected at a frequency of 1 per 20 or fewer investigative samples. A relative percent difference (RPD) of 50 percent will be used as an advisory limit for analytes detected in both the investigative and field duplicate groundwater samples at concentrations greater than or equal to 5 times their quantitation limits. An RPD of 100 percent will be used as an advisory limit for analytes detected in both the investigative and field duplicate soil and soil gas samples at concentrations greater than or equal to 5 times their quantitation limits. Field duplicate samples will not be collected for geotechnical parameters. Professional judgment will be used to qualify associated investigative sample data.

Field precision for field measurements will be assessed through replicate measurement of the same sample, as applicable to the parameter being measured. The precision acceptance criteria for field measurements are identified in Table 3.1 of the FSP.

2.8.2.2 LABORATORY PRECISION CRITERIA

Laboratory precision will be assessed through the calculation of RPDs for laboratory duplicate sample analyses. These will be matrix spike/matrix spike duplicate (MS/MSD) and/or duplicate laboratory control samples (LCS/LCSD) samples. These will be collected/designated a frequency of 1 per 20 or fewer samples. The equation to be used to determine precision is presented in Section 5.3.1 of this QAPP. Laboratory precision acceptance criteria are presented in Table 2.3.

2.8.2.3 FIELD ACCURACY CRITERIA

The criteria for accuracy of the field sample collection procedures will be to ensure that samples are not affected by sources external to the sample, such as or inadequate equipment decontamination procedures or sample contamination by ambient conditions or sample cross-contamination. Field sampling accuracy will be assessed by the data from field equipment blank samples and trip blank samples.

Field equipment blank samples will be collected at a frequency of 1 per 20 or fewer sampling equipment decontamination procedures. Field equipment blank samples (also referred to herein as equipment blank samples) will be collected by routing laboratory-provided deionized water through decontaminated sampling equipment. Equipment blank samples will be analyzed to check procedural contamination and/or ambient conditions and/or sample container contamination at the Site that may cause sample contamination. Equipment blank samples will not be collected for samples collected using pre-cleaned or pre-cleaned, disposable sampling equipment or soil gas samples. A background ambient air sample will be collected for soil gas samples analyzed for VOCs.

Trip blank samples, consisting of volatile organic-free water poured into sample vials at the laboratory, will be provided by the laboratory for the groundwater sampling effort. Trip blank samples are applicable only to aqueous samples to be analyzed for VOCs. Trip blank samples will be handled in a manner consistent with actual field samples, but will not be opened, and will be shipped back to the laboratory with the samples. Trip blank samples will provide a measure of potential cross-contamination of samples by VOCs during shipment and handling. One trip blank sample will be included in each shipping cooler containing groundwater samples for VOC analysis.

Trip blanks for VOCs in soil gas samples will not be collected. The canisters undergo a rigorous cleaning procedure after each use. Before a canister can be shipped to a site, its cleanliness must be certified and documented. Flow control devices also are cleaned by the laboratory prior to field use. A precleaned flow controller will be supplied for each canister used to collect samples, and each flow controller will be used at only one sampling location.

To ensure that canisters have not been contaminated prior to use, the vacuum measured by the laboratory prior to shipping will be compared to the canister vacuum measured in the field prior to sampling. Laboratory-measured vacuums will be recorded and provided with the canisters. Prior to field sampling, the canister vacuum will be measured and recorded on the data sheet using a laboratory-supplied vacuum gauge. If a significant difference in vacuum is noted prior to sampling, the canister may have leaked during transit, potentially contaminating the canister. Canisters exhibiting a significant difference in vacuum when checked prior to sampling will not be used.

Soil gas sampling will be terminated when the canister pressure approaches, but is less than, atmospheric pressure by setting the flow controller for a slightly longer sampling period, which will allow the canister to remain under vacuum. The final vacuum for each canister will be recorded and provided with the canister to the laboratory. The laboratory will measure the vacuum of the samples prior to analysis. Samples with significantly less vacuum than the final field vacuum recorded prior to shipping will be not be analyzed and will be recollected.

Equipment and trip blank samples should not contain target analytes. The equipment and trip blank sample data will be evaluated using the procedures specified in Section 5.3.2 of this QAPP. Accuracy also will be ensured by adhering to all sample handling procedures, sample preservation requirements, and holding time periods.

Accuracy of field measurements will be assessed by analyzing calibration check samples, as applicable to the parameter being measured. Accuracy acceptance criteria for field measurements obtained during the field activities are presented in Table 3.1 of the FSP.

2.8.2.4 LABORATORY ACCURACY CRITERIA

Laboratory accuracy will be assessed by determining percent recoveries from laboratory control sample (LCS) analyses. An LCS will be analyzed at a frequency of 1 per batch of 20 or fewer samples of the same matrix. Accuracy relative to the sample matrix will be assessed by determining percent recoveries from the analysis of matrix spike samples. MS/MSD samples will be collected/designated at a frequency of 1 per 20 or fewer samples of the same matrix. The equation to be used to determine accuracy for this project is presented in Section 5.3.2 of this QAPP. Laboratory accuracy acceptance criteria are presented in Table 2.3.

The accuracy of all organic analyses also will be monitored through the analysis of surrogate compounds. Surrogate compounds are added to each sample, standard, blank, and QC sample prior to sample preparation and analysis. Surrogate compounds are not expected to be found occurring naturally in the samples, but behave analytically similar to the compounds of interest. Consequently, surrogate compound percent recovery data will provide information on the effect that the sample matrix exhibits on the accuracy of the analyses. Surrogate compound percent recovery acceptance criteria are presented in Table 2.4.

2.8.2.5 FIELD REPRESENTATIVENESS CRITERIA

Representativeness is dependent upon the proper design of the sampling program. The representativeness criteria for field sampling will be to ensure that samples are collected from the correct soil locations, that the correct monitoring wells are sampled, and that the proper sampling procedures are followed. The sampling program was designed to provide data representative of conditions at the Site. During development of this program, consideration was given to existing analytical data and physical setting.

2.8.2.6 LABORATORY REPRESENTATIVENESS CRITERIA

The representativeness criteria for laboratory data will be to ensure that the proper analytical procedures are used for sample preparation, sample analysis, and that sample holding times are met. Additionally, the accuracy and precision of the laboratory data affect representativeness. The laboratory representativeness criteria will include achieving the accuracy and precision criteria for the sample analyses.

2.8.2.7 FIELD COMPARABILITY CRITERIA

The criteria for field comparability will be to ensure and document that the proper sampling procedures are followed.

2.8.2.8 LABORATORY COMPARABILITY CRITERIA

The criteria for laboratory data comparability will be to ensure that the analytical methods used for the investigation are comparable to the methods used for previous sampling events, as applicable. The methods identified in Section 3.3.2 of this QAPP are the same or comparable to the methods used to generate data for previous investigations at the Site.

2.8.2.9 FIELD COMPLETENESS CRITERIA

The criteria for field completeness will be 90 percent or more of the field-measured data are usable. The procedure for determining field data usability is provided in Section 3.9.2 of this QAPP. The equation for calculating completeness is presented in Section 5.3.4 of this QAPP.

2.8.2.10 LABORATORY COMPLETENESS CRITERIA

The criteria for laboratory completeness will be 90 percent or more of the laboratory data are determined to be usable for the intended purpose. The procedure for determining laboratory data usability is provided in Section 3.9.2 of this QAPP. The equation for calculating completeness is presented in Section 5.3.4 of this QAPP.

2.8.2.11 FIELD SENSITIVITY CRITERIA

The criteria for field measurement sensitivity are provided in Table 2.2 of this QAPP.

2.8.2.12 LABORATORY SENSITIVITY CRITERIA

The sensitivity criteria for the laboratory analyses are the targeted quantitation limits provided in Table 2.2.

It should be noted that high concentration of target and non-target analytes and matrix interferences may prevent the targeted quantitation limits from being achieved for all samples. Additionally, the method to be used for analyzing soil gas samples for NMOC assumes the samples are collected from a capped landfill. An elevated nitrogen concentration in a sample (e.g., approaching atmospheric concentrations) can affect the data.

The methods selected for analyzing the samples are USEPA methods routinely used to support environmental investigations and data gathering activities and are sufficiently sensitive to achieve the detectability requirements of the project.

2.9 SPECIAL TRAINING/CERTIFICATION REQUIREMENTS

CRA's field sampling team members are required to have received the 40-hour Hazardous Waste Operations and Emergency Response safety training and annual 8-hour refresher courses required by 29 CFR Parts 1910 and 1926. On-Site subcontractor personnel performing intrusive activities, if any, are required to have received the same training. Each subcontractor is responsible for compliance of its personnel with the applicable health and safety regulations.

The laboratory performing sample analysis is accredited by the National Environmental Laboratory Accreditation Program (NELAP), which demonstrates compliance with ANSI/ASQC E4-94 ("Specifications and Guidelines for Quality System for Environmental Data Collection and Environmental Technology Programs", January 1995), and EPA QA/R-2 ("EPA Requirements for Quality Management Plans", March 2001). The laboratory being used for this project is accredited by NELAP for analyses to which accreditation applies.

2.10 DOCUMENTATION AND RECORDS

The documents, records, and reports generated during the project are identified in the following subsections.

2.10.1 FIELD AND LABORATORY RECORDS

Documents and records generated during the project include sample collection records, QC sample records, field measurement records, laboratory records, and data handling records. An overview of these documents and records is provided below. Detailed information regarding these records is provided in subsequent sections of this QAPP.

Sample collection records that will be generated during the sampling activities include field logbooks, chain-of-custody records, and shipping papers.

QC sample records that will be generated during the project to document QC sample collection include field logbooks for recording field duplicate samples and MS/MSD samples. TA-North Canton will maintain quality records for water sent for trip blank samples and both laboratory will maintain sample integrity information. Records of sample preservation will be maintained in field logbooks and by the laboratory.

Field measurements will be recorded in bound logbooks or on standard field forms. Calibration data, where applicable, will also be recorded in these logbooks or on these forms.

Laboratory records that will be maintained for the project include sample receipt documentation, field and laboratory chain-of-custody documentation, sample container documentation, reagent and standard reference material certifications, sample preparation records, sample analysis records (e.g., run logs), instrument/raw data, QC data, calibration data, corrective action reports, and final reports.

Data handling records that will be maintained include verification of computer programs used to manipulate or reduce raw data into final results and data validation reports. The laboratory will maintain documentation of data reduction, review, and verification procedures as necessary for the analyses conducted during the investigation. CRA will maintain checklists, notes, and reports generated during the external data validation process.

2.10.2 DATA REPORTING FORMAT

Field data will be recorded in bound logbooks or on standard forms. The details for recording field data are provided in Section 3.2.2.1 of this QAPP. Field data will be generated primarily from direct-reading meters or consist of field readings or observations. These data will be tabulated and included in project reports or submittals.

Laboratory reports for all samples except for laboratory reports for soil gas samples that will be used for risk assessment purposes will consist of the following data deliverables:

1. Case Narrative
   a) date of issuance;
   b) any deviations from intended analytical strategy;
   c) laboratory lot or project number;
   d) number of samples and respective matrices;
   e) project name and number;
   f) condition of samples "as received";
   g) discussion of whether or not sample holding times were met;
   h) discussion of technical problems or other observations that may have created analytical difficulties; and
   i) discussion of any laboratory quality control checks that failed to meet project criteria.

2. Chemistry Data Package
   a) dates of sample collection, receipt, preparation, and analysis;
   b) cross-reference of laboratory to project sample identification numbers;
   c) description of data qualifiers used;
   d) methods of sample preparation and analysis;
   e) sample results (including estimated concentrations for analytes detected at concentrations less than reporting limits), reporting limits, and method detection limits in tabular format;
   f) summaries of MS/MSD and LCS/LCSD data, LCS data, method blank data, surrogate compounds data;
   g) fully executed chain-of-custody document.

Method detection limit studies, instrument detection limit studies, and method performance and validation studies will be maintained by the laboratory. Complete data packages, including raw data, will be obtained from the laboratory for any samples requiring review of these deliverables as deemed necessary during the data validation process.

Laboratory reports for soil gas samples that will be used for risk assessment purposes will include the data deliverables described above, all raw data, and will be fully validated. Estimated concentrations will not be reported for soil gas sample parameters.

Data deliverables for geotechnical testing will consist of tabular and graphical displays of results, as appropriate to the testing being conducted.

2.10.3 DATA ARCHIVING AND RETRIEVAL

All records, including field and laboratory data, generated during the project will be maintained by the laboratory and CRA consistent with their respective record retention policies.

3.0 DATA GENERATION AND ACQUISITION

The design and implementation of the measurement systems that will be used during the investigation, including sampling procedures, analytical procedures, and data handling and documentation are detailed in the following subsections.

3.1 SAMPLING PROCESS DESIGN

The rationale for the sampling program and schedule for sampling and analytical activities and reviews are provided in the RD Work Plan and FSP.

3.1.1 SAMPLING METHODS

Sampling methods are provided in the FSP.

3.1.2 FIELD EQUIPMENT AND SAMPLE CONTAINER CLEANING PROCEDURES

Equipment cleaning/decontamination procedures are provided in the FSP. All sample containers will be provided by the laboratory. The containers will be precleaned in accordance with the USEPA guidance document entitled "Specifications and Guidance for Contaminant-Free Sample Containers" (EPA 540/R-93/051), as applicable. Certificates of analysis for each lot of containers will be available from the container vendors.

Evacuated canisters used to collect soil gas samples will be precleaned and certified by the laboratory in accordance with the requirements of the analytical method.

3.1.3 FIELD EQUIPMENT MAINTENANCE, TESTING, AND INSPECTION REQUIREMENTS

Field equipment will be inspected and tested prior to being shipped to the field. Maintenance logs for all field equipment will be maintained by CRA. Prior to use in the field, the equipment will be checked again, generally during field calibration, and the information will be recorded in the field logbook. All equipment shipped back from the field will be inspected and tested upon return. Any required maintenance will be completed and documented prior to the equipment being returned to service. CRA's QA Officer is ultimately responsible for ensuring these functions have been performed.

Critical spare parts for field equipment and replacement field equipment are available at each CRA office and can be shipped for overnight delivery, picked up at the CRA office, or delivered to the field when the need is identified. Alternately, field equipment vendors can provide replacement equipment if needed. The replacement equipment can be shipped for overnight delivery as necessary. A list of critical spare parts for field equipment is provided in Table 3.1.

3.1.4 INSPECTION AND ACCEPTANCE REQUIREMENTS FOR SUPPLIES AND SAMPLE CONTAINERS

The field supplies for the project consist of calibration solutions for field instrument calibration and calibration checks, laboratory-grade detergent, distilled water for rinsing field instruments and equipment, water for trip and equipment blank samples, and containers to collect the samples.

Trip blank water, equipment blank water, and sample containers will be provided by the laboratory. The laboratory will maintain or have access to its vendor's documentation of the purity/cleanliness of these materials. The laboratory's QA Officer is ultimately responsible for ensuring that these materials are acceptable for the project. The acceptability of these materials for use will be evaluated by reviewing lot analysis certificates, as applicable. Water and containers that do not meet the laboratory's acceptability requirements will not be shipped to the field.

3.2 SAMPLE HANDLING AND CUSTODY REQUIREMENTS

The procedures for sample handling, labeling, shipping, and chain-of-custody documentation are provided in the subsections that follow.

3.2.1 SAMPLE HANDLING

The procedures to be used to collect samples are provided in the FSP. The number of containers, container volume, container type (material of construction), sample preservation, holding time periods, packaging, and shipping requirements for the analyses are identified in Table 3.2.

The sample numbering system for the project has been designed to uniquely identify each sample from each sampling program and event. This numbering system is provided in the FSP.

Field duplicate samples will be uniquely numbered to prevent laboratory bias of field QC samples. Samples designated for MS/MSD analysis will be identified as such in the remarks column of the chain-of-custody document.

Samples of soil and groundwater for chemical analysis will be placed in shipping coolers containing bagged, cubed ice immediately following collection. Samples will be shipped to the laboratory via an express courier service generally on the day they are collected. However, samples that are collected after the courier service has picked up the shipment for the day (generally only at remote sites) and samples collected on a Sunday or holiday will be shipped on the next business day.

The laboratory will group samples in sample delivery groups (SDGs) by sample matrix. An SDG is a group of 20 or fewer field samples (including field QC samples) received by the laboratory.

3.2.2 SAMPLE CUSTODY

Chain of custody is the sequence of possession of an item. An item (such as a sample or final evidence file) is considered to be in a person's custody if the item is in actual possession of a person, the item is in the view of the person after being in his/her actual possession, or the item was in a person's physical possession but was placed in a secure area by that person. Field, laboratory, and final evidence file custody procedures are described in the subsections that follow.

3.2.2.1 FIELD CUSTODY PROCEDURES

Logbooks will used to record field data collection activities. Entries into field logbooks will be described in as much detail as possible to ensure that a particular situation could be reconstructed solely from logbook entries. Field logbooks will be bound field survey books or notebooks with pre-printed, consecutively numbered pages. Each logbook will be identified by a project-specific document number.

The title page of each logbook will contain the following information:

- person to whom the logbook is assigned;
- logbook number;
- project name;
- project start date; and
- end date.

Entries into the logbook will contain a variety of information. At the beginning of each day's logbook entry, the date, start time, weather conditions, and the names of all sampling team members present will be entered. The names of individuals visiting the Site or field sampling team and the purpose of their visit will also be recorded in the field logbook.

All field measurements obtained and samples collected will be recorded in the field logbook or on standard field forms. All entries will be in ink, signed, and dated with no erasures. If an incorrect entry is made, the incorrect information will be crossed out with a single strike mark that is initialed and dated by the person making the erroneous entry. The correct information will be entered into the logbook adjacent to the original entry.

Whenever a sample is collected or a measurement is made, a detailed description of the location will be recorded in the logbook. Photographs taken at a location, if any, will also be noted in the logbook. All equipment used to obtain field measurements will be recorded in the field logbook. In addition, the calibration data for all field measurement equipment will be recorded.

Samples will be collected following the sampling procedures documented in the FSP. The equipment used to collect samples, time of sample collection, sample description, volume and number of containers, and preservatives added (if applicable) will be recorded in the field logbook. Each sample will be uniquely identified using the sample numbering system provided in the FSP.

The following packaging and shipping procedures will ensure that the chain-of-custody of samples collected for chemical analysis remains intact:

1. The field sampler is personally responsible for the care and custody of the samples until they are transferred to another person or the laboratory. As few people as possible will handle the samples.
2. All sample containers will be identified by using sample labels that include the unique sample identification number and the date and time of collection. Sample labels will be completed for each sample using waterproof ink.
3. Samples will be accompanied by a properly completed chain-of-custody form. The sample identification numbers and required analyses will be listed on the chain-of-custody form. When transferring the possession of samples, the individuals relinquishing and receiving the samples will sign and record the date and time on the form. The chain-of-custody form documents sample custody transfers from the sampler to another person, to the laboratory, or to/from a secure storage area.
4. Samples will be properly packaged for shipment (see Table 3.2) and dispatched to the laboratory for analysis with a separate signed chain-of-custody form enclosed in and secured to the inside top of each shipping cooler. Shipping coolers will be secured with custody tape for shipment to the laboratory. The custody tape will be covered with clear plastic tape to prevent accidental damage to the custody tape.
5. If samples are collocated (split) with a government agency or other entity, it is the responsibility of that entity to prepare its own chain-of-custody form for the samples. Information regarding the identity of the entity and the samples that are being collocated will be recorded in the field logbook.
6. All sample shipments will be accompanied by the chain-of-custody form identifying its contents. The chain-of-custody form is a four part carbonless-copy form. The form is completed by the sampling team which, after signing and relinquishing custody to the shipper, retains the bottom (goldenrod) copy. The shipper, if different than the sampling team members, retains the pink copy after relinquishing custody to the laboratory. The yellow copy is retained by the laboratory and the fully executed white copy is returned as part of the data deliverables package.
7. If the samples are sent by common carrier, a bill of lading (e.g., FedEx airbill) will be used and copies will be retained as permanent documentation. Commercial carriers are not required to sign the chain-of-custody form as long as the form is sealed inside the sample cooler and the custody tape remains intact.

CRA's QA Officer will be responsible for ensuring field documentation is complete.

3.2.2.2 LABORATORY CUSTODY PROCEDURES

Laboratory sample custody begins when the samples are received at the laboratory. The field sample identification numbers, laboratory sample identification numbers, date and time of sample collection, date and time of sample receipt, and requested analyses will be entered into the sample receiving log.

Following log-in, all samples will be stored within an access-controlled location and will be maintained properly preserved (as defined in Table 3.2) until completion of all laboratory analyses. Unused sample aliquots and sample extracts will be maintained properly preserved for a minimum of 60 days following receipt of the final report by CRA. The laboratory will be responsible for the disposal of unused sample aliquots, sample containers, and sample extracts in accordance with all applicable local, state, and federal regulations.

The laboratory will be responsible for maintaining analytical logbooks and laboratory data. All laboratory records will be maintained consistent with the laboratory's record retention policy.

3.2.2.3 FINAL EVIDENCE FILES CUSTODY PROCEDURES

The final evidence file for the project will be maintained by CRA and will consist of the following:

1. Project plans;
2. Project log books;
3. Field data records;
4. Sample identification documents;
5. Chain-of-custody records;
6. Correspondence;
7. References, literature;
8. Final data packages;
9. Data validation memos/reports;

10. Miscellaneous - photos, maps, drawings, etc.; and
11. Final reports.

The final evidence file materials will be the responsibility of the evidentiary file custodian with respect to maintenance and document removal. Document retention will be consistent with the requirements of Section XXV of the Consent Decree.

3.3 ANALYTICAL METHOD REQUIREMENTS

The field and laboratory analytical methods that will be used during the investigation are detailed in the following subsections.

3.3.1 FIELD ANALYTICAL METHODS

The field methods that will be used to analyze samples collected during the project are presented in Table 3.3. The field measurements will be obtained consistent with the SOPs in Attachment A.

3.3.2 LABORATORY ANALYTICAL METHODS

The laboratory methods that will be used to analyze samples collected during the project are presented in Table 3.3. The quantities and types of QC samples for the project are presented in Table 2.1.

3.4 QUALITY CONTROL REQUIREMENTS

The field and laboratory QC requirements for the investigation are discussed in the following subsections.

3.4.1 FIELD SAMPLING QUALITY CONTROL

Field QC requirements include analyzing reference standards for instrument calibration and for routine calibration checks. Field QC samples for this project include equipment

blank samples to check procedural contamination and/or ambient conditions and/or sample container contamination at the Site that may cause sample contamination, trip blank samples to determine the existence and magnitude of sample contamination resulting from shipping and/or storage, and field duplicate samples to assess the overall precision of the sampling and analysis event. The frequency of collection for these field QC samples was provided in Section 2.8 of this QAPP. The evaluation of field QC data is provided in Section 3.9.2 of this QAPP.

3.4.2 ANALYTICAL QUALITY CONTROL

The laboratory QC requirements for the analyses include analyzing method blanks, initial calibration standards, calibration verification standards, internal standards, surrogate compound spikes, interference check samples, serial dilution samples, MS/MSD samples, and LCSs. The acceptance criteria for MS/MSD, LCSs, and surrogate compounds are provided in this QAPP. The analysis frequency and acceptance criteria for the remaining QC checks will be consistent with the SOPs in Attachment A.

3.5 INSTRUMENT/EQUIPMENT TESTING, INSPECTION, AND MAINTENANCE REQUIREMENTS

The procedures used to verify that instruments and equipment are functional and properly maintained are described in the following subsections.

3.5.1 FIELD INSTRUMENT MAINTENANCE

Specific preventive maintenance procedures to be followed for field equipment are those recommended by the manufacturer. Field instruments will be checked and calibrated daily before use. The maintenance schedule and procedures for field instruments are presented in Table 3.1.

3.5.2 LABORATORY INSTRUMENT MAINTENANCE

As part of their QA programs, the laboratory will conduct routine preventive maintenance to minimize the occurrence of instrument failure and other system malfunctions. Designated laboratory employees will regularly perform routine scheduled maintenance

and repair of (or coordinate the repair of) all instruments. All maintenance that is performed is documented in maintenance logbooks. All laboratory instruments are maintained in accordance with manufacturer's specifications.

Table 3.1 provides examples of the frequency at which components of key analytical instruments or equipment will be serviced.

3.6 CALIBRATION PROCEDURES AND FREQUENCY

The procedures for maintaining the accuracy for all the instruments and measuring equipment that are used for conducting field and laboratory analyses are described in the following subsections. These instruments and equipment will be calibrated prior to each use or according to a periodic schedule.

3.6.1 FIELD INSTRUMENTS/EQUIPMENT

Equipment to be used during field sampling will be examined to confirm that it is in operating condition. This includes checking the manufacturer's operating manual to ensure that all maintenance requirements are being observed. Individual calibration records will be reviewed to ensure that any prior equipment problems have not been overlooked and all necessary repairs to equipment have been completed. Field instrument calibration will be performed as described in the SOPs in Attachment A.

3.6.2 LABORATORY INSTRUMENTS

Calibration of laboratory equipment will be based on approved written procedures. Records of calibration, repairs, or replacement will be filed and maintained by the designated laboratory personnel performing these quality control activities. These records generally will be filed at the location where the work is performed and will be subject to a QA audit. The laboratory will have trained staff and in-house spare parts available for instrument repair or will maintain service contracts with vendors. Specific calibration procedures and frequencies are detailed in the SOPs.

3.7 INSPECTION/ACCEPTANCE CRITERIA FOR SUPPLIES AND CONSUMABLES

The procedures that will be used to ensure that supplies and consumables used in the field and laboratory will be available as needed and free of contaminants are detailed in the following subsections.

3.7.1 FIELD SUPPLIES AND CONSUMABLES

Supplies and consumables for field measurements and sampling will be obtained from various vendors and will include calibration solutions, sample containers, laboratory detergent, distilled water, laboratory-supplied equipment blank water, and laboratory-supplied trip blank water. Additional field supplies and consumables include disposable sampling supplies and personnel protective equipment. All field supplies will be consumed or replaced with sufficient frequency to prevent deterioration or degradation that may interfere with the analyses.

3.7.2 LABORATORY SUPPLIES AND CONSUMABLES

Vendors for general labware and reagents used by the laboratory include VWR Scientific Products and Fisher Scientific. Vendors for chromatography supplies and organic standards may include Ultra Scientific, Supelco, Accustandard, Restek, ChemService, Cambridge Isotopes, and Aldrich Chemical. The lot numbers of reagents and standards will be recorded and dates of receipt, first use, and expiration will be documented by the laboratory. Certificates of analysis will be maintained on file to document reagent/standard purity.

The SOPs provide details on identifying contaminants in reagents and standards, determining deterioration of reagents and standards, and the corrective actions required if contaminants or deterioration are identified. The laboratory's QA Officer is ultimately responsible for the ensuring the acceptability of supplies and consumables.

3.8 DATA ACQUISITION REQUIREMENTS (NON-DIRECT MEASUREMENTS)

Historical data from previous studies and monitoring events are discussed in Section 4.0 of the RD Work Plan. Any historical data used for the RD will have been validated by CRA, USEPA, or USEPA's contractors.

3.9 DATA MANAGEMENT

The procedures for managing data from generation to final use and storage are detailed in subsections that follow.

3.9.1 DATA RECORDING

Field data will be recorded in field logbooks and consist of measurements from direct-reading instruments or direct measurements. Field staff are responsible for recording field data, and CRA's QA Officer or designee is responsible for identifying and correcting any recording errors.

Laboratory data are recorded in a variety of formats. Data from instruments are recorded on magnetic media, strip charts, or bench sheets. The analytical methods provide the data recording requirement for each preparation and analysis method.

3.9.2 DATA VALIDATION

Validation of field data for this project will primarily consist of checking all data for transcription errors and reviewing all information recorded in field logbooks. Data transcribed from the field logbook into summary tables for reporting purposes will be verified for correctness by CRA's QA Officer or designee. Any limitations on the use of field data will be included in the reports.

Validation of the analytical data will be performed by CRA's QA Officer or designee using an SOP based on the "USEPA Contract Laboratory Program National Functional Guidelines for Organic Data Review", EPA 540/R-99/008, October 1999 and "USEPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review", EPA 540-R-04-004, October 2004. The data validation SOP is provided in Attachment B.

All data will be validated using the QC deliverables specified in Section 2.10.2 of this QAPP. As noted in Section 2.10.2, data being used for risk assessment will be fully validated (i.e., including raw data review).

3.9.3 DATA REDUCTION

Field data reduction procedures will be minimal in scope compared to those implemented for laboratory data. Only direct reading instrumentation will be employed in the field. These data will be recorded in field logbooks or on standard forms immediately after the measurements are obtained.

Laboratory data reduction consists of producing the final results from raw data. The procedures, calculations, and specific equations used by the laboratory for data reduction are detailed in the SOPs.

3.9.4 DATA TRANSMITTAL/TRANSFER

Field measurements will be entered into a standard Microsoft Excel spreadsheet format, as necessary. CRA's QA Officer is responsible for verifying the correctness of the field data after the data are transferred to spreadsheet format.

TA-North Canton and TA-Knoxville will provide data in electronic format as electronic data deliverables (EDDs) that are compatible with EarthSoft's EQuIS database product, which is CRA's database for chemistry and geographical data. EDDs are generated directly from the laboratory information management system (LIMS), thereby eliminating the possibility of manual transcription errors. Laboratory EDDs are imported into EQuIS, and the data are maintained in the database for manipulation and presentation.

CRA's QA Officer is responsible for verifying the correctness of the analytical database after the laboratory data have been imported. This is accomplished by comparing the data from the database to the hardcopy analytical reports for a minimum of 10 percent of the sample results. If discrepancies between the database and hardcopy analytical reports are identified, a complete verification of the database will be performed or a new EDD will be submitted, imported, and verified as described previously.

Laboratory reports, outputs from the project database (data summary tables comparing validated data to evaluation criteria), and data validation memoranda will be transferred to CRA's Project Manager for use following completion of data validation process. Consistent with paragraph 35 of the CD, validated analytical data will be provided to USEPA within sixty (60) days of each sampling activity in the electronic format described at: http//www.epa.gov/region5superfund/edman.

3.9.5 DATA ANALYSIS

Laboratory data will be evaluated as described in the RD Work Plan. It is anticipated that commercially-available software, such as ArcView, or CRA's Electronic Database Access Tool (e:DAT) may be used to facilitate the evaluation/visualization of the data. The actual software used and input parameters/assumptions will be identified in project reports, as necessary. There are no extreme or unique computer hardware required to use these software.

3.9.6 DATA ASSESSMENT

Assessment of laboratory data by the laboratory will be performed using the procedures detailed in the SOPs. These assessments include determining the mean, standard deviation, percent relative standard deviation (RSD), percent difference, RPD, and percent recovery for certain QC elements.

Assessment of QC data for data validation purposes will include determining percent recovery, RPD, and percent completeness. The statistical equations to determine percent recovery, RPD, and percent completeness are provided in Section 5.3 of this QAPP.

3.9.7 DATA TRACKING

Data generated in the field will be recorded in field logbooks or on standard field forms. There are no unique or special tracking requirements for these data. The data will be transcribed for analysis and reporting as discussed in Section 3.9.4 of this QAPP, and the original field logbooks and field forms will be maintained in the final evidence file.

Laboratory data tracking procedures will be consistent with the laboratory's standard procedures for tracking data from generation to reporting. The laboratory's LIMS will also

provide a means for tracking data in the laboratory. The laboratory's Operations Manager is ultimately responsible for data tracking in the laboratory.

Tracking analytical data in the database includes recording the laboratory generating the data, the dates when the EDDs were received and imported, the date when qualifiers were applied to the results, and the level of data validation performed. CRA's Project Manager is ultimately responsible for tracking data from entry into the database to reporting.

3.9.8 DATA STORAGE AND RETRIEVAL

Laboratory data will be stored in hardcopy and/or electronic format for a minimum period of 5 years. Electronic instrument data are maintained on magnetic media (i.e., magnetic tape) for this same time period.

CRA's Project Manager is responsible for project data storage and retrieval. Final evidence files, which will include a copy of all laboratory data will be maintained by CRA.

3.9.9 DATA SECURITY

Laboratory data security is the responsibility of the laboratory's Operations Manager. Archived data cannot be accessed without authorization, and the name and purpose of personnel accessing archived data are recorded. The laboratory's LIMS is password protected and access rights are restricted by job function. CRA's data security procedures include limiting project database access to database managers and analysts and general building security procedures.

4.0 ASSESSMENT/OVERSIGHT

The following subsections describe the procedures used to ensure proper implementation of this QAPP and the activities for assessing the effectiveness of the implementation of the project and associated QA/QC activities.

4.1 ASSESSMENTS AND RESPONSE ACTIONS

Assessments consisting of internal and external audits may be performed during the project. Internal technical system audits of both field and laboratory procedures, if conducted, will verify that sampling and analysis are being performed in accordance with the procedures established in the FSP and this QAPP.

An internal field technical system audit of field activities, including sampling and field measurements, may be conducted by the QA Officer or designee at the beginning of the field sampling activities to identify deficiencies in the field sampling and documentation procedures. The field technical system audit, if conducted, will include examining field sampling records, field instrument operating records, field instrument calibration records, and chain-of-custody documentation. In addition, sample collection, handling, and packaging in compliance with the established procedures will be reviewed during the field audit. Any deficiencies identified will be documented and corrective actions will be taken to rectify the deficiencies.

Corrective action resulting from internal field technical system audits will be implemented immediately if data may be adversely affected from the use of unapproved or improper use of approved methods. CRA's QA Officer will identify deficiencies and recommended corrective action to CRA's Project Manager. Implementation of corrective actions will be performed by CRA's QA Officer and field team. Corrective action will be documented in the field logbook and/or the project file. Follow-up audits will be performed as necessary to verify that deficiencies have been corrected, and that the QA/QC procedures described in this QAPP, the FSP, and the RD Work Plan are maintained throughout the project.

An external field technical system audit may be conducted by USEPA at any time during the field operations. These audits may or may not be announced.

An internal laboratory technical system audit may be conducted during the project by the laboratory QA Officer or designee. The laboratory technical system audit generally is conducted on an annual basis and includes examining laboratory documentation regarding sample receiving, sample log-in, storage and tracking, chain-of-custody procedures, sample preparation and analysis, instrument operating records, data handling and management, data tracking and control, and data reduction and verification. The laboratory QA Officer will evaluate the results of the audit and provide a final report to section managers and the Operations Manager that includes any deficiencies and/or noteworthy observations.

Corrective action resulting from deficiencies identified during internal laboratory technical system audits will be implemented immediately. The Operations Manager or section leaders, in consultation with the laboratory supervisor and staff, will approve the required corrective action to be implemented by the laboratory staff. The laboratory QA Officer will ensure implementation and documentation of the corrective action. All problems requiring corrective action and the corrective action taken will be reported to the laboratory Project Manager. Follow-up audits will be performed as necessary to verify that deficiencies have been corrected.

An external laboratory audit may be conducted at the discretion of USEPA. These audits may or may not be announced. External laboratory audits, if conducted, may include, but not be limited to, reviewing laboratory analytical procedures, laboratory on-site audits, and/or submitting performance evaluation samples to the laboratory for analysis.

4.2 REPORTS TO MANAGEMENT

Quality Assurance Management Reports will be prepared for the project. Minimally, these reports will include the results of periodic data quality validation and assessment, data use limitations, and any significant QA problems identified and corrective actions taken.

CRA's QA Officer will be responsible within the organizational structure for preparing these reports. CRA's Project Manager will be provided with these reports, which will be provided to USEPA with the results of monitoring events. Project reports will also include a summary of the data quality information contained in the periodic reports.

5.0 DATA VERIFICATION/VALIDATION AND USABILITY

The QA activities that will be performed to ensure that the project data are scientifically defensible, properly documented, of known quality, and meet the project objectives are described in the following sections.

5.1 DATA REVIEW, VERIFICATION, AND VALIDATION REQUIREMENTS

All field and laboratory data will be reviewed, verified, and validated. These terms are defined as follows:

- Data review is the in-house examination to ensure that the data have been recorded, transmitted, and processed correctly.
- Data verification is the process for evaluating the completeness, correctness, and conformance/compliance of a specific data set against the method, procedural, or contractual specifications.
- Data validation is an analyte- and sample-specific process that extends the evaluation of data beyond method, procedure, or contractual compliance (i.e., data verification) to determine the quality of a specific data set relative to the end use.

The procedures and criteria used to verify and validate field and laboratory data are presented in Section 5.2. Field data and logbooks will be reviewed to ensure that the requirements of the sampling program, including the number of samples and locations, sampling, and sample handling procedures, were fulfilled.

Laboratory data review consists of raw data being reduced to results and checked by the responsible analyst. A second review of the data reduction procedure is conducted by another analyst or senior chemist. After the data are verified (see Section 5.2), a draft report is reviewed by the laboratory Project Manager. Final reports are generated, signed, and transmitted after approval of the draft by the Project Manager.

5.2 VERIFICATION AND VALIDATION METHODS

Field data will be verified by reviewing field documentation and chain-of-custody records. Data from direct-reading field instruments will be verified by reviewing calibration and operating records and the QC data specified in Section 2.8.2 of this QAPP.

Verification of sample collection procedures consists of reviewing sample collection documentation for compliance with the requirements of the FSP and QAPP. If alternate sampling procedures were used, the acceptability of the procedure will be evaluated to determine the affect on the usability of the data. Data usability will not be affected if the procedure used is determined to be an acceptable alternative that fulfills the measurement performance criteria in Section 2.8.2 of this QAPP.

The laboratory will internally verify its data by reviewing and documenting sample receipt, sample preparation, sample analysis (including internal QC checks), and data reduction and reporting. Any deviations from the acceptance criteria, corrective actions taken, and data determined to be of limited usability (i.e., laboratory-qualified data) will be noted in the laboratory reports.

Verification of laboratory data conducted by CRA will consist of reviewing the final reports to ensure that the methods used to analyze the samples were consistent with the requirements of this QAPP. Sample handling records will also be reviewed to ensure that sample integrity remained intact from collection to laboratory receipt and that samples were properly preserved. Chain-of-custody documentation and sample condition upon laboratory receipt will be reviewed. Laboratory results, holding time periods, and QC data will be reviewed to determine compliance with the measurement performance criteria in Section 2.8.2 of this QAPP and the analytical methods.

Data validation will be conducted by CRA consistent with the procedure identified in Section 3.9.2 of this QAPP. The results of the data verification procedure will identify data that do not meet the measurement performance criteria in Section 2.8.2 of this QAPP. Data validation will determine whether the data are acceptable, of limited usability (qualified as estimated), or rejected. Data qualified as estimated will be reviewed and a discussion of the usability of estimated data will be included in the data validation memoranda. The results of data verification/validation will be summarized in data validation memoranda provided to CRA's Project Manager for use in interpreting the results and for use in project reports.

Data determined to be unusable may require corrective action to be taken. Potential types of corrective action may include resampling by the field team or reanalysis of samples by the laboratory. The corrective actions taken are dependent upon the ability to mobilize the field team and whether or not the data are critical for project DQOs to be achieved.

CRA's Project Manager will be responsible for approving the implementation of any corrective action deemed to be necessary during data verification/validation.

5.3 USABILITY/RECONCILIATION WITH DATA QUALITY OBJECTIVES

The overall usability of the data for the investigation will be assessed by evaluating the PARCCS of the data set to the measurement performance criteria in Section 2.8.2 of this QAPP using basic statistical quantities, as applicable. The procedures and statistical formulas to be used for these evaluations are presented in the following subsections.

5.3.1 PRECISION

Precision will be evaluated by assessing the RPD data from field duplicate samples. Analytical precision will be evaluated by assessing the RPD data from either duplicate spiked sample analyses or duplicate LCS sample analyses. The RPD between two measurements is calculated using the following simplified formula:

$$RPD = \frac{|R_1 - R_2|}{R_1 + R_2} \times 200$$

where:

R_1 = value of first result
R_2 = value of second result

RPD data will provide the means to evaluate the overall variability attributable to the sampling procedure, sample matrix, and laboratory procedures. It should be noted that the RPD of two measurements can be very high when the concentrations approach the quantitation limit of an analysis. RPDs will only be calculated when the concentrations of an analyte detected in both samples are greater than or equal to 5 times the quantitation limit for the analyte.

5.3.2 ACCURACY/BIAS

The data from method blank samples, trip blank samples, MS/MSD samples, surrogate compound spikes, and LCSs will be used to determine accuracy and potential bias of the sample data.

The data from method blank samples provide an indication of laboratory contamination that may result in bias of sample data. Sample data associated with method blank contamination will have been identified during the data verification/validation process. Sample data associated with method blank contamination are evaluated during the data validation procedure to determine if analytes detected in samples associated with contaminated method blanks are "real" or are the result of laboratory contamination. The procedure for this evaluation involves comparing the concentration of the analyte in the sample to the concentration in the method blank sample taking into account adjustments for sample preparation and dilution factors. In general, the sample data are qualified as not detected if the sample concentration is less than 5 times (10 times for common laboratory contaminants) the method blank concentration. Typically, the quantitation limit for the affected analyte is elevated to the concentration detected in the sample.

The data from equipment and trip blank samples provide an indication of field conditions that may result in bias of sample data. Sample data associated with contaminated equipment and trip blank samples will have been identified during the data verification/validation process. The evaluation procedure and qualification of sample data associated with equipment and trip blank contamination is performed in a similar manner as the evaluation procedure for method blank sample contamination.

Matrix spike sample data provide information regarding the accuracy/bias of the analytical methods relative to the sample matrix. Matrix spike samples are field samples that have been fortified with target analytes prior to sample preparation and analysis. The percent recovery data provide an indication of the effect that the sample matrix may have on the preparation and analysis procedure. Sample data exhibiting matrix effects will have been identified during the data verification/validation process.

Surrogate spike recoveries provide information regarding the accuracy/bias of organic analyses on an individual sample basis. Surrogate compounds are not expected to be found in the samples and are added to every sample prior to sample preparation. The percent recovery data provide an indication of the effect that the sample matrix may have on the preparation and analysis procedure. Sample data exhibiting matrix effects will have been identified during the data verification/validation process.

Analytical accuracy/bias will be determined by evaluating the percent recovery data of LCSs. LCSs are artificial samples prepared in the laboratory using a blank matrix fortified with analytes from a standard reference material that is independent of the calibration standards. LCSs are prepared and analyzed in the same manner as the field samples. The

percent recovery data from LCS analyses will provide an indication of the accuracy and bias of the analytical method for each analyte or analyte group.

Percent recovery is calculated using the following formula:

$$\%R = \frac{SSR - SR}{SA} \quad X \ 100$$

where:

SSR = Spiked Sample Result
SR = Sample Result or Background
SA = Spike Added

The percent recovery for surrogate compounds and LCSs are determined by dividing the measured value by the true value and multiplying by 100.

Accuracy/bias will be determined by comparing the percent recovery data to the measurement performance criteria in Section 2.8.2 of this QAPP.

5.3.3 SAMPLE REPRESENTATIVENESS

Representiveness of the samples will be assessed by reviewing sample holding times, the results of field audits, if conducted, and the data from field duplicate samples. Sample representativeness will be considered acceptable if holding time periods are met, the results of field audits indicate that the approved sampling methods or alternate acceptable sampling methods were used to collect the samples, and the field duplicate RPD data are acceptable.

5.3.4 COMPLETENESS

Completeness will be assessed by comparing the number of valid (usable) sample results to the total possible number of results within a specific sample matrix and/or analysis. Percent completeness will be calculated using the following formula:

$$\% \text{ Completeness} = \frac{\text{Number of Valid (usable) measurements}}{\text{Number of Measurements Planned}} \quad X \ 100$$

Completeness will be considered acceptable if 90 percent of the data are determined to be valid.

5.3.5 COMPARABILITY

The comparability of data sets will be evaluated by reviewing the sampling and analysis methods used to generate the data for each data set. Comparability will be determined to be acceptable if the sampling and analysis methods specified in this QAPP and any approved QAPP revisions or amendments are used for generating the data.

Comparability of data from split samples (samples that are collected at the same time from the same location and split equally between two parties using sample containers from the same source or vendor), if collected, will be evaluated by determining the RPD of detected analytes in both samples following data verification/validation. Analytes that are detected in only one of the two samples will be assessed by reviewing the data validation reports for both data sets and determining the cause of the discrepancy, if possible. Comparability of split sample data will be considered acceptable if the RPD for detected analytes with concentrations greater than or equal to 5 times their respective quantitation limits does not exceed RPD acceptance criteria for field duplicate samples.

5.3.6 SENSITIVITY AND QUANTITATION LIMITS

Laboratory reports will include both method detection limits and method reporting limits. Analytes detected between the method detection limit and method reporting limit will be reported and flagged appropriately. These limits will be reviewed for the samples to ensure that the sensitivity of the analyses was sufficient to achieve the detectability requirements. All relevant QC data will be reviewed to assess compliance with the measurement performance criteria specified in Section 2.8.2 of this QAPP. Sensitivity will be considered acceptable if quantitation/detection limits for the samples are sufficient to achieve the detectability requirements for the investigation.

It should be noted that quantitation limits may be elevated as a result of high concentrations of target compounds, non-target compounds, and matrix interferences (collectively known as sample matrix effects). In these cases, the sensitivity of the of the analyses will be evaluated on an individual sample basis relative to the applicable evaluation criteria. The need to investigate the use of alternate analytical methods may be

required if the sensitivity of the analytical methods identified in this QAPP cannot achieve the evaluation criteria as a result of sample matrix effects.

5.3.7 DATA LIMITATIONS AND ACTIONS

Data use limitations will be identified in data validation reports. Data that do not meet the measurement performance criteria specified in this QAPP will be identified and the impact on the project quality objectives will be assessed and discussed in these reports and project reports. Field information will be reviewed to ensure that all sampling procedures and field measurements were conducted in accordance with the requirements of this QAPP. Field measurements obtained or data from samples collected using procedures inconsistent with the requirements of this QAPP will be evaluated using the procedures in Section 5.1 of this QAPP. Specific actions for field or laboratory data that do not meet the measurement performance criteria depends on the use of the data, and may require that additional samples are collected or the use of the data be restricted.

6.0 REFERENCES

EPA Requirements for Quality Assurance Project Plans, EPA QA/R-5, EPA/240/R-02/010, March 2001.

Guidance for Quality Assurance Project Plans, EPA QA/G-5, EPA/240/R-02/009, December 2002.

Region 5 Instructions on the Preparation of a Superfund Division Quality Assurance Project Plan, Revision 0, U.S. EPA Region 5 Superfund Division, June 2000.

USEPA Contract Laboratory Program National Functional Guidelines for Organic Data Review, EPA 540/R-99/008, October 1999.

USEPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review, EPA 540-R-04-004, October 2004.

FIGURES

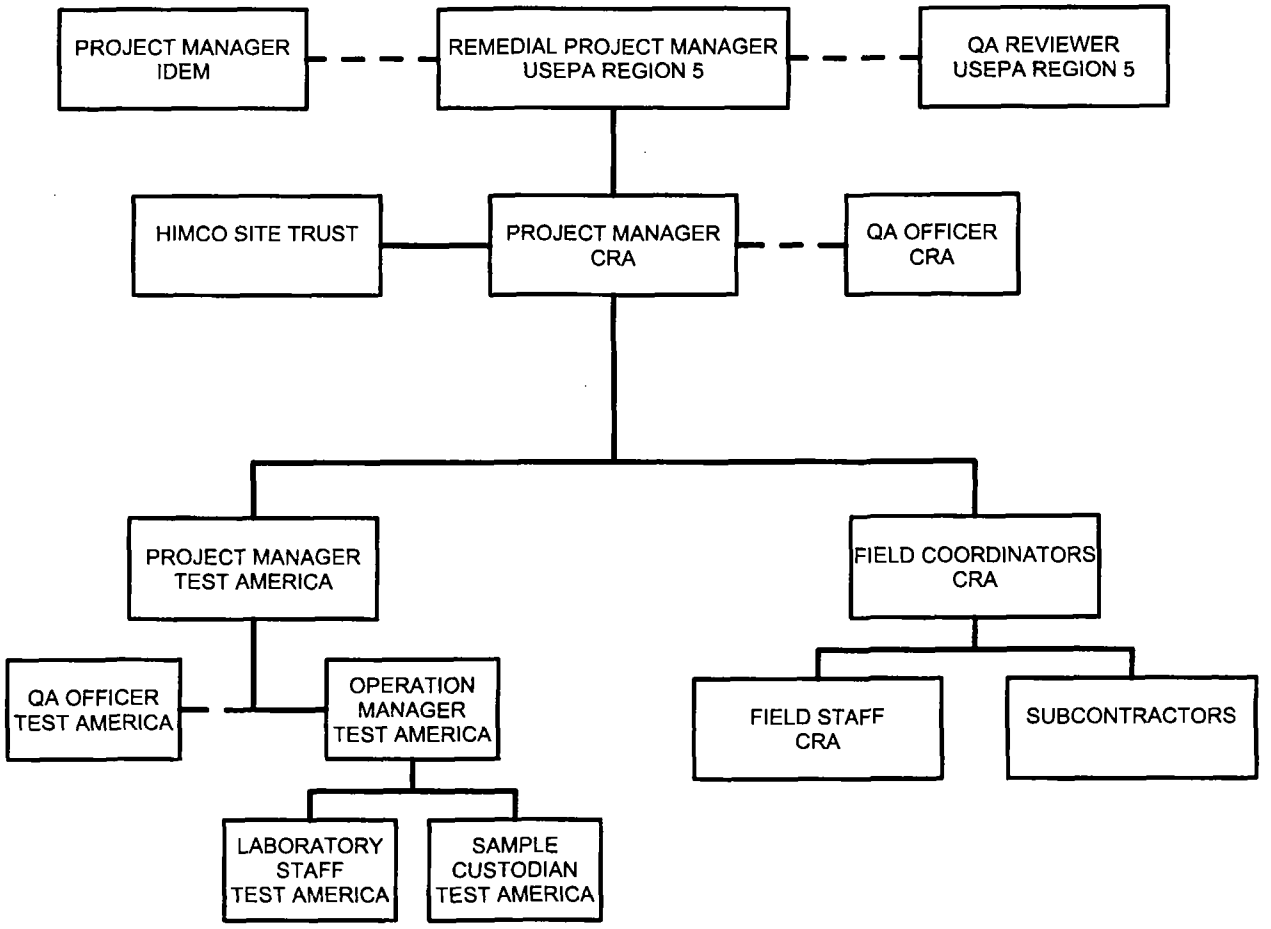

figure 2.1

PROJECT QA/QC ORGANIZATION
HIMCO SITE REMEDIAL DESIGN
Elkhart, Indiana

TABLES

TABLE 2.1

SUMMARY OF SAMPLING AND ANALYSIS PROGRAM
HIMCO SITE
ELKHART, INDIANA

Location/Task	*Sample Matrix*	*Field Parameters*	*Laboratory Parameters*[2]	*Approximate Number of Samples*	*QC Samples*[1] *Field Blanks*	*Field Duplicates*	*MS/MSD*[3]	*Total*
Test Pit Sampling	Soil	PID screening	TCL SVOCs, TAL Metals, Total cyanide.	15	1	1	1	18
Landfill Cover Soil Borings	Soil	PID screening	Grain size distribution, pH, organic content, NPK content	27	0	0	0	27
			TCL VOCs	TBD[4]	0	1 per 20	1 per 20	TBD
Soil Gas Probe Installation (single probes)	Soil	FID/PID screening, water level, gas pressure, methane, oxygen, carbon dioxide	None	24	0	0	0	24
Soil Gas Probe Nests Installation (each nested pair)	Soil	FID/PID screening	Grain size distribution, porosity/water-filled porosity, dry bulk density, vapor permeability, fraction of organic carbon	6	0	0	0	6
Vertical Aquifer Sampling	Groundwater	None	TCL VOCs, TAL Metals, bromide, sulfate, chloride	126	7	7	7	147
Groundwater Sampling	Groundwater	pH, DO, temperature, conductivity, ORP, turbidity, water level	TCL VOCs, TCL SVOCs, TAL Metals, bromide, sulfate, chloride	39[5]	2	2	2	45

TABLE 2.1

SUMMARY OF SAMPLING AND ANALYSIS PROGRAM
HIMCO SITE
ELKHART, INDIANA

Location/Task	*Sample Matrix*	*Field Parameters*	*Laboratory Parameters*[2]	*Approximate Number of Samples*	*QC Samples*[1] *Field Blanks*	*Field Duplicates*	*MS/MSD*[3]	*Total*
Soil Gas Sampling	Gas	FID/PID screening water level, gas pressure, methane, oxygen, carbon dioxide	VOCs, nitrogen, hydrogen sulfide, carbon monoxide, NMOC	31	0	2	1	34

Notes:

[1] One trip blank sample will be included in each cooler containing groundwater samples for VOC analysis.

[2] TCL - Target Compound List (TCL), SVOCs - Semi-volatile Organic Compounds (SVOCs), TAL - Target Analyte List, VOCs - Volatile Organic Compounds, NMOC - Non-Methane Organic Compounds, NPK - Nitrogen, Phosphorus, Potassium.

[3] Matrix spike/matrix duplicate (MS/MSD) analyses will be performed for organic analyses. MS/MSD samples will be collected with extra sample volume for water samples, at a frequency of 1 per 20 or fewer investigative samples. Triple the normal sample volume will be collected for VOCs and double the normal volume for SVOCs. No additional sample volume is required for inorganic analyses. Duplicate laboratory control samples (LCS/LCSD) will be analyzed at a frequency of 1 per 20 or fewer soil gas samples.

[4] To be determined based on headspace PID screening. A soil sample will be collected for VOC analysis if headspace PID reading is greater than 10 ppm above background PID readings.

[5] Number based on baseline monitoring of 39 wells to be monitored quarterly for 2 years.

TABLE 2.2

TARGET ANALYTES AND QUANTITATION LIMITS
HIMCO SITE
ELKHART, INDIANA

	Targeted Quantitation Limit [1]
Volatile Organic Compounds - Soil (µg/kg)	
1,1,1-Trichloroethane	5.0
1,1,2,2-Tetrachloroethane	5.0
1,1,2-Trichloro-1,2,2-trifluoroethane	5.0
1,1,2-Trichloroethane	5.0
1,1-Dichloroethane	5.0
1,1-Dichloroethene	5.0
1,2,4-Trichlorobenzene	5.0
1,2-Dibromo-3-chloropropane	5.0
1,2-Dibromoethane	5.0
1,2-Dichlorobenzene	5.0
1,2-Dichloroethane	5.0
1,2-Dichloropropane	5.0
1,3-Dichlorobenzene	5.0
1,4-Dichlorobenzene	5.0
2-Butanone	20
2-Hexanone	20
4-Methyl-2-pentanone	20
Acetone	20
Benzene	5.0
Bromodichloromethane	5.0
Bromoform	5.0
Bromomethane	5.0
Carbon disulfide	5.0
Carbon tetrachloride	5.0
Chlorobenzene	5.0
Chloroethane	5.0
Chloroform	5.0
Chloromethane	5.0
cis-1,2-Dichloroethene	5.0
cis-1,3-Dichloropropene	5.0
Cyclohexane	10
Dibromochloromethane	5.0
Dichlorodifluoromethane	5.0
Ethylbenzene	5.0
Isopropylbenzene (Cumene)	5.0
Methyl Acetate	10
Methyl tert Butyl Ether	5.0
Methylcyclohexane	10
Methylene chloride	5.0

TABLE 2.2

TARGET ANALYTES AND QUANTITATION LIMITS
HIMCO SITE
ELKHART, INDIANA

	Targeted Quantitation Limit [1]
Volatile Organic Compounds - Soil (µg/kg)	
Styrene	5.0
Tetrachloroethene	5.0
Toluene	5.0
trans-1,2-Dichloroethene	5.0
trans-1,3-Dichloropropene	5.0
Trichloroethene	5.0
Trichlorofluoromethane	5.0
Vinyl chloride	5.0
Xylenes (total)	10
Semi-volatile Organic Compounds - Soil (µg/kg)	
1,1'-Biphenyl	330
2,2'-oxybis(1-Chloropropane)	330
2,4,5-Trichlorophenol	830
2,4,6-Trichlorophenol	330
2,4-Dichorophenol	330
2,4-Dimethylphenol	330
2,4-Dinitrophenol	830
2,4-Dinitrotoluene	330
2,6-Dinitrotoluene	330
2-Chloronaphthalene	330
2-Chlorophenol	330
2-Methylnaphthalene	330
2-Methylphenol	330
2-Nitroaniline	830
2-Nitrophenol	330
3,3'-Dichlorobenzidine	330
3-Nitroaniline	830
4,6-Dinitro-2-methylphenol	830
4-Bromophenylphenyl ether	330
4-Chloro-3-methylphenol	330
4-Chloroaniline	330
4-Chlorophenyl phenyl ether	330
4-Methylphenol	330
4-Nitroaniline	830
4-Nitrophenol	830
Acenaphthene	330
Acenaphthylene	330
Acetophenone	330

TABLE 2.2

TARGET ANALYTES AND QUANTITATION LIMITS
HIMCO SITE
ELKHART, INDIANA

	Targeted Quantitation Limit[1]
Semi-volatile Organic Compounds - Soil (µg/kg)	
Anthracene	330
Atrazine	330
Benzaldehyde	330
Benzo(a)anthracene	330
Benzo(a)pyrene	330
Benzo(b)fluoranthene	330
Benzo(g,h,i)perylene	330
Benzo(k)fluoranthene	330
bis(2-Chloroethoxy)methane	330
bis(2-Chloroethyl)ether	330
bis(2-Ethylhexyl)phthalate	330
Butylbenzylphthalate	330
Caprolactam	330
Carbazole	330
Chrysene	330
Dibenz(a,h)anthracene	330
Dibenzofuran	330
Diethylphthalate	330
Dimethylphthalate	330
Di-n-butyphthalate	330
Di-n-octylphthalate	330
Fluoranthene	330
Fluorene	330
Hexachlorobenzene	330
Hexachlorobutadiene	330
Hexachlorocyclopentadiene	330
Hexachloroethane	330
Indeno(1,2,3-cd)pyrene	330
Isophorone	330
Naphthalene	330
Nitrobenzene	330
N-Nitroso-di-n-propylamine	330
N-Nitrosodiphenylamine (diphenylamine)	330
Pentachlorophenol	830
Phenanthrene	330
Phenol	330
Pyrene	330
Pyridine	660

TABLE 2.2

TARGET ANALYTES AND QUANTITATION LIMITS
HIMCO SITE
ELKHART, INDIANA

	Targeted Quantitation Limit [1]
TAL Inorganics - Soil (mg/kg)	
Aluminum	40
Antimony	12
Arsenic	2
Barium	40
Beryllium	1
Cadmium	1
Calcium	1,000
Chromium	2
Cobalt	10
Copper	5
Iron	20
Lead	0.6
Magnesium	1,000
Manganese	3
Mercury	0.1
Nickel	8
Potassium	1,000
Selenium	1
Silver	2
Sodium	1,000
Thallium	2
Vanadium	10
Zinc	4
Cyanide	0.25
Field Parameters (meter units as ppm)	
Organic Vapors	1
Volatile Organic Compounds - Water (µg/L)	
1,1,1-Trichloroethane	1
1,1,2,2-Tetrachloroethane	1
1,1,2-Trichloro-1,2,2-trifluoroethane	1
1,1,2-Trichloroethane	1
1,1-Dichloroethane	1
1,1-Dichloroethene	1
1,2,4-Trichlorobenzene	1
1,2-Dibromo-3-chloropropane	2
1,2-Dibromoethane	1
1,2-Dichlorobenzene	1

TABLE 2.2

TARGET ANALYTES AND QUANTITATION LIMITS
HIMCO SITE
ELKHART, INDIANA

	Targeted Quantitation Limit[1]
Volatile Organic Compounds - Water (µg/L)	
1,2-Dichloroethane	1
1,2-Dichloropropane	1
1,3-Dichlorobenzene	1
1,4-Dichlorobenzene	1
2-Butanone	10
2-Hexanone	10
4-Methyl-2-pentanone	10
Acetone	10
Benzene	1
Bromodichloromethane	1
Bromoform	1
Bromomethane	1
Carbon disulfide	1
Carbon tetrachloride	1
Chlorobenzene	1
Chloroethane	1
Chloroform	1
Chloromethane	1
cis-1,2-Dichloroethene	1
cis-1,3-Dichloropropene	1
Cyclohexane	1
Dibromochloromethane	1
Dichlorodifluoromethane	1
Ethylbenzene	1
Isopropylbenzene (Cumene)	1
Methyl Acetate	10
Methyl tert Butyl Ether	5
Methylcyclohexane	1
Methylene chloride	1
Styrene	1
Tetrachloroethene	1
Toluene	1
trans-1,2-Dichloroethene	1
trans-1,3-Dichloropropene	1
Trichloroethene	1
Trichlorofluoromethane	1
Vinyl chloride	1
Xylenes (total)	1

TABLE 2.2

TARGET ANALYTES AND QUANTITATION LIMITS
HIMCO SITE
ELKHART, INDIANA

	Targeted Quantitation Limit[1]
Semi-volatile Organic Compounds - Water (µg/L)	
Acenaphthene	0.2
Acenaphthylene	0.2
Anthracene	0.2
Benzo(a)anthracene	0.2
Benzo(a)pyrene	0.2
Benzo(b)fluoranthene	0.2
Benzo(g,h,i)perylene	0.2
Benzo(k)fluoranthene	0.2
bis(2-Chloroethoxy)methane	1
bis(2-Chloroethyl)ether	1
2,2'-oxybis(1-Chloropropane)	2
bis(2-Ethylhexyl)phthalate	1
4-Bromophenylphenyl ether	2
Butylbenzylphthalate	1
Carbazole	1
4-Chloroaniline	2
2-Chloronaphthalene	1
4-Chlorophenyl phenyl ether	2
Chrysene	0.2
Dibenz(a,h)anthracene	0.2
Dibenzofuran	1
Di-n-butyphthalate	1
3,3'-Dichlorobenzidine	5
Diethylphthalate	1
Dimethylphthalate	1
2,4-Dinitrotoluene	5
2,6-Dinitrotoluene	5
Di-n-octylphthalate	1
Fluoranthene	0.2
Fluorene	0.2
Hexachlorobenzene	0.2
Hexachlorobutadiene	1
Hexachlorocyclopentadiene	10
Hexachloroethane	1
Indeno(1,2,3-cd)pyrene	0.2
Isophorone	1
2-Methylnaphthalene	0.2
Naphthalene	0.2
2-Nitroaniline	2

TABLE 2.2

TARGET ANALYTES AND QUANTITATION LIMITS
HIMCO SITE
ELKHART, INDIANA

	Targeted Quantitation Limit[1]
Semi-volatile Organic Compounds - Water (µg/L)	
3-Nitroaniline	2
4-Nitroaniline	2
Nitrobenzene	1
N-Nitrosodiphenylamine	1
N-Nitroso-di-n-propylamine	1
Phenanthrene	0.2
Pyrene	0.5
1,2,4-Trichlorobenzene	1
4-Chloro-3-methylphenol	2
2-Chlorophenol	1
2,4-Dichlorophenol	2
2,4-Dimethylphenol	2
2,4-Dinitrophenol	5
4,6-Dinitro-2-methylphenol	5
2-Methylphenol	1
4-Methylphenol	1
2-Nitrophenol	2
4-Nitrophenol	5
Pentachlorophenol	5
Phenol	1
2,4,5-Trichlorophenol	5
2,4,6-Trichlorophenol	5
TAL Metals - Water (µg/L)	
Aluminum	50
Antimony	2
Arsenic	1
Barium	200
Beryllium	1
Cadmium	1
Calcium	5000
Chromium	10
Cobalt	50
Copper	25
Iron	100
Lead	3
Magnesium	5000
Manganese	15
Mercury	0.2

TABLE 2.2

TARGET ANALYTES AND QUANTITATION LIMITS
HIMCO SITE
ELKHART, INDIANA

	Targeted Quantitation Limit[1]
TAL Metals - Water (µg/L)	
Nickel	40
Potassium	5000
Selenium	5
Silver	10
Sodium	5000
Thallium	1
Vanadium	50
Zinc	20
Water Quality Parameters (mg/L)	
Bromide	0.5
Chloride	1
Sulfate	1
Volatile Organic Compounds - Soil Gas ($\mu g/m^3$)	
1,1,1-Trichloroethane	1.1
1,1,2,2-Tetrachloroethane	2.1
1,1,2-Cl 1,2,2-F ethane (113)	1.5
1,1,2-Trichloroethane	1.1
1,1-Dichloroethane	0.81
1,1-Dichloroethene	0.79
1,2,4-Trichlorobenzene	3.0
1,2,4-Trimethylbenzene	2.0
1,2-Cl-1,1,2,2-F ethane (114)	1.4
1,2-Dibromoethane	1.5
1,2-Dichlorobenzene	1.2
1,2-Dichloroethane	0.81
1,2-Dichloropropane	0.92
1,3,5-Trimethylbenzene	2.0
1,3-Dichlorobenzene	1.2
1,4-Dichlorobenzene	1.2
2-Butanone	0.59
2-Hexanone	0.82
4-Ethyl Toluene	0.98
4-Methyl-2-Pentanone	0.82
Acetone	2.4
Benzene	0.64
Benzyl Chloride	1.0

TABLE 2.2

TARGET ANALYTES AND QUANTITATION LIMITS
HIMCO SITE
ELKHART, INDIANA

	Targeted Quantitation Limit[1]
Volatile Organic Compounds - Soil Gas ($\mu g/m^3$)	
Bromodichloromethane	1.3
Bromoform	2.1
Bromomethane	0.78
c-1,2-Dichloroethene	0.79
c-1,3-Dichloropropene	0.91
Carbon Disulfide	3.1
Carbon Tetrachloride	1.3
Chlorobenzene	0.9
Chloroethane	0.53
Chloroform	0.97
Chloromethane	0.82
Dibromochloromethane	1.7
Dichlorodifluoromethane (12)	0.99
Ethylbenzene	0.87
Hexachlorobutadiene	2.1
Methylene Chloride	0.69
o-Xylene	0.87
p,&m-Xylene	0.87
Styrene	0.85
t-1,2-Dichloroethene	0.79
t-1,3-Dichloropropene	0.91
Tetrachloroethene	1.4
Toluene	0.75
Trichloroethene	1.1
Trichlorofluoromethane (11)	1.1
Vinyl Acetate	3.5
Vinyl Chloride	0.51
Landfill Gases	
Nitrogen	1%
Hydrogen sulfide	1%
Carbon monoxide	1%
NMOC	10 ppmv

TABLE 2.2

TARGET ANALYTES AND QUANTITATION LIMITS
HIMCO SITE
ELKHART, INDIANA

	Targeted Quantitation Limit[1]
Field Measurements	
pH	2 Standard Units
Temperature	0.1 °C
Conductivity	0.1 mmho/cm
Dissolved Oxygen	1 mg/L
ORP	1 mV
Turbidity	0.1 NTU
Methane	1%
Oxygen	1%
Carbon dioxide	1%

NoteS:

[1] The targeted quantitation limits are based on wet weight. The limits provided by the laboratory on a dry weight basis will be higher. Targeted quantitation are presented for guidance and may not be achievable for all samples as a result of matrix interferences or high concentrations of target and non-target compounds.

[2] NC - No Criteria; NA - Not Applicable

TABLE 2.3

PERCENT RECOVERY AND RELATIVE PERCENT DIFFERENCE CONTROL LIMITS
HIMCO SITE
ELKHART, INDIANA

Analyses	*% Recovery Control Limits*[1]	
	LCS/LCSD	*MS/MSD*
Volatile Organic Compounds - Soil	75-129 (27)	55-138 (20)
Benzene	75-127 (22)	49-139 (22)
Chlorobenzene	55-142 (27)	43-147 (27)
1,1-Dichloroethene	71-130 (24)	46-147 (24)
Toluene	71-131 (23)	46-143 (23)
Trichloroethene		
Volatile Organic Compounds - Water		
Benzene	80-116 (20)	78-118 (20)
Chlorobenzene	76-117 (20)	76-117 (20)
1,1-Dichloroethene	63-130 (20)	62-130 (20)
Toluene	76-119 (20)	70-119 (20)
Trichloroethene	75-122 (20)	62-130 (20)
Volatile Organic Compounds - Soil Gas		
1,1-Dichloroethene	70-130 (30)	NA
Methylene Chloride	70-130 (30)	NA
Trichloroethene	70-130 (30)	NA
Toluene	70-130 (30)	NA
1,1,2,2-Tetrachloroethane	70-130 (30)	NA
Semi-volatile Organic Compounds - Soil		
Acenaphthene	46-110 (30)	10-200 (30)
4-Chloro-3-methylphenol	42-110 (30)	32-117 (30)
2-Chlorophenol	39-110 (30)	32-110 (30)
2,4-Dinitrotoluene	55-116 (30)	42-118 (30)
4-Nitrophenol	24-117 (30)	10-125 (30)
N-Nitrosodi-n-propylamine	40-114 (30)	30-121 (30)
Pentachlorophenol	10-110 (30)	10-182 (30)
Phenol	39-110 (30)	10-144 (30)
Pyrene	58-113 (30)	10-200 (30)
Semi-volatile Organic Compounds - Water		
Acenaphthene	40-110 (30)	36-110 (30)
4-Chloro-3-methylphenol	39-110 (30)	33-110 (30)
2-Chlorophenol	27-110 (30)	26-110 (30)
2,4-Dinitrotoluene	52-123 (30)	46-119 (30)
4-Nitrophenol	12-130 (30)	13-127 (30)
N-Nitrosodi-n-propylamine	37-121 (30)	25-119 (30)
Pentachlorophenol	26-110 (30)	23-110 (30)
Phenol	14-112 (30)	16-110 (30)
Pyrene	55-120 (30)	54-115 (30)

TABLE 2.3

PERCENT RECOVERY AND RELATIVE PERCENT DIFFERENCE CONTROL LIMITS
HIMCO SITE
ELKHART, INDIANA

Analyses	*% Recovery Control Limits*[1]	
	LCS/LCSD	*MS/MSD*
TAL Inorganics - Soil		
Aluminum	80-120 (20)	75-125 (20)
Antimony	80-120 (20)	75-125 (20)
Arsenic	80-120 (20)	75-125 (20)
Barium	80-120 (20)	75-125 (20)
Beryllium	80-120 (20)	75-125 (20)
Cadmium	80-120 (20)	75-125 (20)
Calcium	80-120 (20)	75-125 (20)
Chromium	80-120 (20)	75-125 (20)
Cobalt	80-120 (20)	75-125 (20)
Copper	80-120 (20)	75-125 (20)
Iron	80-120 (20)	75-125 (20)
Lead	80-120 (20)	75-125 (20)
Magnesium	80-120 (20)	75-125 (20)
Manganese	80-120 (20)	75-125 (20)
Mercury	81-116 (20)	11-192 (20)
Nickel	80-120 (20)	75-125 (20)
Potassium	80-120 (20)	75-125 (20)
Selenium	80-120 (20)	75-125 (20)
Silver	80-120 (20)	75-125 (20)
Sodium	80-120 (20)	75-125 (20)
Thallium	80-120 (20)	75-125 (20)
Vanadium	80-120 (20)	75-125 (20)
Zinc	80-120 (20)	75-125 (20)
Cyanide	68-123 (20)	50-134 (20)
TAL Metals - Water		
Aluminum	77-123 (20)	63-128 (20)
Antimony	57-110 (20)	44-153 (20)
Arsenic	86-118 (20)	82-123 (20)
Barium	80-120 (20)	75-125 (20)
Beryllium	84-120 (20)	77-124 (20)
Cadmium	89-114 (20)	78-117 (20)
Calcium	80-120 (20)	75-125 (20)
Chromium	80-120 (20)	75-125 (20)
Cobalt	80-120 (20)	75-125 (20)
Copper	80-120 (20)	75-125 (20)
Iron	77-122 (20)	75-125 (20)
Lead	80-120 (20)	75-125 (20)
Magnesium	80-120 (20)	75-125 (20)
Manganese	80-120 (20)	75-125 (20)

TABLE 2.3

PERCENT RECOVERY AND RELATIVE PERCENT DIFFERENCE CONTROL LIMITS
HIMCO SITE
ELKHART, INDIANA

Analyses	*% Recovery Control Limits* [1]	
	LCS/LCSD	*MS/MSD*
TAL Metals - Water		
Mercury	82-123 (20)	69-134 (20)
Nickel	80-120 (20)	75-125 (20)
Potassium	80-120 (20)	75-125 (20)
Selenium	80-120 (20)	75-125 (20)
Silver	80-120 (20)	75-125 (20)
Sodium	80-120 (20)	75-125 (20)
Thallium	82-113 (20)	69-117 (20)
Vanadium	80-120 (20)	75-125 (20)
Zinc	80-120 (20)	75-125 (20)
Water Quality Parameters		
Bromide	90-110 (20)	80-120 (20)
Chloride	90-110 (20)	80-120 (20)
Sulfate	90-110 (20)	80-120 (20)

Note:

[1] Values in parentheses are the maximum RPD values allowed for MS/MSD or LCS/LCSD analytes. Laboratory control limits are updated on a periodic basis and the control limits in effect when the samples are analyzed will be used for data validation purposes.

TABLE 2.4

SURROGATE COMPOUND PERCENT RECOVERY CONTROL LIMITS
HIMCO SITE
ELKHART, INDIANA

Analysis	*Surrogate Compound*	*% Recovery Control Limits (water)*	*% Recovery Control Limits (soil)*	*% Recovery Control Limits (soil gas)*
VOCs	1,2-Dichloroethane-d4	61-128	61-130	70-130
	4-Bromofluorobenzene	74-116	47-158	70-130
	Toluene-d8	76-110	60-143	70-130
	Dibromofluoromethane	73-122	59-138	NA
TCL SVOCs	2-Fluorobiphenyl	28-110	34-110	NA
	2-Fluorophenol	10-110	26-110	NA
	2,4,6-Tribromophenol	22-120	10-118	NA
	Nitrobenzene-d_5	27-111	24-112	NA
	Phenol-d_5	10-110	28-110	NA
	Terphenyl-d_{14}	37-119	41-119	NA

Note:

[1] Laboratory control limits are updated on a periodic basis and the control limits in effect when the samples are analyzed will be used for data validation purposes.

TABLE 3.1

ROUTINE PREVENTIVE MAINTENANCE PROCEDURES AND SCHEDULES
HIMCO SITE
ELKHART, INDIANA

Instrument	*Maintenance Procedures/Schedule*	*Spare Parts in Stock*
Gas Chromatograph/Mass Spectrometer	1. Replace pump oil as needed. 2. Change septa weekly or as often as needed. 3. Change gas line dryers as needed. 4. Replace electron multiplier as often as needed. 5. Replace gas jet splitter as needed. 6. Replace GC injector glass liner weekly or as often as needed. 7. Replace GC column as needed. 8. Check to ensure that gas supply is sufficient for the day's activity and the delivery pressures are set as described in the SOP. 9. Check to ensure the pressure on the primary regulator never falls below 100 psi.	1. Syringes 2. Septa 3. Various electronic components 4. Glass jet splitters 5. GC columns 6. Glass liners
Gas Chromatograph	1. Change septa weekly or as often as needed. 2. Change gas line dryers as needed. 3. Replace GC injector glass liner weekly or as often as needed. 4. Replace GC column as needed. 5. Clean/replace GC detector as needed. 6. Check to ensure that gas supply is sufficient for the day's activity and the delivery pressures are set as described in the SOP. 7. Check to ensure the pressure on the primary regulator never falls below 100 psi.	1. Syringes 2. Septa 3. Detectors 4. Glass liners 5. GC columns

TABLE 3.1

ROUTINE PREVENTIVE MAINTENANCE PROCEDURES AND SCHEDULES
HIMCO SITE
ELKHART, INDIANA

Instrument	*Maintenance Procedures/Schedule*	*Spare Parts in Stock*
Purge and Trap Sample Concentrator	1. Replace trap as needed. 2. Decontaminate the system after running high concentration samples or as required by blank analysis. 3. Leak check system daily and as often as needed. 4. Check to ensure the gas supply is sufficient for the day's activity and the delivery pressures are set as described in the SOP. 5. Check to ensure the pressure on the primary regulator never run below 100 psi.	1. Traps 2. Spargers 3. Various electronic components/ circuits 4. Plumbing supplies - tubing, fittings
Inductively Coupled Plasma Spectrometer	1. Clean torch assembly and mixing chamber when discolored or after eight hours of running high dissolved solid samples. 2. Clean nebulizer as needed. 3. Check to ensure the gas supply is sufficient for the day's activity and the delivery pressures are set as described in the SOP.	1. Torch and mixing chamber 2. Nebulizer
Cold Vapor Mercury Analyzer	1. Clean quartz window as necessary. 2. Check to ensure the gas supply is sufficient for the day's activity and the delivery pressures are set as described in the SOP. 3. Check tubing daily and replace as necessary	1. Mercury lamp 2. Tubing

TABLE 3.1

ROUTINE PREVENTIVE MAINTENANCE PROCEDURES AND SCHEDULES
HIMCO SITE
ELKHART, INDIANA

Instrument	*Maintenance Procedures/Schedule*	*Spare Parts in Stock*
Autoanalyzer	1. Inspect pump tubes after each 8-hour run; replace if discolored or distorted. 2. Inspect colorimeter daily; replace lamp as necessary.	1. Pump tubes 2. Colorimeter lamp
Ion Chromatograph	1. Change pre-column as needed. 2. Replace injection loop monthly or as often as needed. 3. Replace column as needed. 4. Clean/replace conductivity detector as needed.	1. Syringes 2. Injection loops 3. Pre-columns 4. Detectors 5. Chromatography column
Electric Water Level Meter	1. Check battery and replace if needed (as applicable). 2. Check connection between probe and tape periodically. Repair with electrical tape if required. 3. After use, wash the probe and reel in soap and rinse thoroughly with distilled water.	1. Probes 2. Tapes 3. Cable reels 4. Batteries
pH Meter	1. Check battery and replace if needed (as applicable). 2. Clean electrode at frequency recommended in manual using appropriate cleaning solution. 3. Store electrode properly filled with appropriate filling electrolyte solution.	1. pH buffers 2. Electrolyte filling solution 3. Electrodes
Conductivity Meter	1. Check battery and replace if discharged. 2. Clean probe at frequency recommended in manual using appropriate cleaning solution.	1. Standard conductivity solutions 2. Electrodes

TABLE 3.1

ROUTINE PREVENTIVE MAINTENANCE PROCEDURES AND SCHEDULES
HIMCO SITE
ELKHART, INDIANA

Instrument	*Maintenance Procedures/Schedule*	*Spare Parts in Stock*
Turbidity Meter	1. Check battery before use and replace if discharged. 2. Clean sample cells before use and avoid scratches. 3. Check lamp before use. Replace if not functioning.	1. Standard turbidity solutions 2. Lamps 3. Batteries
ORP Probe	1. Check battery before use and replace if discharged. 2. Keep electrode properly filled with appropriate filling solution. 3. After use, rinse probe thoroughly with distilled water.	1. Batteries 2. Filling Solution
DO Probe	1. Check battery before use and replace if discharged. 2. Keep electrode properly filled with appropriate filling solution. 3. Check membrane and o-ring after each use. 4. After use, rinse probe thoroughly with distilled water.	1. Batteries 2. Filling Solution 3. Membranes 4. O-Rings
Photoionization Detector	1. Check battery, and recharge when low. 2. Clean UV lamp, ion chamber, and fan if calibration cannot be achieved, or if readings are erratic.	1. Battery charger 2. UV lamps

TABLE 3.2

CONTAINER, PRESERVATION, HOLDING TIMES, SHIPPING, AND PACKAGING REQUIREMENTS
HIMCO SITE
ELKHART, INDIANA

Analyses	*Sample Containers*[1]	*Preservation*[2]	*Maximum Holding Time from Sample Collection*[3]	*Volume of Sample*	*Shipping*	*Packaging*
Groundwater						
TCL VOCs	Three 40-mL septum top vials per analysis	Iced HCl to pH<2	14 days for analysis	Fill completely	Federal Express Priority 1	Bubble Wrap
TCL SVOCs	Two 1-L amber glass bottles	Iced	7 days for extraction 40 days after extraction for analysis	Fill to neck of bottle	Federal Express Priority 1	Bubble Wrap
TAL Metals	One 1-L polyethylene bottle	HNO3 to pH<2	6 months for analysis (mercury - 28 days)	Fill to neck of bottle	Federal Express Priority 1	Bubble Wrap
Chloride, Sulfate, Bromide	One 1-L polyethylene bottle	Iced	28 days for analysis	Fill to neck of bottle	Federal Express Priority 1	Bubble Wrap
Soil						
TCL VOCs	Three 5-g discrete samplers[4]	Iced	14 days for extraction 40 days after extraction for analysis	Fill completely	Federal Express Priority 1	Bubble Wrap
TCL SVOCs + Pyridine	One 500-mL glass jar	Iced	14 days for extraction 40 days after extraction for analysis	Fill to shoulder of jar	Federal Express Priority 1	Bubble Wrap
TAL Inorganics	One 500-mL glass jar	Iced	6 months for analysis (mercury - 28 days) (cyanide - 14 days)	Fill to shoulder of jar	Federal Express Priority 1	Bubble Wrap
Geotechnical, Agricultural Testing	Two 500-mL glass jars per category	None	None	Fill to shoulder of jar	Federal Express Priority 1	Bubble Wrap
Soil Gas						
VOCs, nitrogen, hydrogen sulfide, NMOC, and carbon monoxide	One 6-liter evacuated canister	None	30 days from collection to completion of analysis	Fill nearly complete	Federal Express Priority 1	Fiberboard Box

Notes:

[1] Where possible, analyses will be combined into the minimum number of sample containers with respect to sample preservation requirements.

[2] Samples requiring refrigeration will be shipped in coolers containing bagged, cubed ice. Following laboratory receipt and log-in, these samples will be stored by the laboratory at 0° to 6°C.

[3] Maximum holding times presented are technical holding times and are based on the time elapsed from sample collection.

[4] En Core discrete sampler or equivalent sampling method in SW-846 Method 5035.

TABLE 3.3

SUMMARY OF ANALYTICAL METHODS
HIMCO SITE
ELKHART, INDIANA

Parameter[1]	*Preparation Method*[2]	*Analysis Method*
Soil		
TCL VOCs	SOP for SW-846 5035	SOP for SW-846 8260B
TCL SVOCs	SOP for SW-846 3550B	SOP for SW-846 8270C
TAL Metals	SOP for SW-846 3050B/7471A	SOP for SW-846 6010B/7471A
Cyanide	SOP for SW-846 9013	SOP for SW-846 9012A
Grain Size Distribution	ASTM D 421	ASTM D 422/D 1140
Organic Content	ASTM D 2974	ASTM D 2974
Moisture Content	ASTM D 2216	ASTM D 2216
Bulk Dry Density	NA	Calculation
Specific Gravity	ASTM D 854	ASTM D 854
Porosity	NA	Calculation
Groundwater		
TCL VOCs	SOP for SW-846 5030A	SOP for SW-846 8260B
TCL SVOCs	SOP for SW-846 3520C	SOP for SW-846 8270C
TAL Metals	SOP for SW-846 3010A/7470A	SOP for SW-846 6010B/7470A
Chloride	SOP for EPA 300.0A	SOP for EPA 300.0A
Bromide	SOP for EPA 300.0A	SOP for EPA 300.0A
Sulfate	SOP for EPA 300.0A	SOP for EPA 300.0A
Soil Gas		
VOCs	SOP for EPA TO-15	SOP for EPA TO-15
Nitrogen	40 CFR Part 60 Method 3C	40 CFR Part 60 Method 3C
Hydrogen sulfide	40 CFR Part 60 Method 15	40 CFR Part 60 Method 15
Carbon Monoxide	40 CFR Part 60 Method 25C	40 CFR Part 60 Method 25C
NMOC	40 CFR Part 60 Method 25C	40 CFR Part 60 Method 25C
Field Measurements		
Field pH	NA	See Attachment A[3]
Field Temperature	NA	See Attachment A
Field Conductivity	NA	See Attachment A
Field ORP	NA	See Attachment A
Field DO	NA	See Attachment A
Field Turbidity	NA	See Attachment A
Field Soil Gas Screening	NA	See Attachment A

Notes:

[1] VOCs - Volatile Organic Compounds
SVOCs - Semi-volatile Organic Compounds

[2] SW-846 - "Test Methods for Evaluating Solid Wastes, Physical/Chemical Methods", EPA SW-846, 3rd Edition with Updates I through IIIB.
ASTM - "Annual Book of ASTM Standards", American Society for Testing and Materials.
SM - "Standard Methods for the Examination of Water and Wastewater", APHA, 19th Edition, 1995.
RSK - Internal Standard Operating Procedure from U.S. EPA's R.S. Kerr Laboratory.

[3] Laboratory Standard Operating Procedures (SOPs) are presented in Attachment A. SOP numbers are provided on the attachment cover page.

ATTACHMENTS

A

ATTACHMENT A

FIELD AND LABORATORY STANDARD OPERATING PROCEDURES

ATTACHMENT A

FIELD AND LABORATORY STANDARD OPERATING PROCEDURES

		Title	*SOP Number*
A.	Field SOPs		
	1.	Simultaneous Measurement of pH, Temperature, Conductivity, Oxidation-Reduction Potential, and Dissolved Oxygen (DO) in Water using Multi Probe Meter System	YSI-MPS-Flow
	2.	Turbidity	Turb-Nelph
	3.	Gas Extraction Monitor	GEM-500
B.	Laboratory SOPs		
	1.	Sample Receiving and Sample Control	NC-SC-0005
	2.	Quality Control Program	QA-003
	3.	Statistical Evaluation of Data and Development Control Charts	NC-QA-0018
	4.	Determination of Volatile Organics by GC/MS	CORP-MS-0002NC
	5.	Extraction and Cleanup of Organic Compounds from Waters and Soils	CORP-OP-0001NC
	6.	GC/MS Analysis Based	CORP-MS-0001NC
	7.	Acid Digestion for Aqueous Samples	CORP-IP-0003NC
	8.	Acid Digestion of Soils	CORP-IP-0002NC
	9.	Inductively Coupled Plasma- Atomic Emission Spectroscopy, Spectrometric Methods for Trace Elements Analyses	NC-MT-012
	10.	Inductively Coupled Plasma-Mass Spectrometry	NC-MT-0002
	11.	Preparation and Analysis of Mercury in Aqueous Samples by Cold Vapor Atomic Absorption	CORP-MT-0005NC
	12.	Preparation and Analysis of Mercury in Solid Samples by Cold Vapor Atomic Absorption Spectroscopy	NC-MT-011
	13.	Cyanide, Preparation Method	NC-WC-0032
	14.	Cyanide, Automated Pyridine- Barbituric Acid	NC-WC-0031
	15.	Ion Chromatography, Determination of Inorganic Anions	NC-WC-0084
	16.	Total Solids, Percent Moisture, Total Settleable Solids, Ash and Total Volatile Solids	NC-WC-0004
	17.	VOA Canister Analysis	KNOX-MS-0001
	18.	Sample Receipt and Log In	KNOX-SC-0003

SIMULTANEOUS MEASUREMENT OF PH, TEMPERATURE, CONDUCTIVITY, OXIDATION-REDUCTION POTENTIAL, AND DISSOLVED OXYGEN (DO) IN WATER USING MULTI PROBE METER SYSTEM

Scope and Application: This method is applicable to surface water, wastewater and groundwater.

Method: Potentiometric/Electrometric

References: "Methods for Chemical Analysis of Water and Wastes", EPA-600/4-79-020, revised March 1983, Method 150.1 (pH)

"Methods for Chemical Analysis of Water and Wastes" EPA-600/4-79-020, revised March 1983, Method 120.1 (Conductivity, Temperature)

"Standard Methods for the Examination of Water and Wastewater", APHA, 19th edition, 1995, Method 2580B. (ORP)

"Methods for Chemical Analysis of Water and Wastes", EPA-600/4-79-020, revised March 1983, Method 360.1 (DO)

Resolution: pH - 0.01 SU

Temperature - 0.01 °C

Conductivity - 0.001 mS/cm

ORP - 0.1 mV

DO - 0.01 mg/L

Barometric Pressure – 0.1 mm Hg

Optimum Range: pH 0.00 to 14.00

Temperature -5 to 45 °C

Conductivity 0 to 200 mS/cm

ORP – 999 to +999 mV

DO 0.2 to 20 mg/L

Barometric Pressure – 500 to 800 mm Hg

Sample Handling: Determined on site

Reagents and Apparatus:

YSI Model 556 Multi-Probe System (with optional barometer)

YSI Model 5563 Probe Module (includes temperature, DO, and conductivity sensors)

YSI Model 5565 pH/ORP Probe Kit

YSI Model 5083 Flow Cell

pH buffer solutions, pH 4.00, 7.00, and 10.0 (NIST traceable)

Conductivity solution, approx. 10 mS/cm (NIST traceable)

Zobell Solution (ORP calibration standard)

Distilled or deionized water in wash bottle.

General Calibration Procedure (pH, Conductivity, ORP):

1. Press "On/Off" key to display run screen. Press escape, arrow down to "Calibrate" and press "Enter". Highlight appropriate parameter to be calibrated and press "Enter".

2. Pre-rinse sensor and transport cup with small volume of calibration solution and discard.

3. Add approximately 60 mL of appropriate calibration solution (i.e., pH buffer, potassium chloride, Zobell solution) to transport cup.

4. Immerse probe module into solution and remove bubbles from sensors by rotating module. Securely screw probe module into transport cup.

5. Enter value of calibration standard into keypad and press enter.

6. Allow temperature to equilibrate for at least one minute prior to taking reading. When readings show no significant change for approximately 30 seconds, press "Enter" to obtain reading. After calibration has been accepted, screen will prompt user to press "Enter" again, which will return meter to "Calibration" screen.

7. Rinse probe module, sensors, and transport cup with distilled water and dry.

8. Repeat Steps 2 through 7 for next calibration standard (pH only).

9. When calibration for a parameter is complete, press "Escape" to return to "Calibrate" screen for next parameter.

10. Repeat Steps 2 through 9 for Conductivity, ORP, and pH. Refer to operation manual for troubleshooting tips.

Dissolved Oxygen Calibration Procedure by Water-Saturated Air Technique

1. Allow DO sensor to polarize for 20 minutes before calibrating.

2. Access "Calibrate" screen. Arrow down to Dissolved Oxygen and press "Enter".

3. Select "DO %" and press "Enter".

4. Place approximately 1/8 inch of water in the bottom of transport cup, place probe module in transport cup, and secure loosely to ensure DO sensor is vented to atmosphere. DO and temperature sensors must not be immersed in water. Press "Enter".

5. Allow 10 minutes for air in transport cup to become saturated and the temperature to equilibrate.

6. When readings show no significant change for approximately 30 seconds, press "Enter" to obtain reading. After calibration has been accepted, screen will prompt user to press "Enter" again, which will return meter to "Calibration" screen.

7. Rinse probe module, sensors, and transport cup with distilled water and dry.

Notes:

1. Temperature is factory-calibrated and field calibration is not possible.

2. Barometer is factory-calibrated, but sensor drift can occur over time. Barometer reading from an independent barometer should be used to check instrument reading at least monthly. Refer to Section 10.10 of operation manual for barometer calibration.

Procedure for Water Samples without Flow-Cell:

1. Set up and calibrate meter.

2. Select Run from main menu options.

3. Immerse probe module with probe sensor guard installed into sample or surface water. Ensure that sensors are completely immersed in sample.

4. Move probe module rapidly through sample and allow DO readings to stabilize. Store data for uploading or transcribing.

5. Remove probe sensor guard and rinse probe module with distilled water and dry.

6. Repeat steps 3 through 5 for each sample.

7. Check calibration after every 10 or fewer samples and after the last sample.

8. Store probe in transport cup when not in use. Refer to operations manual for long-term probe and sensor storage.

Procedure for Water Samples with Flow-Cell:

1. Set up and calibrate meter.

2. Install probe module in flow-cell. Connect tubing from well pump discharge to flow-cell inlet. Connect tubing from flow-cell outlet to purge water collection point.

3. Activate well pump and allow groundwater to pass through flow-cell. Ensure that sensors are completely immersed by sample. Do not exceed pumping rate of 1.5 L per minute.

4. Select Run from main menu options.

5. Store data for uploading or transcribing after each time or water volume interval.

6. Rinse probe module and flow-cell with distilled water and dry.

7. Repeat steps 2 through 6 for each monitoring well location/sample.

8. Check calibration after every 10 or fewer samples and after the last sample.

9. Store probe in transport cup when not in use. Refer to operations manual for long-term storage.

Quality Control:

1. Check calibration after every 10 or fewer samples and after the last sample. Calibration check results must be ± 10% of the true value.

   If the result is outside the control limit, rinse probe and sensors and analyze calibration check solution again. If still outside the control limit, recalibrate and flag affected data for all samples analyzed since the last in-control calibration.

2. Rinse flow-cell with distilled or deionized water after use. Clean with detergent, tap water rinse, and distilled or deionized water rinse at end of day.

Interferences:

Interferences in pH measurements occur with presence of weak organic and inorganic salts and oil and grease. Clean electrode as recommended in operations manual.

Interferences in DO measurements generally occur due to membrane coating. Clean probe as specified in the operations manual.

Interferences in ORP measurements occur when the platinum electrode surface becomes coated. Clean the ORP sensor as specified in the operations manual

TURBIDITY

Scope and Application: This method is applicable to surface water, wastewater and groundwater.

Method: Nephalometric

Reference: "Methods for Chemical Analysis of Water and Wastes:", EPA-600/4-79-020, revised March 1983, Method 180.1

Sensitivity: 0.01 Nephalometric Turbidity Unit (NTU)

Optimum Range: 0 - 20; 0 - 200 NTU

Sample Handling: Determined on site

Reagents and Apparatus:

1. Direct reading turbidity meter, HF Scientific Model DRT-15C
2. Cuvettes with screw tops
3. Battery charger
4. 0.02 NTU (nominal) reference standard
5. Distilled or deionized water in wash bottle.

Calibration Check and Operation

The turbidimeter has been calibrated by the manufacturer and electronic calibration using freshly-prepared formazin standards should be performed by the manufacturer when the electronic printed circuit board, the photodetectors, or the light source has been replaced.

The procedures for calibration checks and the operation of the meter follows:

1. For accurate measurements in the low range rotate the cuvettes in the well to obtain the minimum reading. Mark the cuvette with one of the adhesive dots provided with the instrument so that orientation of the cuvette will be identical each time it is placed in the instrument.

2. To operate the turbidimeter, switch to the "20" range and place the Reference Standard (0.02 NTU) in the optical well.

3. With the light shield in place over the well, adjust the Reference Adjust knob to cause the meter to read the reference standard value on the scale. The unit is now ready for use in either range.

4. To make a measurement of a sample, clean one of the cuvettes and fill to within approximately 1/2" of top with sample. Place the top on the cuvette and carefully clean the outside surface of the cuvette with a lint free wiper such as KimWipes. Place the sample in the well and place the light shield over the well. Select the appropriate range for best readability. Record results in field logbook.

5. Repeat steps 3 and 4 for each sample.

Quality Control:

1. Calibration check results must be ±10% of the true value. If the result is outside of ±10%, clean cuvettes and check solution again. If still outside the control limit, recalibrate the meter and reanalyze all samples analyzed since the last in-control calibration.

2. All glassware is to be detergent and water washed, tap rinsed and distilled or deionized water rinsed prior to analyses.

Interferences:

Interferences in turbidity measurements are generally due to dirty or scratched cuvettes. Handle only the top one-third of the cuvettes and wipe clean using a lint-free wiper (KimWipes or equivalent).

GAS EXTRACTION MONITOR

Scope and Application: This method is applicable to screening methane, carbon dioxide, and oxygen content in landfill gas.

Method: Infrared Gas Analyzer

Sensitivity: ±1 percent methane by volume
±1 percent carbon dioxide
±1 percent oxygen by volume

Optimum Range: 0 to 100 percent methane
0 to 100 percent carbon dioxide
0 to 25 percent oxygen

Sample Handling: Determined on site

Reagents and Apparatus:

1. Landtec Gas Extraction Monitor, GEM-500;
2. Calibration gas (commercially available standard cylinders containing methane, carbon dioxide, oxygen);
3. Calibration apparatus and tubing; and
4. Battery chargers.

Setting Up Gas Extraction Monitor:

1. Ensure the inlet filter is clean by using an Allen key to unscrew the inlet port from the instrument body. Replace inlet filter if needed.
2. Thread the inlet port back into the instrument body and tighten.
3. Check to ensure the sample hose's filter/water trap assembly is clean by disassembling the threaded plastic housing. Replace the filter if needed. Re-thread the plastic housing back together and tighten.

Field Calibration in Procedure:

1. Turn the instrument on by pressing the "Red" button. Press button [0] to exit the MAIN MENU Screen. Press button [1] to enter the GENERAL UTILITIES Screen.

2. Press button [9] for more OPTIONS. Press button [5] for GAS CALIBRATION Screen.

3. Press button [1] to enter the ZERO METHANE Screen. Ensure the instrument is in fresh air.

4. Press button [5] to turn on the GEM-500 sample pump, let purge for approximately 1 minute.

5. Press button [1] to perform the instrument ZERO calibration. If "CH_4 Not Zeroed" was displayed, ensure the instrument is in clean air and re-zero the instrument. If "CH_4 Zeroed" appeared on the display, press the [0] button twice to return to the GAS CALIBRATION Screen.

6. Press button [3] to enter the O_2 CALIBRATION Screen. Press button [2] to calibrate O_2 Span Screen.

7. Press button [5] to turn on the GEM-500 sample pump, let purge for approximately 1 minute.

8. Press button [1] and input the oxygen concentration of the atmosphere (20.8 percent) on keyboard of the GEM-500.

9. Press button [1] to confirm the calibration.

10. Press button [0] until the MAIN MENU Screen appears. The instrument is ready for field use.

Procedure:

1. Connect GEM-500 to a "T" connector of the gas probe so as to measure methane concentration. The "T" connection will be connected to the sample port. Record initial readings for the GEM-500. The valve will then be closed and the "T" connection removed from the gas probe.

2. A personal sampling pump will be added to the sampling train with its intake connected to the sample port and its discharge connected to the "T" connector (GEM-500 is still connected to the "T" connection). The personal sampling pump will be turned on and operated at a low flow rate. Readings will be collected every 30 seconds.

3. Readings will be collected until three consecutive readings are recorded that are within 10 percent of the average of the last three readings. If the aforementioned stabilization criteria cannot be attained, then readings will be recorded until such time as a maximum of five readings have been collected.

4. Configure GEM-500 so as to measure oxygen concentration and record reading in the field logbook.

5. Configure GEM-500 so as to measure carbon dioxide concentration and record reading in the field logbook.

6. Disconnect personal pump from sampling port. The sampling train will continue to operate for a period of 1 minute, drawing in ambient air, to purge the train of sample.

7. Repeat steps 1 through 6 for each sample.

Quality Control:

1. Calibration check results must be within 10 percent of the true value. If the result is outside of 10 percent, recalibrate the instrument s specified above. Record the calibration standard in the field logbook.

2. Duplicate samples are not analyzed since the headspace readings will vary considerably as volatilization in the soil occurs.

Interferences:

In the event that the GEM-500 is operating during the winter months, the instrument will be stored and maintained in an ambient temperature operating range between 10°F and 104°F.

TestAmerica

THE LEADER IN ENVIRONMENTAL TESTING

TestAmerica North Canton

SOP No. NC-SC-0005, Rev. 6.4
Effective Date: 10/02/06
Cover Page

Title: Sample Receiving and Sample Control

[Method: None]

Approvals (Signature/Date):

Technology Specialist	12/12/07 Date	Health & Safety Coordinator	12-14-07 Date
Quality Assurance Manager	12/13/07 Date	Laboratory Director	12/14/07 Date

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Revision Date: 10/02/06
Page: 1 of 26

STL STANDARD OPERATING PROCEDURE

TITLE: SAMPLE RECEIVING AND SAMPLE CONTROL

(SUPERSEDES: REVISION 6.3, 04/20/04)

Reviewed by:	Technology Specialist	12/4/06 Date
Approved by:	Quality Assurance Manager	10/4/06 Date
Approved by:	Environmental Health and Safety Coordinator	10-4-06 Date
Approved by:	Laboratory Director	12/5/06 Date

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1. SCOPE AND APPLICATION

1.1. It is the responsibility of Sample Receiving and Control personnel to perform the procedures described herein in full compliance with this SOP.

1.2. It is the responsibility of the Laboratory Director, QA Manager, and departmental Supervisor of the facility to assure that the procedures described are performed in full compliance with this SOP. It is also their responsibility to supply adequate training, materials, and equipment to enable personnel to perform this SOP correctly.

1.3. Analyst

1.3.1. It is the responsibility of the analyst to provide the correct request(s) for bottles to the sample custodian by using the QuantIMS program, PSR024.01 (as described in section 11.25) and to return all bottles to the custodian.

1.3.2. It is the responsibility of the analyst or designee to fill all bottle requests in a timely fashion and document the transfers on the request/return forms (Appendix 17.2.5).

1.3.3. It is the responsibility of the analyst or designee to correctly document the bottle information required (Appendix 17.2.5).

1.4. Sample Custodian

1.4.1. It is the responsibility of the sample custodian or designee to ensure that the returned bottle is the same as the one relinquished and to return it to the proper storage area.

1.4.2. This document accurately reflects current laboratory standard operating procedures (SOP) as of the date above. All facility SOPs are maintained and updated as necessary.

2. SUMMARY OF METHOD

2.1. Not applicable.

3. DEFINITIONS

3.1. Sample Custodian refers to sample control personnel or designee.

3.2. Refer to the glossary in the Laboratory Quality Manual (LQM), latest version

4. INTERFERENCES

4.1. Not applicable.

5. SAFETY

5.1. Procedures shall be carried out in a manner that protects the health and safety of all STL associates.

5.2. Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Cut resistant gloves must be worn when unpacking coolers, aliquoting total solids samples, purging samples, and any other task that presents a strong possibility of getting cut. If personnel are required to perform any portion of the procedure in laboratory areas, appropriate personal protective equipment and precautions must be utilized. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.3. The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure/Unusual Hazards
Hydrochloric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Nitric Acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Sodium Hydroxide	Corrosive	2 Mg/M3-Ceiling	Severe irritant. Effects from inhalation of dust or mist vary from mild irritation to serious damage of the upper respiratory tract, depending on severity of exposure. Symptoms may include sneezing, sore throat or runny nose. Contact with skin can cause irritation or severe burns and scarring with greater exposures. Causes irritation of eyes, and with greater exposures it can cause burns that may result in permanent impairment of vision, even blindness.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure/Unusual Hazards
Sulfuric Acid	Corrosive Oxidizer Dehydrator Poison Carcinogen	1 Mg/M3-TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

5.4. Exposure to chemicals must be maintained as low as reasonably achievable, therefore, unless they are known to be non-hazardous, all samples must be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation where possible. All samples with stickers that read "Caution/Use Hood!" **must** be opened in the hood. Contact the EH&S Coordinator if this is not possible. Solvent and waste containers will be kept closed unless transfers are being made.

5.5. The preparation of standards and reagents will be conducted in a fume hood with the sash closed as far as the operation will permit.

5.6. All work must be stopped in the event of a known or potential compromise to the health and safety of a STL associate. The situation must be reported immediately to the EH&S Coordinator and the Laboratory Supervisor.

5.7. This document accurately reflects current standard operating procedures (SOP) as of the date above. All facility SOPs are maintained and updated as necessary by the laboratory QA department.

6. EQUIPMENT AND SUPPLIES

6.1. Thermometers

6.2. PPE such as gloves, lab coats, safety glasses, etc.

6.3. Utility knives

6.4. pH paper

6.5. Copier, printer, computer and label generator

6.6. Carts

7. REAGENTS AND STANDARDS

7.1. Not applicable.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Not applicable.

9. QUALITY CONTROL

9.1. Nonconformance and Corrective Action

9.1.1. Any deviations from QC procedures must be documented as a nonconformance, with applicable cause and corrective action approved by the facility QA Manager.

10. CALIBRATION AND STANDARDIZATION

10.1. Not applicable.

11. PROCEDURE

11.1. Any deviations from this procedure must be documented as a nonconformance, with a cause and corrective action described.

11.2. The procedures listed in this document describe the responsibilities of Sample Control personnel in ensuring that data is transmitted correctly from the client samples to all personnel involved with sample analysis and review.

11.3. The intent of the sample custodian maintenance program is to show custody of individual bottles based on work order number as well as bottle control numbers. This program acts as an internal chain of custody.

11.4. The sample control group opens each cooler and removes the enclosed sample documents. Coolers are prioritized based on rush status and expirable tests. If a COC (chain-of-custody) is marked rush, the following occurs:

24 hour TAT – flag with red folder
48 hour TAT – flag with blue folder
72 hour TAT – flag with yellow folder
1 week TAT – flag with green folder

11.5. If tests on the COC are expirable, the cooler is marked with a manila folder.

11.6. Rush and expirable coolers are to be unpacked first and logged as soon as possible. The lab groups are to be notified with any rush 72 hours or less.

11.7. The following information is documented on the Cooler Receipt/ Narrative Form (Appendix 17.2.1).

11.7.1. Samples were received via overnight courier, client drop off, or other means.

11.7.2. Presence of the custody seals on the outside of the cooler

11.7.3. Presence of the custody papers.

11.7.4. The custody papers were properly filled out (ink, signed, match labels)

11.7.5. The custody papers were signed in the appropriate place

11.7.6. Presence of the shipper's packing slip

11.7.7. Presence of packing material information: if yes, type of packing material

11.7.8. The temperature of the cooler is taken by one of the following methods that best reflect the condition/temperature of the samples upon receipt: temp vial, coolant/sample, between bottles, IR, Ice/H_2O slurry.

11.7.8.1. If temp vial is present, the temperature of the temp vial is taken as soon as it is removed from the cooler. A temperature probe is inserted into the temp vial to obtain the temperature.

11.7.8.2. In the use of the coolant/sample methods, the temp is taken by placing the thermometer probe between the coolant and the sample(s).

11.7.8.3. In the use of between bottles method, the thermometer probe is placed between two sample bottles and the temperature recorded.

11.7.8.4. The IR gun is used on a single bottle, sometimes the temp blank, that best reflects the cooler temperature.

11.7.8.5. If the Ice/H_2O slurry method is used, the temperature is taken from the ice/slurry mixture. This method is only used if all sample bottles are in contact with the slurry.

11.7.8.6. If the temperature is outside 4°C ± 2°C, the anomaly is recorded on the cooler receipt form. The project manager is contacted when the temperature is >6°C.

11.7.9. Condition of bottles upon receipt (good condition, broken, etc.)

11.7.10. Complete bottle labels (date, time, client ID)

11.7.11. Information on bottle labels and tags agree with custody papers

11.7.12. Correct bottles used for the tests indicated

11.7.13. VOA bottles were checked for the presence of air bubbles. Any bubbles exceeding 6 mm in diameter are narrated and the PM is contacted.

11.7.14. Sufficient amount of sample sent in each bottle

11.7.15. pH's are taken, on all preserved samples less Volatiles, TOC, and TOX by removing sample lids and using a droplet of sample from in the lid to test the pH. The pH's are then recorded on the cooler receipt form. The pH paper strips are then discarded.

11.7.15.1. In determining if the sample is preserved to the correct pH for Navy samples, the sample custodian or receiving personnel must take an aliquot of sample out of the sample container either by pouring out a small aliquot or using a disposable pasteur pipette and place a drop of the sample on a pH paper strip.

11.7.16. Purchased prepared vials of preservatives are used if samples are not at the correct pH. The pH is adjusted by adding the appropriate preservative in 5 mL increments up to a maximum of 20 mL per liter of sample or unless there is a reaction. Sulfides are preserved with 5 mL Sodium hydroxide and 1 mL Zinc acetate. The pH adjustment and final pH are noted on the cooler receipt form. The Lot Number of the pre-made preservative is located on the Cooler Receipt Form. It is the responsibility of the Sample Receiving Group to change the lot number when a new shipment arrives.

11.7.17. The concentrations of the preservatives used:

4N Sodium Hydroxide
1N Zn Acetate
1:1 HCL (18%)
1:4 $HN0_3$ (18%)
1:2 H_2SO_4 (33%)

11.7.18. If the Project Manager was notified of any discrepancy/non-conformance at log-in, the information is recorded on cooler receipt form with the name of the Project Manager, date contacted, name of sample custodian who contacted the Project Manager, and how contacted.

11.8. The Sample Control person is to remove all sample containers. Any broken, leaking, or dirty sample containers are to be placed inside the fume hood. Dirty sample containers are to be cleaned appropriately, so as not to contaminate the sample storage area. The Sample Control person is to wear disposable latex gloves, safety glasses, and a lab coat while handling any samples.

11.9. Any cooler received emitting strong vapors/fumes when opened will be taken to the High Hazard Room and unpacked in either of its hoods.

11.9.1. Any problems concerning exposure while unpacking samples must be immediately reported to the Group Leader or Supervisor.

11.10. Any volatile sample(s) suspected (e.g., odor) or known (client information or site history) to be high in volatile concentration is stored in a separate designated volatile area.

11.11. The Sample Control person is to examine all documents and compare information from sample container labels and Chain-of-Custody Records to insure that there is no discrepancy between documents, ensuring that all documents are properly completed and signed.

11.12. If any problems or discrepancies are noted during the sample receiving process that compromise sample integrity, such as limited sample volume, sample identification cannot be determined from the COC, incorrect pH levels (or preservatives if known), or broken, leaking samples, the Project Manager is notified. They in turn will contact the client in an attempt to solve discrepancies.

11.13. Expirable tests (hold time 48 hours or less) must be written on the top of the bottles from which they are to be analyzed. If more than one method exists for the analysis, the method must also be written.

11.14. Any sample requiring a Total Solid result is split off for analysis. Splitting these samples is the responsibility of the receiving group. A small representative portion (approx. 5-10 grams) from each sample is put into a small plastic snap-top container designated for the TS analysis. If the TS container is not labeled with a QuantIMS label at the time of splitting off, the TS container must be labeled with handwritten client ID. Containers designed for VOC analysis must not be opened/used for TS aliquot. When only one solid container is received for VOC analysis, receiving group must **not** split off because of possible contamination or possible lost volatiles. An empty TS container with a QuantIMS label is given to the VOC analysis group for each solid. The VOC group will aliquot for the TS when they open container for analysis. TS plastic containers are placed into baggies by lot (project) and the baggies are put into a box inside the walk-in cooler door.

11.15. When samples need to be composited, the following procedure is followed, unless there are specific instructions from the client.

11.15.1. Equal aliquots are weighed from each container and mixed thoroughly and transferred to a new container.

11.15.2. The amount aliquoted is recorded on the Cooler Receipt Form.

11.16. If all samples recorded on the Chain-of-Custody Record were received by the laboratory and there are no problems observed with the sample shipment, the Sample Control person will sign the Chain-of-Custody Record in the "Received for Laboratory by:" box on the document. If problems are noted, sign for shipment and note the problems. All discrepancies are recorded on Cooler Receipt Form.

11.17. A quote must reflect what is on the chain-of-custody. Any discrepancies must be resolved by the Project Manager. Likewise, if there is not an associated quote in QuantIMs, the samples are placed on hold until a quote is completed by the Project Manager.

11.18. In the event that a project is on hold until the next day or longer, all associated paperwork is placed into a black folder and all samples and black folder are put into cold storage. Any project that is on hold must be recorded on the dry-erase board posted on walk-in cooler door.

11.19. The Sample Control person will enter each sample into the laboratory computer (QuantIMS), where a unique lot number is assigned to each project received, and sequential sample numbers are designated for each client identification within the lot.

11.19.1. Lot Numbers: The lot number is nine characters in length and is based on the date of receipt. Lot number A9J010121 is described as follows:

A - STL location where the samples were received.

(A = North Canton, B = Tampa, C = Pittsburgh, etc.)

9 - Last digit of the year (i.e. 1999).

J - Month (i.e. A = January, B = February, J = October, etc.)

01 - The next 2 numeric characters identify the day of the month, in this case, the first day of the month.

0121 - The next 4 numeric characters are the sequential assignment of numbers specific to each lot received. Each day the first lot logged in receives the number "0101", the second lot receives the number "0102", etc..

For example:

If four bottles were submitted under Client ID numbers AB100-AB103 and the laboratory identification number generated by the computer is A9K100101, then the assigned laboratory number recorded on the Sample Log-In Sheet would be as follows.

Client ID Sample Number	Assigned Laboratory Number
AB 100	A9K100101-001
AB 101	A9K100101-002
AB 102	A9K100101-003
AB 103	A9K100101-004

11.19.2. Sample Numbers: The samples in each lot are assigned a sample number that is attached to the lot number and are reset at each new lot. For example: the first and second samples in the lot above are labeled A9J010121-001 and A9J010121-002.

11.19.3. Sample Suffixes: Each sample also has a 1 character field (which is not a required field for all samples) called the suffix which identifies the sample as specified below.

Client Sample	no suffix
Method Blank	B
Laboratory Control Sample	C
Laboratory Control Sample Duplicate	L
Matrix Spike	S
Matrix Spike Duplicate	D
Sample Duplicate	X
Serial Dilution	P
Sample Confirmation	Y
Post Digestion Spike	Z
Re-analysis	I

Example: A9J010121-001X is a sample duplicate for sample A9J010121-001.

11.19.4. Work Order Numbers: Each test requested by the client for an individual sample receives an individual 8 digit work order number assigned by QuantIMS. Work order number A5WE1-2-1C is described as follows:

A5WE1 - In addition to the three digit sample identification described in 4.7.2 (i.e. - 001 and - 002), the first 5 characters of the work order number also identifies each unique sample. This identification is generated in QuantIMS using a sequential logic that is beyond the scope of this SOP to describe.

2 - The "modifier" indicates the type of run. In this case this is the second time the sample had to be run. If it needs reprepped and run again, the number would indicate a "3". The original analysis work order number assigns "1" to the modifier position.

1C - The "suffix" is the identification of the specific test for that sample. The suffix in this case is not always sequential, but is unique to the test to be performed on the sample.

Example: A5WE1-2-1C is the assigned 8 digit work order number for the reanalysis of the chloride test on the sample A5WE1. A5WE1-1-05 could be the 8 digit work order number for the analysis of SW846 8270 on sample A5WE1.

11.19.5. Each sample container with the same client ID has a unique number. Each container will be labeled with the same 5 digit work order number and then will contain a suffix beginning with –001, -002, -003, etc. For example, if 5 containers are submitted from the same sample point and the LIMS-generated work order number is CREE4, LIMS will generate 5 labels: CREE4-001, CREE4-002, CREE4-003, CREE4-004, CREE4-005. The specific bottle number is the number used for sample request/removal paperwork.

11.19.6. Labels that read "Caution-Use Hood!" shall be affixed to all containers for a given sample that are thought to be a safety hazard (for example, high in contaminants, flammable, etc.), or known to emit noxious odors (this includes all DuPont samples). The Sample Receiving group is notified of potential hazards by the Project Manager, COC, quote, or client.

11.19.6.1. Samples that are known or expected to contain high concentration of Cyanide (250 ppm or more) or Sulfide (500 ppm or more) need to be unpacked in a fume hood. The Sample Control Group must put a special sticker on these sample bottles indicating to the Lab Groups that the samples are high in either Cyanide or Sulfide so the Lab Groups can take the necessary safety precautions.

11.19.7. Expirable tests must be given to the lab groups the day they are received. The expirable test/method is written on top of the bottle and the bottle must be put in the red bin designated for expirables. The work order or sample ID must be recorded on the expirable logsheet along with the record of the test to be run, special method if necessary and the initials of the person relinquishing the sample. The Wet Chem lab group checks this bin throughout the day and is responsible for signing out the sample container when they take it.

11.19.8. Once all sample containers have been properly labeled and all the information has been recorded on the Sample Lot Summary; the Sample Control person will place the samples into the proper storage locations. These locations are as follows:

11.19.9. Organic extractable samples (Semivolatiles, Pesticides/PCBs) are to be placed into the walk-in refrigerators located in Sample Receiving.

11.19.10. Volatile samples are to be stored in the double-door refrigerator located in the Sample Custodian area.

11.19.11. Samples known or suspected to be of high concentration are not stored in these refrigerators located in Sample Receiving.

11.19.12. Inorganic samples are to be placed into the walk-in refrigerators located in Sample Receiving.

11.19.13. Preserved metal samples are placed in a non-refrigerated room located in the Sample Custodian area. Metals samples that need to be lab filtered and/or preserved are stored in the walk-in cooler. All metals for Navy projects are stored in the walk-in cooler.

11.20. One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and approved by a Technical Specialist and QA Manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file.

11.21. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

11.21.1. For clients who request a show of sample transfer from sample receipt to storage, a sample control record is printed. (see Appendix 17.2.4.). STL LIMS will generate this record for Expanded Deliverable and CLP designated samples. This record is referred to as an internal chain of custody (COC). This form can also be generated from the STL North Canton website.

11.22. The completed sample control record is attached to the summary package. The sample control record can be manually printed using the SAM S31 command in QuantIMS. Note: The report package for the lot must be "D" (Expanded Deliverable) or "C" (CLP) for the report to print.

11.23. Samples received after hours are signed for by an STL North Canton employee and placed in the walk-in cooler to be processed the following business morning.

11.24. Samples are requested by an analyst through the QuantIMS program PSR024.01. This program is accessed from the Sample Receiving Menu (SAM) by selecting option S24 (Sample Removal Requests). Bottles are requested based on method code, workorder number, prep code, QA batch number, lot number, or method group.

11.25. Each bottle has an associated lot number, sample workorder number, and bottle suffix number (Appendix 17.2.7).

11.26. When an analyst requests bottles and exits the request program, a requisition (Appendix 17.2.5) prints in the custodian's work area. This requisition identifies the requestor and the method/parameter requested. The requestor fills the requisition, recording each bottle number on the form. The bottle(s)

is/are signed out to the custody of the requestor by indicating the name and the date of transfer. The request is relinquished and accepted by the requestor's initials.

11.27. When bottles are returned, the sample custodian records the return on the original requisition form and re-enters custody of the bottles to the sample control area. The custodian initials and dates the return on the form (Appendix 17.2.5).

11.28. When sample bottles are consumed in the analysis process, the empty container is returned to the custodian. The custodian marks a "C" by the appropriate sample on the request form to indicate a consumed sample (Appendix 17.2.5).

11.29. Samples returned after the custodian has left at the end of the day are placed in the walk-in cooler by a custodian designee and recorded as received by the custodian the next working day.

11.29.1. All request forms remain in the sample custodian area while samples are being analyzed. The final form is also kept in the sample custodian area after samples have been analyzed and reported.

11.29.2. When a sample custodian is not available, a designee gets the samples, and all request paperwork is completed properly.

11.30. Subcontracting of samples

11.30.1. Samples that are logged but not analyzed at the laboratory are subcontracted to different laboratories for analysis including other STL facilities.

11.30.2. The LIMs system will automatically print a Sample Analysis Requisition for these samples upon completion of the log-in process (Appendix 17.2.6).

11.30.3. This form contains information necessary for sample analysis. The original form is sent to the subcontracted laboratory and a copy is attached to the summary package. The Sample Analysis Requisition form must have a relinquished signature with a date and time. Any additional information necessary for sample analysis must be handwritten on the form (e.g. list of compounds, homogenizing of samples, limited quantity, etc.). In order to track subcontracted samples, the lab purchase order number on the Sample Analysis Requisition form must be recorded in the subcontracted sample PO book located in the receiving log-in area. (Appendix 17.2.7).

11.30.4. A sample analysis request (SAR) can be printed from LIMS or the STL North Canton website by entering the Lot Number.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Not applicable.

13. METHOD PERFORMANCE

13.1. Training Qualifications:

13.1.1. The group/team leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience.

13.1.2. The only personnel authorized to execute this SOP are the Sample Log-In persons.

14. POLLUTION PREVENTION

14.1. This method does not contain any specific modifications that serve to minimize or prevent pollution.

15. WASTE MANAGEMENT

15.1. All waste will be disposed of in accordance with Federal, Sate, and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in Section 13 of the Corporate Safety manual for "Waste Management and Pollution Prevention".

15.2. All samples may be disposed of 30 days after the report date except for those samples associated with special client retention. Shelves are purged in chronological order. All lots on a specific shelf must be noted. If a lot can be disposed of, a disposal date must be recorded.

15.3. Disposal dates are recorded on a print-out of lots according to a storage location. When clearing samples that cannot yet be disposed of because of special client retention, samples are boxed or stored on carts. Stored samples must have a specific date listed in which samples can be disposed of, or a note that indicates "SAVE" and client name or reason.

15.4. All lots assigned to a certain shelf can be obtained from QuantIMS.

15.4.1. UTL – "Enter"

15.4.2. Type "wrk" – "Enter"

15.4.3. Type "2" by option

15.4.4. Choose one query name and "Enter"

15.4.5. SLOIS for metals shelves

15.4.6. CLOIS for cooler shelves C1 – C272

15.4.7. WLOIS for cooler shelves W1-163

15.4.8. Type "1" next to "select records"

15.4.9. Enter the shelf location 3x where prompted (appears on two different screens). Then hit "Enter".

15.4.10. Dates need to be updated every four to six months so shelf locations only print most recent lots assigned.

15.4.11. "F3" to run query and "Enter".

15.4.12. At save definition type "Y" and run option "2" and "Enter".

15.5. Solid samples that are non-regulated waste are placed in a cubic yard container for disposal.

15.6. Regulated solid waste is placed in the "MIXED WASTE" container.

15.7. Water samples designated for disposal are placed on carts and disposed of in one of the following areas: sample receiving, wet chemistry, or extractions. Acidified samples are poured into a drum and neutralized as close to a fume hood as possible in one of the following areas: sample receiving, wet chemistry, or extractions.

15.8. Solvent waste must be disposed of in clearly labeled waste cans.

15.9. Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices of STL. They must have training on the hazardous waste disposal practices upon initial assignment to these tasks, followed by an annual refresher training.

16. REFERENCES

16.1 STL Quality Management Plan (QMP), current version.

16.1.1 STL Laboratory Quality Manual (LQM), current version

16.1.2 Corporate Quality Management Plan (QMP), current version

16.1.3 STL Corporate Safety Manual, M-E-0001, and STL North Canton Facility Addendum and Contingency Plan, current version

16.2 Associated SOPs and Policies, latest version

16.2.1 QA Policy, QA-003

16.2.2 Navy/Army SOP, NC-QA-0016

17 MISCELLANEOUS

17.1 Wherever "Sample Control" is mentioned in all SOPs, it is assumed to include the sample custodian or any alternate that is designated by the Sample Control Coordinator.

17.2 Appendices

17.2.1 Appendix I – Cooler Receipt Form/Narrative

17.2.2 Appendix II - Preservative Preparation

17.2.3 Appendix III - Preservative Requirements

17.2.4 Appendix IV – Sample of Internal Chain of Custody

17.2.5 Appendix V - Sample of Custodian Removal Request

17.2.6 Appendix VI – Sample of Client Analysis Summary

17.2.7 Appendix VII - Laboratory Generated Bottle Label

Appendix I - Cooler Receipt/Narrative Form

STL Cooler Receipt Form/Narrative Lot Number:_____

North Canton Facility

Client:_____ Project:_____ Quote#:_____

Cooler Received on:_____ Opened on:_____ by: _____

(Signature)

Fedx ☐ Client Drop Off ☐ UPS ☐ Airborne ☐ FAS ☐ Other:_____

Cooler ☐ Safe ☐ Foam Box ☐ Client Cooler ☐ Other:_____

STL Cooler No#:_____

1. Were custody seals on the outside of the cooler? Yes ☐ No ☐ Intact? Yes ☐ No ☐ NA ☐

   If YES, Quantity_____

   Were the custody seals signed and dated? Yes ☐ No ☐ NA ☐

2. Shipper's packing slip attached to this form? Yes ☐ No ☐ NA ☐

3. Were custody papers included inside the cooler and relinquished? Yes ☐ No ☐

4. Did you sign the custody papers in the appropriate place? Yes ☐ No ☐

5. Packing material used:

Peanuts ☐ Bubble Wrap ☐ Vermiculite ☐ Foam ☐ None ☐ Other :_____

6. Cooler temperature upon receipt _____ °C (see back of form for multiple coolers/temp)

METHOD: Temp Vial ☐ Coolant & Sample ☐ Against Bottles ☐ IR ☐ ICE/H_20 Slurry ☐

COOLANT: Wet Ice ☐ Blue Ice ☐ Dry Ice ☐ Water ☐ None ☐

7. Did all bottles arrive in good condition (Unbroken)? Yes ☐ No ☐

8. Did all bottle labels and tags agree with the custody papers? Yes ☐ No ☐

9. Were samples at the correct pH? (record on back) Yes ☐ No ☐ NA ☐

10. Were correct bottles used for the tests indicated? Yes ☐ No ☐

11. Were air bubbles >6 mm in any VOA vials? Yes ☐ No ☐ NA ☐

12. Was a sufficient amount of sample sent in each bottle? Yes ☐ No ☐

Contacted PM _____ Date:_____ by:_____ via Voice Mail ☐ Verbal ☐ Other ☐

Concerning:_____

√	MACRO	MACRO
	1. CHAIN OF CUSTODY	
	SR1A	The chain of custody and sample bottles did not agree. The following discrepancies occurred_____
	2. SAMPLE CONDITION	
	SR2A	Sample(s)_____ were received or requested after the recommended holding time had expired.
	SR2B	Sample(s) _____ were received with insufficient volume.
	SR2C	Sample(s) _____ were received in a broken container.
	3. SAMPLE PRESERVATION	
	SR3A	Sample(s) _____ were further preserved in sample receiving to meet recommended pH level(s). *Nitric Acid Lot #120503-HNO3; Sulfuric Acid Lot # 101503-H2SO4; Sodium Hydroxide Lot # 111401-NaOH; Hydrochloric Acid Lot # 100902-HCl; Sodium Hydroxide and Zinc Acetate Lot # 112801-CH3COO2ZN/NaOH*
	SR3B	Sample(s)_____ were received with bubble > 6 mm in diameter (cc: PM)
	4. Other (see below or back)	

Appendix II - Preservative Preparation

Preservative Preparation

(If purchased preservative solution vials are not used)

1:1 Hydrochloric Acid (18%):	Slowly add 1000 mL concentrated HCl to 1000 mL reagent water and mix. Store in a well-labeled plastic coated acid bottle.
1:2 Sulfuric Acid (33%):	In a 2000 mL beaker, SLOWLY and CAREFULLY add 500 mL concentrated H_2SO_4 to 1000 mL reagent water and mix. A cool water bath may be needed to cool the solution and beaker. Store in a well labeled plastic acid bottle.
NOTE:	*All preparations must be performed in a hood and proper personal protective equipment must be worn. All reagents and final preservative solution must be documented in applicable reagent logbooks.*

Appendix III - Preservative Requirements

PRESERVATIVES, CONTAINERS, AND VOLUMES

Parameter	Container	Preservative[1,2]	Volume	Parameter	Container	Preservative [1,2]	Volume
Asbestos	P	None	250 mL	Radiological Alpha, Beta, Radium	P	HNO_3	4 L
Acidity	P	None	250 mL	Hardness	P	HNO_3	250 mL
Alkalinity (Sep)	P	None	250 mL	Metals	P	HNO_3	1 L
BOD	P	None	250 mL	Dissolved Metals*	P	HNO_3	1 L
Carbonaceous BOD	P	None	250 mL	Total Organic Carbon (TOC)	G	HCl	2 x40 mL
Bromide (Br)	P	None	250 mL	Chemical Oxygen Demand	P	H_2SO_4	250 mL
Chloride (Cl)	P	None	250 mL	Total Organic Halogens	G	H_2SO_4	250 mL
Chromium, $^{6+}$	P	None	250 mL	COD	P	H_2SO_4	250 mL
R. Chlorine	P	None	100 mL	Ammonia Nitrogen (NH_3)	P	H_2SO_4	500 mL
Color	P	None	50 mL	TKN	P	H_2SO_4	1L
Conductivity	P	None	250 mL	Nitrate/Nitrite	P	H_2SO_4	250 mL
Corrosivity	P	None	250 mL	Oil & Grease	G	H_2SO_4	1 L
Dissolved Oxygen	G	None	300 mL	Phenols	G	H_2SO_4	1 L
Fecal Coliform	P	None	125 mL	Total Phosphorus	P	H_2SO_4	250 mL
Flashpoint	G	None	100 mL	TON	P	H_2SO_4	1 L
Fluoride	P	None	250 mL				
Nitrate	P	None	250 mL	TRPH - IR 418.1	G	HCl	2 L
Nitrite	P	None	250 mL	VOC 601	G	HCl	3x40 mL
pH	P	None	50 mL	VOC 8010	G	HCl	3x40 mL
Elemental PO_4	G	None	250 mL	VOC 624	G	HCl	8x40 mL
Orthophosphate	P	None	250 mL	BTEX 8020	G	HCl	3x40 mL

PRESERVATIVES, CONTAINERS, AND VOLUMES

Parameter	Container	Preservative[1,2]	Volume	Parameter	Container	Preservative [1,2]	Volume
TDS	P	None	250 mL	VOC 8240	G	HCl	3x40 mL
TSS	P	None	250 mL	THM/502.2	G	HCl	2x40 mL
Total Solids	P	None	250 mL	502.2	G	HCl & Asc. Acid	2x40 mL
TVS	P	None	250 mL	VOC 624	G	HCl	3x40 mL
T. Coliform	P	None	125 mL	VOC 602	G	HCl	3x40 mL
Settleable Solids	P	None	1L	465 C & D	G	HCl	4x40 mL
Silica	P	None	250 mL	BTEX 8021	G	HCl	3x40 mL
Sulfate	P	None	250 mL	VOC	G	HCl	3x40 mL
Sulfite	P	None	250 mL	VOC 8260	G	HCl	3x40 mL
Surfactants (MBAS)	P	None	250 mL	VOC and VOA	G	HCl	3x40 mL
Turbidity	P	None	250 mL	VOC 8010/8020	G	HCl	3x40 mL
TPH-GC	G	None	2 L				
				Total Cyanide	P	NaOH[3]	250 mL
BNAs	G	None	2 L	Amenable Cyanide	P	NaOH	250 mL
BNA + Dioxin	G	None	2 L	Free Cyanide	P	NaOH	250 mL
PNA/PAH	G	None	2 L	Sulfide	P	Zn Acetate & NaOH	1 L
Pesticides	G	None	2 L	Formaldehyde	G	None	500 mL
Reactive Cyanide	P	None	1 L	Carbonate	P	None	250 mL
Reactive Sulfide	P	None	1 L	Bicarbonate	P	None	250 mL
PCB	G	None	2 L	TPH - Diesel (Ext.)	G	None	2 L
Pesticides + PCBs	G	None	2 L	TPH - Gasoline (P&T)	G	HCl	2x40 mL
Herbicides	G	None	2 L	Glycols 8015	G	None	2x40 mL
OPPs	G	None	2 L	BTEX & MTBE	G	HCl	3x40 mL

PRESERVATIVES, CONTAINERS, AND VOLUMES

Parameter	Container	Preservative[1,2]	Volume	Parameter	Container	Preservative [1,2]	Volume
				601/602	G	HCl	3x40 mL

* Filtered in field

[1] HCl, HNO_3, and H_2SO_4 to pH < 2. NaOH to pH > 12

[2] Temperature = 4°C ± 2°C except for aqueous metals

[3] Samples to be analyzed for Cyanide should be field-filtered for Residual Chlorine. If Residual Chlorine is detected, ascorbic acid (0.6 g) should be added.

Appendix IV – Sample Internal Chain of Custody

	Lot: A4B180167 Quote: 49535						
	Project Number: 4500068724						
	PO Number:						
	Site: WOOSTER NWF/NPDES OUTFALL						
	Contact: Rich Kuhn Received: 02/18/04 12:10						
	Analytical Due Date: 02/25/04						
	Report Due Date: 03/03/04						
0	Client Sample ID	Date	Time	WATER	MS 8260 LL	PH LIQ	A4B180167
1	217	2/17/04	10:00	WG	X	X	REPORT QC. NPDES. 1 WEEK TAT.

Appendix V - Sample Custodian Removal Request Form (LIMS Generated)

PSR024 2/18/04 16:08:32 MT SAMPLE CUSTODIAN REMOVAL REQUEST PAGE 001

REQUESTED BY: GIRARDS2

METHOD: C8 Fluoride (300.0, Ion Chromatography)

STORAGE LOCATION	WORK ORDER #	PICKED CNTR#	MATRIX CONTROL #	CLIENT #	ANALYSIS	LOTID	SMP#	SFX	MATRIX DESCRIPTION	QTY RCVD	QTY REQD
None	F8KPP-1-AL	___ ___ ___	931601	001628	I-88-C8	A4A020103	003		WATER	1	1
None	F8KPQ-1-AL	___ ___ ___	931602	001628	I-88-C8	A4A020103	004		WATER	1	1
None	F8KPT-1-AL	___ ___ ___	931603	001628	I-88-C8	A4A020103	005		WATER	1	1
None	F8KPV-1-AL	___ ___ ___	931604	001628	I-88-C8	A4A020103	006		WATER	1	1

13. RELINQUISHED BY DATE/TIME **RECEIVED BY**

_____ _____ _____

_____ _____ _____

_____ _____ _____

_____ _____ _____

_____ _____ _____

_____ _____ _____

_____ _____ _____

_____ _____ _____

***** END OF REPORT *****

Appendix VI - Sample Analysis Requisition

Severn Trent Laboratories, Inc.
Laboratory SAMPLE ANALYSIS Report
Report
REQUISTION

Package:

STL Valparaiso

2400 CUMBERLAND DRIVE
Valparaiso, IN 46383

STL Valparaiso Lab RequestSR056490Need Analytical Report
2004-02-24

Project Manager:
Sample I.D.
Analysis Required

Client Code:

Work Order Number	Client Sample ID	Sampling Date
A4B100272-1	F9DED	MW-65A	2004-02-04
A4B100272-2	F9DEK	MW-66A	2004-02-05

Appendix VII - Laboratory Generated Bottle Label

F9P8N-001 3543
A4B180106-001 2/18/04
2XL/1X500ML 7:30
P1-02/18/04-GRAB
SW46

SF9P8N-002 3543
A4B180106-001 2/18/04
2XL/1X500ML 7:30
P1-02/18/04-GRAB
SW46

F9P8N-003 3543
A4B180106-001 2/18/04
2XL/1X500ML 7:30
P1-02/18/04-GRAB
SW46

Controlled Copy No. ____

Implementation Date: 9-24-07

Policy No.: QA-003
Revision No.: 6
Revision Date: 09/19/07
Page 1 of 20

APPROVAL:

Dorothy J. Leeson, Quality Assurance Manager

Opal Davis-Johnson, Laboratory Director

TESTAMERICA NORTH CANTON POLICY
Quality Control Program

Supersedes: Revision 5, Revision Date 09/27/04

OBJECTIVE:

This policy describes the TestAmerica North Canton program of routine analytical quality control (QC) activities. The objective is to generate QC data that demonstrate that the analytical process is in control and that the data meet client and method requirements. The policy outlines QC requirements for a variety of regulatory programs, with the stipulation that when lacking specific direction from our clients, TestAmerica North Canton will default to routine RCRA program QC requirements.

SCOPE:

This policy is to be enforced and followed throughout the laboratory.

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POLICY:

1. Assessments of QC data relative to control limits determine the acceptability of sample test results. Whenever control criteria are not met, the data must be evaluated to determine appropriate corrective action. The initial evaluation is made by the analyst, frequently in conjunction with data review software and/or senior analysts or supervisors. Further technical evaluation of the data or data review software output is conducted by second-party data reviewers. Corrective action decisions, particularly whether or not to reanalyze samples, should be done in consultation with the client to the extent possible when operating under project-specific QA plans. Requirements for assessment and corrective action are described in the attachments to this policy. Details concerning technical data review and documentation of the reviews are described in the Laboratory Quality manual (LQM).

2. The TestAmerica North Canton standard QC program is to be communicated to the client prior to acceptance of work. At the same time, every effort must be made to understand the client's special project requirements. Generally, laboratory project managers serve as a liaison between the clients and the laboratory staff to ensure that requirements are properly communicated in writing to both parties. In the event that alternative QC procedures are not specified by our clients, these standard QC protocols must be followed to ensure the generation of legally and scientifically defensible analytical data.

3. Successful implementation of this QC program requires that it is clearly understood by all TestAmerica staff. Training based on this policy will be conducted periodically and provided to new personnel as appropriate for their functions.

4. TestAmerica North Canton QC program applies to the following:

   RCRA and SW-846 Projects

   All routine analytical projects performed using SW-846 methods must comply with the requirements described in the TestAmerica North Canton Laboratory Quality Manual (LQM) and Attachment I to this policy. The Quality Control sections of analytical standard operating procedures (SOPs) referencing SW-846 methods must be consistent with the requirements in Attachment I.

   CWA and 40 CFR Part 136 Projects

   Any analytical work conducted in support of an NPDES permit or other Clean Water Act compliance activities, must meet the quality control specifications shown in the LQM. The quality control requirements for the specific methods listed in the LQM define the minimum requirements that must be given in laboratory analytical SOPs.

   Other Programs or Projects with Clearly Defined QC Requirements

   The differences between the TestAmerica North Canton standard QC program and special project requirements must be specified in project documents. These documents may include Quality Assurance Project Plans (QAPjPs), Quality Assurance Program Plans

(QAPPs), Sampling and Analysis Plans (SAPs), project-specific Quality Assurance Summaries (QASs), SOPs, contracts, or other approved documents.

Documents describing special project requirements must be reviewed and approved by appropriate QA and operations staff.

If the special project requirements appear to result in modifications that contradict federal or state regulatory requirements, the variance must be noted in writing and communicated to the client. A record of this communication must be retained as a permanent part of the project file.

Any special client project requirements must be communicated to TestAmerica North Canton's analysts in advance of releasing samples for analysis, and the work must be clearly differentiated in the analytical documentation, otherwise Attachment I requirements will be followed.

Projects Without Specific QC Requirements

Any projects for which no specific QC program is specified must follow the requirements shown in Attachment I.

5. Analytical SOPs must include a quality control section that addresses these general QC requirements. As relevant, specific method QC requirements should be given precedence to these general requirements.

ATTACHMENT I

QC for RCRA PROJECTS AND PROJECTS WITHOUT DEFINED QC REQUIREMENTS

1.0 Introduction

This Quality Control (QC) Program is based on the requirements in "Test Methods for Evaluating Solid Waste", USEPA SW-846, Third Edition with promulgated updates. It applies whenever SW-846 analytical methods are used. It also applies in whole or in part whenever project requirements fail to specify some aspect of QC practices described here. It does not apply when other well defined QC programs (e.g., DoD QSM) are specified. This policy represents TestAmerica North Canton base QC program for environmental analyses.

Details concerning instrument calibrations, tunes, and QC that are required for specific methods (e.g., interference check samples for ICP) are not given here. Refer to the method standard operating procedures (SOPs) for information about the frequency, assessment and corrective action required for additional QC elements.

2.0 Definitions

2.1 Batch Definition – a batch is a group of no greater than 20 samples, excluding QC samples (LCS, Method Blank, MS, MSD) which are processed similarly with respect to the procedure. All sample setups must be initiated within a 24-hour period from the initial preparation or extraction and without interruption of the process. All samples within the batch must be treated with the same lots of reagents, the same processes, and the same personnel.

2.2 Surrogates - Surrogates are organic compounds similar in chemical behavior to the target analytes, but that are not normally found in environmental samples. Surrogates are added to all samples in a batch to monitor the effects of both the matrix and the analytical process on accuracy.

2.3 Method Blank - The method blank (MB) is a control sample prepared using the same reagents used for the samples. As part of a QC batch, it accompanies the samples through all steps of the analytical procedure. The method blank is used to monitor the level of contamination introduced to a batch of samples as a result of laboratory processing.

2.4 Instrument/Calibration Blank - The instrument blank is prepared using the same solvents and reagents (e.g. hexane, methylene chloride, or reagent water) used to dilute the prepared sample extracts or digests. Unlike the method blank, it is analyzed without being subject to the

preparation steps of the analytical procedure. It is used to monitor laboratory or reagent contamination introduced at the instrumental analysis phase of work. For procedures without a separate preparation step, an instrument blank is equivalent to the method blank, and serves the same purpose.

2.5 Laboratory Control Sample - A laboratory control sample (LCS) is prepared using a well characterized matrix (e.g. reagent water or Ottawa sand) that is spiked, with known amounts of representative analytes. Alternate matrices (e.g. glass beads) may be used for soil analyses when Ottawa sand is not appropriate. As part of a QC batch, it accompanies the samples through all steps of the analytical process. The LCS is used to monitor the accuracy of the analytical process independent of possible interference effects due to sample matrix. Information regarding precision of the method can be determined over time.

2.6 Matrix Spike and Matrix Spike Duplicate

2.6.1 Matrix Spike - A matrix spike (MS) is a replicate portion of one field sample in the QC batch that is spiked with known amounts of target analytes. An MS is spiked with the same analytes at the same concentrations that are added to the LCS. Any client sample that is not a field blank can be used for a matrix spike as long as there is sufficient quantity. As part of the QC batch, it accompanies the field samples through all steps of the analytical process. Matrix spike data are only meaningful for the sample in which they are prepared and samples from the same site.

2.6.2 Matrix Spike Duplicate - A matrix spike duplicate (MSD) consists of an additional portion of the same sample used to prepare the MS. This portion is spiked and processed exactly as the MS.

2.6.3 The MS and MSD results are used to determine the effect of the sample matrix on the precision and accuracy of results. Due to the potential variability of the matrix of each sample, the MS and MSD results may not have immediate bearing on any samples except the one spiked.

2.7 Sample Duplicate - A sample duplicate is a second aliquot of an environmental sample, taken from the same sample container when possible, that is processed with the first aliquot of that sample. That is, sample duplicates are processed as independent samples within the same QC batch. Any client sample that is not a field blank can be used for a sample duplicate as long as there is sufficient quantity. The sample and duplicate results are compared to determine the effect of the sample matrix on the precision of the analytical process. As with the MS/MSD results, the sample duplicate precision results are not necessarily representative of the precision for other samples in the batch.

2.8 Duplicate Control Sample - A duplicate laboratory control sample (LCSD or DCS) may be prepared at the request of the client. It is required for some projects particularly when insufficient sample volume is received to prepare and analyze an MS/MSD pair. LCS/LCSD pairs provide additional information regarding the precision of the measurement process.

3.0 Batch QC Elements & Batch Processing

3.1 A QC batch is designed to determine the quality of the analytical results obtained for a group of up to 20 field samples in terms of accuracy and precision. With some exceptions as described in Sections 3.6 through 3.8 below, the minimum QC elements for each QC batch are

- one method blank (MB),
- one laboratory control sample (LCS),
- one matrix spike (MS), and
- one matrix spike duplicate (MSD).

3.2 The identity of each QC batch must be documented and traceable, i.e., each batch of field samples must be clearly associated with the applicable QC samples.

3.3 To the extent possible, samples that require a preparation step should be analyzed together with their associated QC samples. If the samples in a given QC batch require separate analytical runs, the minimum batch QC in each run is an acceptable MB or instrument/calibration blank.

3.4 For analytical procedures that do not include a separate extraction or digestion (e.g., volatile organic analysis by purge and trap), the QC batch must be analyzed sequentially using the same instrument and instrument configuration within the same calibration event. That is, the same calibration curve, calibration factors, or response factors must be in effect throughout the analysis.

3.5 Field QC samples (e.g., trip blanks, equipment rinsates, and field duplicates) count as individual samples, therefore, they add to the QC batch count. Samples that require simple reanalysis (e.g., dilutions to adjust a sample extract to the working range of the instrument), as opposed to reextraction or digestion and reanalysis, do not count as additional samples in the QC batch. For procedures without a separate preparation, a reanalysis within the same calibration event (as defined in Section 3.4) does not add to the batch count.

3.6 MS/MSD pairs are not the only acceptable means of demonstrating precision.

3.6.1 As requested by clients or required by some methods, batch precision may also be demonstrated through the analysis of sample duplicates. However, the client should be

advised that a duplicate is less likely to provide usable precision statistics depending on the likelihood of finding concentrations below reporting limits.

3.6.2 A duplicate LCS (LCSD or DCS) may be used to demonstrate method batch precision independent of client's matrix. LCSDs are prepared at the client's request, and are often used when the client has not supplied sufficient sample quantity to prepare an MS, MSD or duplicate.

3.6.3 On-going monitoring of LCS results can be used to determine long-term precision and accuracy for a method.

3.7 Some methods including isotope-dilution methods, pH and ignitability for example, do not use all of the QC elements listed in Section 3.1. Method exceptions to these requirements are listed in the TestAmerica North Canton LQM QC tables and in the laboratory analytical SOPs.

3.8 Deviations from these QC elements must either be noted in project planning documents (QAPPs, QAPjPs, SAPs, SOWs, QAS, or equivalent) or in a nonconformance memo (see SOP CORP-QA-0010 for details).

4.0 Data Evaluation and Corrective Action

4.1 General Guidelines

4.1.1 Any QC component that is outside of established control limits is considered an out-of-control event. All out-of-control events must be documented and the associated data evaluated. Depending on the specific circumstances, evaluation can lead to a variety of actions. The following sections and the flowcharts describe the appropriate corrective action for the most common QC failures. However, it is not possible to address all possible data evaluation scenarios in this policy. The guiding principle for all evaluations is that the data and corrective action decisions must be defensible using TestAmerica North Canton policies, procedures or scientific evidence, and justified in the project records.

4.1.2 If reanalysis for QC failures is conducted and the second analysis confirms a QC problem that is outside of the laboratory's control, further testing is not necessary. The problem must be documented and the data properly qualified in the project report.

4.1.3 QC failures that are not corrected by reanalysis are documented in the TestAmerica North Canton electronic Nonconformance System (Clouseau) as described in SOP CORP-QA-0010.

4.1.4 QC failures due to sample matrix interferences (particularly MS, MSD and sample surrogate failures) do not have to be documented in the Clouseau system unless there is a holding time violation. Other forms (e.g., Organic Data Review Checklist) may be used to document matrix QC failures. In either case, matrix QC failures must be communicated to the laboratory project manager and significant matrix QC failures must be discussed in the final report case narrative.

4.1.4 When ongoing, systematic problems are identified, work must stop until it can be demonstrated that the system is in control again.

4.2 Method Blank (MB) Evaluation (see Figure 1)

4.2.1 Method Blank Acceptance Criteria

The results of the method blank shall be one of the QC measures used to assess batch acceptance. Results are acceptable if all analyte concentrations in the MB meet the following criteria:

- Organics -The blank contamination is less than 1/10 of the measured concentration of any sample in the associated preparation batch , or
- Inorganics – The blank contamination is less than 1/20 of the measured concentration of any sample in the associated preparation batch, or
- The blank contamination is less than the concentration present in the samples and is less than 1/10 of the regulatory limit, or
- The same contaminants were not found in the associated samples, or
- MB results are less than or equal to the reporting limit.

Note: Positive method blank results slightly below the reporting limit should still be evaluated by the analyst for potential impact on sample results at or near the reporting limit.

Note: DoD project requirements are noted in NC-QA-0016, Supplemental Practices for DoD Project Work.

Note: For Ohio VAP projects, the method blank contamination must be below the reporting limit.

4.2.2 Corrective Action for Method Blank Failure

- If the method blank does not meet the acceptance criteria, the source of contamination must be investigated and measures taken to correct, minimize or eliminate the problem. Samples associated with the contaminated blank shall be reprocessed for analysis or, under the following circumstances, may be reported as qualified (qualifier flags or narrative comments):

- MB contamination at a level less than the reporting limit with sample results at levels near the RL, based on analyst's judgement shall be flagged, if flags are requested by client.
- Analyte concentrations in samples are greater than 10 times blank contamination for Organics and 20 times the blank contamination for Inorganics, or
- The contaminant is a common blank contaminant (see below) and the MB concentration is less than 5 times the RL for organics or less than two times the RL for inorganics. Note that some programs do not recognize common lab contaminants.

Common Laboratory Contaminants:

Analyte	Method
Methylene Chloride	Volatile Organics (GC or GC/MS)
Acetone	Volatile Organics (GC or GC/MS)
2-Butanone	Volatile Organics (GC or GC/MS)
Phthalate Esters	Semi-Volatile Organics (GC or GC/MS)
Copper	Metals (ICP or ICPMS)
Zinc	Metals (ICP or ICPMS)
Iron	Metals (ICP or ICPMS)
Lead	Metals (Trace ICP or ICPMS)
Barium	Metals (ICPMS)
Chromium	Metals (ICPMS)
Manganese	Metals (ICPMS)
Calcium	Metals (ICPMS)
Magnesium	Metals (ICPMS)
Potassium	Metals (ICPMS)
Sodium	Metals (ICPMS)

4.3 Laboratory Control Samples (LCS) Evaluation (see Figure 2)

4.3.1 Acceptance Criteria

The LCS recovery for the control analytes must be within established control limits. The percent recovery is calculated as follows:

$$\text{LCS Percent Recovery} = \frac{X}{t} \times 100$$

Where: X = observed concentration
t = concentration of spike added

4.3.2 Corrective Action for LCS Failure

- check calculations,
- check instrument performance,
- reanalyze the LCS, and if still outside of control limits,
- reprepare and reanalyze all samples in the QC batch.

Notes: 1. It is acceptable to report the data if the LCS recovery is out high and analyte of concern was not detected in any of the samples.

2. In the case of volatile analyses, if the LCS fails, a new LCS may be reprepared and reanalyzed within the same tune period.

3. In the case where all target requested analytes are within control, but some other LCS compounds are out of control, the LCS may still be considered acceptable for reporting.

4.4 Duplicate Laboratory Control Samples (LCS/LCSD or DCS) Evaluation (see Fig. 2)

4.4.1 Acceptance Criteria

The recovery for each spike of the pair must be within established control limits. The formula used to calculate LCSD recoveries is the same as the formula for LCS spike recoveries. If a batch includes samples requiring LCS control and samples requiring both LCSs and LCSDs, the LCS used will be the first LCS that passes control criteria.

The relative percent difference (RPD) for the pair is calculated as follows:

$$\text{RPD} = \left[\frac{|X_1 - X_2|}{\frac{(X_1 + X_2)}{2}} \right] \times 100$$

Where: X_1 = first observed concentration
X_2 = second observed concentration

4.4.2 Corrective Action for LCS/LCSD Recovery (Accuracy) Failure

- check calculations,
- check instrument performance,
- reanalyze and/or reprepare and reanalyze all samples in the QC batch.

Note: If either LCS/LCSD spikes fails and the batch cannot be reanalyzed, the failure must be documented and noted in the final report. Also see notes under Section 4.3.2.

4.4.3 Corrective Action for LCSD Precision Failure

- Check calculations
- Check instrument performance
- If the RPD is out of control, but both accuracy recoveries are within acceptance criteria, prepare an NCM and qualify report.

Note: Because LCS/LCSD limits are based on the standard deviation of data collected over time and include long-term precision, it would be unusual to fail precision limits while meeting accuracy limits. If this occurs with any frequency, control limits should be reevaluated.

4.5 Surrogate Evaluation (see Figure 3)

4.5.1 Acceptance Criteria

Surrogate recoveries must be within established control limits. Method QC (MB, LCS, and/or LCSD) results are not acceptable unless the surrogate recoveries for those QC samples are within control limits. If MS/MSD, duplicate or field samples require dilutions beyond the threshold stated in the analytical SOPs, routine surrogate control limits do not apply and recoveries are not evaluated. This should be noted in the final report. The recovery is calculated as follows:

$$\text{Surrogate Percent Recovery} = \frac{X}{t} \times 100$$

Where: X = observed concentration
t = concentration of surrogate added

4.5.2 Corrective Action

4.5.2.1 Surrogate Failures in MB, LCS, or LCSD

- check calculation and instrument performance,
- reanalyze QC sample and/or reanalyze all samples in the QC batch.

Note: For Ohio VAP projects, the batch must be re-extracted if reanalysis does not resolve the problem.

4.5.2.2 Surrogate Failures in Samples or MS/MSD

- check calculation and instrument performance
- evaluate objective evidence of matrix interference (e.g. heterogeneous sample, interfering compounds seen on chromatograms, or interference demonstrated by prior analyses)
- document the failure and note it on the final report

Note: Unless otherwise specified by the client, it may be possible to report qualified results if method QC surrogate recoveries are biased high and analytes were not detected in the field samples. However, all other QC requirements would have to be met and the failure would have to be noted in the final report.

Note: Some client programs require reanalysis to confirm matrix interferences. Chec. special project instructions for this corrective action.

4.6 Matrix Spike and Matrix Spike Duplicates (MS/MSD) Evaluation (see Figure 4)

4.6.1 Acceptance Criteria

MS and MSD recoveries and RPD should be within established control limits. If MS or MSD samples require dilutions beyond the threshold stated in the analytical SOPs, routine control limits do not apply and recoveries are not evaluated, but this should be noted in the final report. The MS and MSD recoveries are calculated as follows:

$$\text{MS or MSD Percent Recovery} = \left[\frac{X_s - X}{t}\right] \times 100$$

Where: X = observed concentration in unspiked sample
X_s = observed concentration in spiked sample
t = concentration of spike added

Note: 1. If sample result is ND, $X = 0$ when no values reported below RL.
If sample result is reported as a value <RL, X = reported value.

2. CLP forms software uses observed recovery, not concentrations.

RPD is defined in Section 4.4.1.

4.6.2 Corrective Action for MS/MSD or MS/MSD RPD Failure (assuming that the LCS is in control)

- check calculation and instrument performance,
- consider objective evidence of matrix interference (e.g. heterogeneous sample, interfering compounds seen on chromatograms, or interference demonstrated by prior analyses);
- document the failure and note on final report;

Note: Some client programs require reanalysis to confirm matrix interferences. Check special project requirements for this corrective action.

4.7 Sample Duplicate

4.7.1 Acceptance Criteria
The RPD for the sample and its duplicate must be within established control limits. The RPD is the same as for the MS/MSD (see Section 4.6.1).

4.7.2 Corrective Action for Duplicate Failure

- check calculation and instrument performance,
- document the QC failure and note on the final report.

5.0 Establishing QC Acceptance Limits

5.1 Initial Control Limits
For new procedures, published method limits can be used until sufficient QC data are acquired (minimum of 20 to 30 data points recommended). However, the published limits may not be appropriate if they are based on a single-operator or single-laboratory study. In this case, the QA Manager may establish default limits until enough data is collected for laboratory established limits to be determined.

5.2 Control limits should be reexamined annually, and reset as needed. If the recalculated limits are consistent with the historical limits, the historical limits may remain unchanged.

5.2 Running the Control Limits Program

Evaluating control charts is an important first step in considering new control limits. This is done with the TraQAr Control Limits program. Only QA personnel who are familiar with the organization of TestAmerica North Canton spike lists are authorized to set control limits. The program collects a specified set of QC data, performs a Grubbs Outlier Test, calculates three standard deviation control limits, compares those limits to the existing limits in the laboratory LIMS, and generates an I-type control chart (ref. ASTM D 6299). This control chart is a plot of results in chronological order to which existing control limits and a centerline have been added. The control chart aids in the examination of the data to be sure that it is representative and appropriate for use in setting new limits. Refer to SOP NC-QA-0018, Statistical Evaluation of Data & Development of Control Charts for complete details, but some specific requirements include the following:

5.2.1 Select QC Type Options:

LCS/DCS - normally used to establish both LCS and MS/MSD control limits.

LCS/DCS Surrogates - normally used to establish surrogate control limits for both LCS and MS/MSD controls. It is rarely used.

MS/MSD - used to set matrix specific control limits, but use of such limits at TestAmerica Denver is generally restricted to materials from a particular site, and currently there is only one example for one client active in the system; this is used rarely.

MS/MSD Surrgates – as above, rarely used

All Surrogates – this option will produce a pooled set of LCS/LCSD, MB, MS/MSD, and sample surrogate results. It is the standard choice for creating surrogate control limits.

5.2.2 Grubbs Outlier Test

The Control Limits program automatically runs the test using a 5% level of significance, i.e., risk of falsely rejecting a data point. The test calculates a value for T based on the difference of the suspect point from the mean value, quantity divided by the calculated standard deviation.

$$T = \frac{|X_i - \overline{X}|}{s}$$ where, X_i is the point being considered for rejection

X bar is the mean, and
s is the standard deviation

The point is rejected if:

$$T > \frac{(N-1)}{\sqrt{N}} \sqrt{\frac{t^2_{(\alpha/2N),N-2)}}{N-2+t^2_{(\alpha/2N),N-2)}}}, \qquad \text{where N = number of points}$$

t = t distribution

Tables for critical values of T are given in John Taylor, Quality Assurance of Chemical Measurements, Lewis Publishers; 1987. If the measured value of T is greater than the value in the critical value, X_i is rejected. This assumes a normal distribution. (see www.itl.nist.gov/div898/handbook/eda for details about the derivation of the critical values of T).

5.3 Examine and Investigate Collected Data

Assuming that an adequate amount of data are collected, the next step involves determining that the data set is representative of the lab's performance, and therefore provides a useful prediction of future performance. A key part of the process is examining the data for bias, discontinuities, and/or trends. Ideally, if conditions are constant over the time period selected and existing limits are appropriate, the data will be evenly distributed around the centerline, with a few points at or slightly outside control limits. The reasons for deviations from the ideal should be investigated to be sure that the collected data are appropriate. Specific conditions requiring further investigation include data sets with no outliers, data with significant bias relative to existing limits, excessive number of outliers, discontinuous patterns, and upward or downward sloping trends.

5.4 Selecting New Control Limits

Generally control limits are based on the following statistics for the historical data

Accuracy: mean recovery ±3*s*
Precision: zero to (mean RPD + 3s)

Where: *s* = standard deviation

If the calculated 3 standard deviation limits are tighter than the method calibration verification criterion (e.g., CCV acceptance limits for ICP = ± 10% of expected value), then the new limits are set to the mean value ± calibration criterion.

5.5 Communicating and Implementing New Control Limits

QA personnel prepare control limit reports comparing the new control limits with the old. This information is sent to the supervisor of the area affected by the new limits. The supervisor is to

review the summary data and sign the documentation to confirm that the data selected are representative of current performance. The supervisor is also confirming that the instrument data systems will be updated on the implementation date--the same date that QuantIMS will be updated. The information is forwarded to clients who have requested it.

6.0 Reporting QC Data

QC data routinely reported with sample results include the LCS, method blank and surrogate standards. Client reporting format requirements are negotiable and documented as part of the project records. Ultimately, all reporting decisions should accommodate the client's requirements.

Figure 1 - Method Blank Evaluation

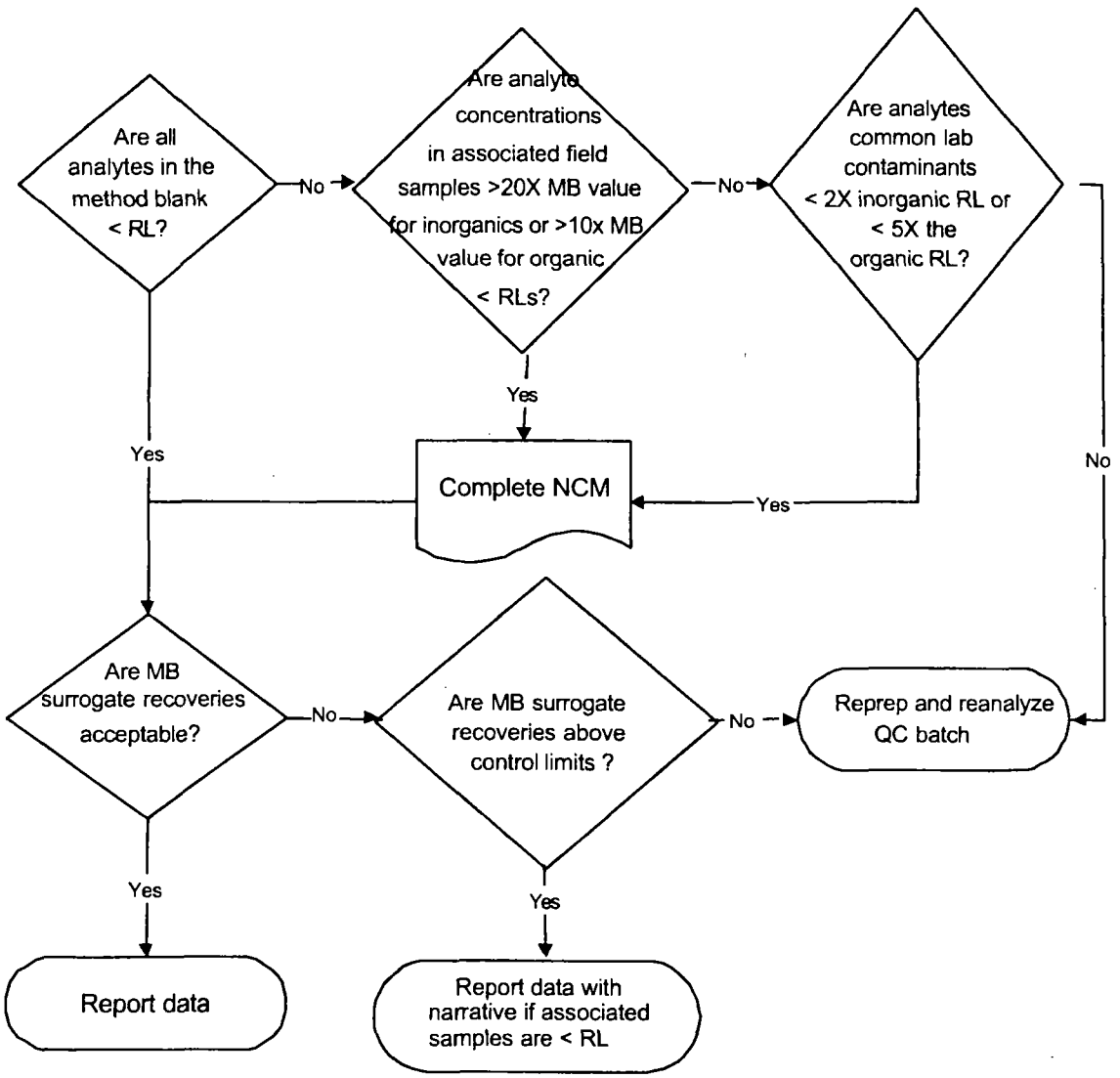


Figure 2 - LCS/LCSD Evaluation

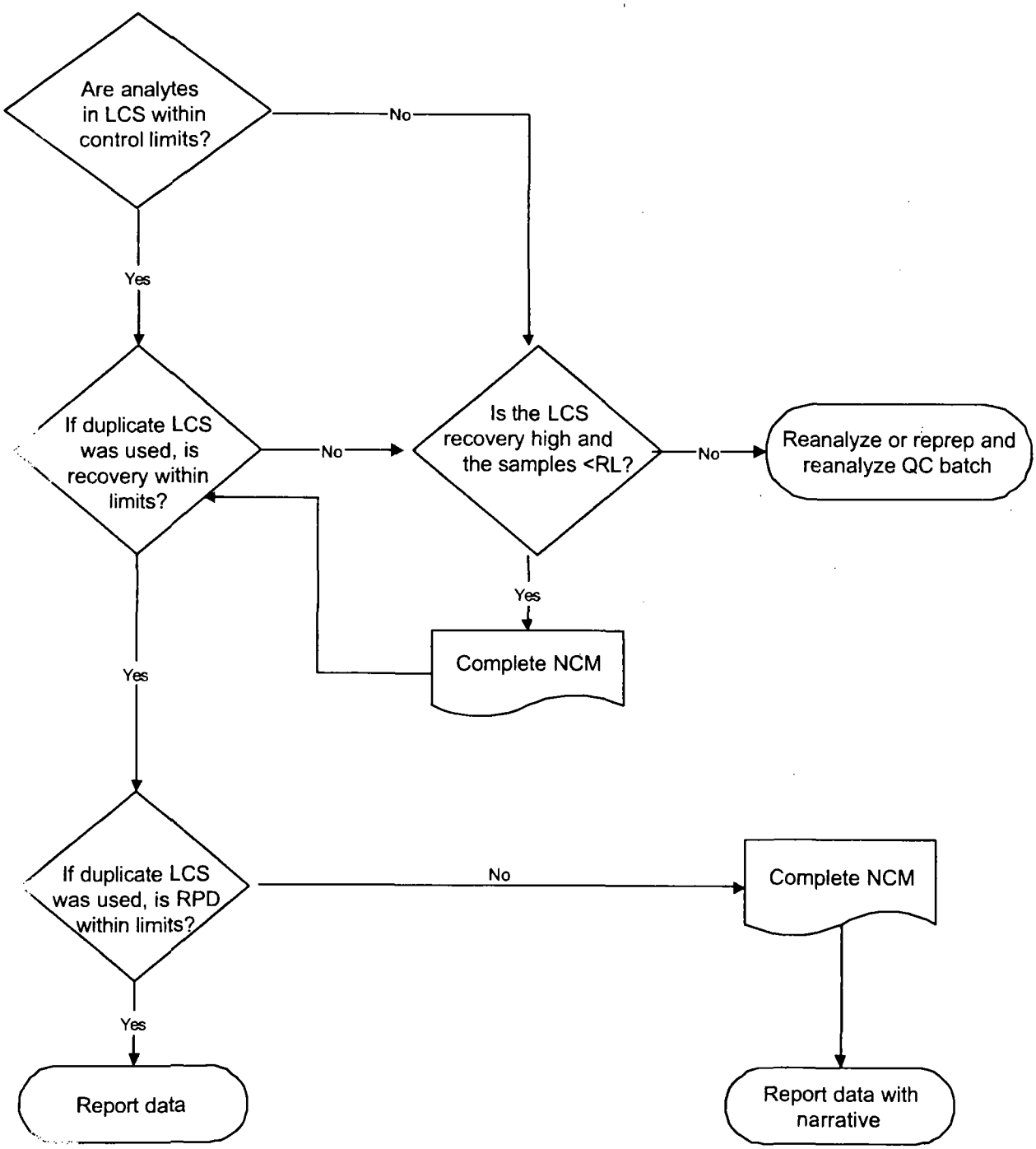


Figure 3 - Surrogate Evaluation

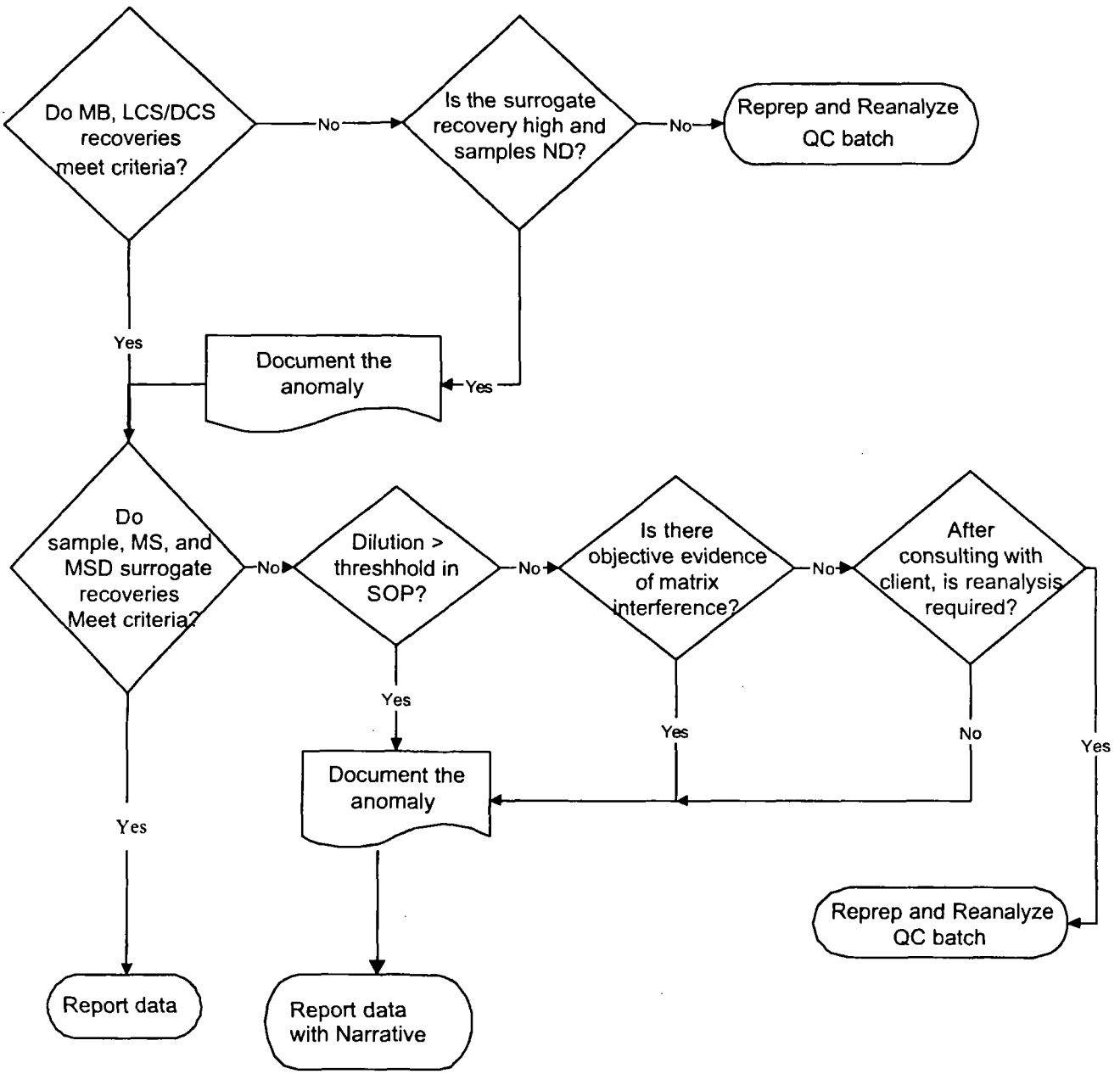
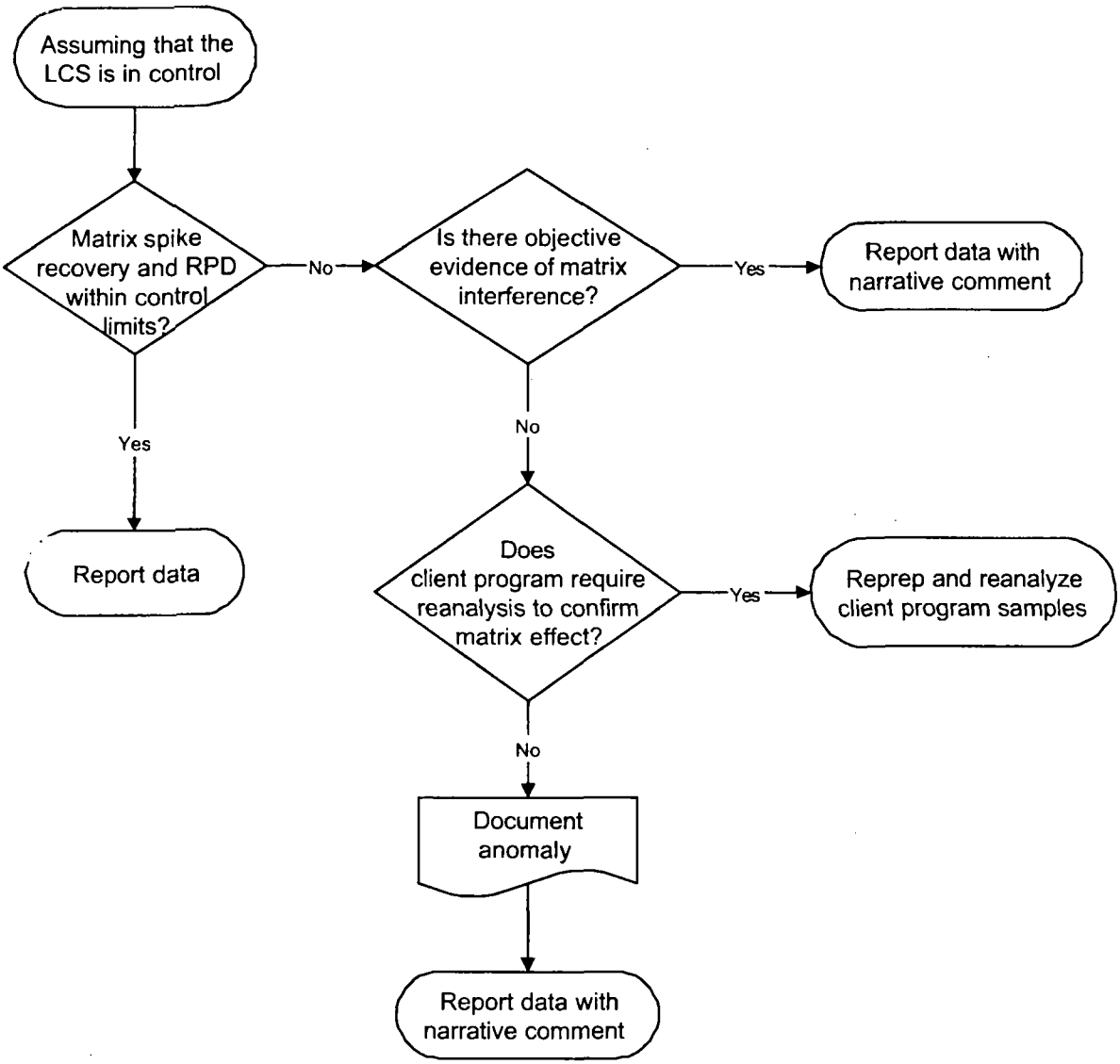


Figure 4 - Matrix Spike/Matrix Spike Duplicate Evaluation



TestAmerica

THE LEADER IN ENVIRONMENTAL TESTING

TestAmerica North Canton

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Title: Statistical Evaluation of Data and Development of Control Charts

[Method: None]

Approvals (Signature/Date):

Dorothy J. Lewis 12/13/07
Quality Assurance Manager Date

Laboratory Director 12/14/07
Laboratory Director Date

Mark T Bruce 12/14/07
Technical Director Date

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STL STANDARD OPERATING PROCEDURE

TITLE: STATISTICAL EVALUATION OF DATA AND DEVELOPMENT OF CONTROL CHARTS

(SUPERSEDES: REVISION 7, DATED 12/08/04)

Approved by: Dorothy J. Leeson — Quality Assurance Manager — 3/20/07 Date

Approved by: [signature] — Laboratory Director — 3/14/07 Date

Approved by: Mark Bruce — Technical Director — 3/13/07 Date

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1. PURPOSE

1.1. The purpose of this SOP is to describe the requirements for: (1) statistically establishing QC acceptance criteria and (2) long-term trend analysis of QC data using control charts at the STL-North Canton Laboratory.

1.2. The control chart is an effective tool for long-term trending because it records in real time the accuracy (bias) and precision of the appropriate parts of the measurement process. The control chart provides the means to demonstrate statistical control.

1.3. This document accurately reflects current standard operating procedures (SOP) as of the date above. All facility SOPs are maintained and updated as necessary by the laboratory.

2. RESPONSIBILITIES

2.1. Analyst

2.1.1. All QC data is entered into the Laboratory Information Management System (LIMS) for statistical evaluation for the generation of control charts. (Data entry may be automated or may be completed from the report generation software as part of the report or review group activities.)

2.1.2. Monitor method performance using established limits and identify any out-of-control situation. Respond to out-of-control conditions. QC Data results are considered out of control when recoveries exceed established control limits.

2.2. Group Leader/Supervisor

2.2.1. Respond to out-of-control conditions.

2.3. QA Department Staff

2.3.1. For analytical methods, coordinate updating of control limits. During this process, review control charts to detect any trends in routine analytical procedures.

2.3.2. Archive control charts and statistically derived QC acceptance data.

2.3.3. Publish statistically derived QC acceptance criteria.

2.3.4. Provide guidance in the development of control charts and in the application of QC samples and acceptance data.

2.3.5. With the Laboratory Director, ensure that Operations staff conforms to the requirements provided in this SOP.

2.4. Project Manager

2.4.1. Incorporate updated limits into project-specific QAPPs.

2.4.2. Submit project-specific control charts to the requesting client.

3. SAFETY

3.1. Procedures shall be carried out in a manner that protects the health and safety of all STL associates.

3.2. Normal office dependent safety precautions must be taken in performing this SOP. If personnel are required to perform any portion of the procedure in the laboratory area, appropriate personal protective equipment and precautions must be utilized.

3.3. All work must be stopped in the event of a known or potential compromise to the health and safety of a STL associate. The situation must be reported **immediately** to a laboratory supervisor and the EH&S Coordinator.

4. PROCEDURE

4.1. Empirical Establishment of QC Acceptance Limits

4.1.1. The assessment of QC sample data shall be performed by comparing precision and accuracy results against control limits. As defined in the following subsections, the control limits used for this comparison shall be either in-house (statistically generated using historical data) control limits or published limits from methods, contracts, or project QA plans.

4.1.2. In-house limits for all QC data must be determined and compared to those limits published in the methods for applicable matrices. Method limits will be employed until sufficient QC data are acquired. A minimum of 20 to 30 of the most recent data points should be used to establish in-house limits based on historical performance data for each major method. Periodically, QC data may need to be reviewed and house limits reestablished whenever a significant change in an analytical process occurs.

4.1.3. Control limits shall be generated for each matrix (i.e., aqueous and soil) for preparative methods, using data from at least 20 of the most recent data points. Limits are generated using a six-month timeframe to ensure the minimum number of points are included.

4.1.4. In-house control limits shall be established for the following samples:

4.1.4.1. Laboratory control sample (LCS) spike recoveries for method required analytes list.

4.1.4.2. Matrix Spike and Matrix Spike Duplicate (MS/MSD) spike recoveries for method required analytes list.

4.1.4.3. Surrogate spike recoveries in LCSs for organic analyses only.

4.1.5. Control limits shall be established for all methods unless specified in project plans such as the Louisville Chemistry Guideline (LCG) or the DoD QSM.

4.1.6. The calculations used to generate the control limits for accuracy (%R) are described in the following subsections.

4.1.6.1. The %R is defined as the observed concentration in LCS divided by the theoretical concentration of the spike or LCS, times 100:

$$\%R = \frac{Found}{True} \times 100$$

4.1.6.2. The mean percent recovery and standard deviation is calculated using the following formulas:

$$\overline{\%R} = \frac{\sum_{i=1}^{n} \%R_i}{n}$$

$$S = \sqrt{\frac{\sum_{i=1}^{n} \left(\%R_i - \overline{\%R}\right)^2}{n-1}}$$

where:

$\%R$ = the mean percent recovery

$\%R_i$ = the percent recovery of an LCS

n = the number of data points

S = the standard deviation of the data set of percent recoveries

4.1.6.3. The warning (95% or 2-sigma) and control limits (99% or 3-sigma) are then calculated from the following equations:

Upper Control Limit = $\overline{\%R} + 3\,s$

Lower Control Limit = $\overline{\%R} - 3\,s$

Upper Warning Limit = $\overline{\%R} + 2\,s$

Lower Warning Limit = $\overline{\%R} - 2\,s$

where:

$\overline{\%R}$ = the mean percent recovery

S = the standard deviation of the data set

4.1.7. Control limits will be recalculated after excluding the following points from the calculations:

4.1.7.1. Samples with values outside control limits due to assignable cause.

4.1.7.2. True outliers as defined in the Grubbs test.

4.1.8. The LIMS is equipped to perform a Grubbs outlier test used to generate the control charts.

4.2. Control Chart Generation – QA Access

4.2.1. A control chart (X chart) is generated using the LIMS or a commercially available software to monitor accuracy and precision by plotting the LCS %R data in a graphical format as follows:

4.2.1.1. The average of the %R determinations for the original data set is established as the midpoint on the Y axis of the graph.

4.2.1.2. The upper and lower warning and control limits are plotted as solid horizontal lines across the graph at their respective points on the Y axis.

4.2.1.3. The calculated %R of each spiked sample is plotted chronologically on the graph to determine whether the recovery is within the warning and control limits of the control chart.

4.2.2. Control charts can be generated from any networked system (see network administrator) as follows:

4.2.2.1. From the Desktop, TraQAr double click the "Control limit " icon button.

4.2.2.2. Select "QA Access"

4.2.2.3. Select "location" (North Canton), "QC Type" (LCS/DCS, MS/MSD, LCS/DCS Surrogates, MS/MSD Surrogates, All Surrogates), "Start and End Date" (default is six months), and then spike list number.

4.2.2.4. Select "QuantIMS Spike List"

4.2.2.5. Select "QC Program"

4.2.2.6. Select "Collect Data". This screen will run and then the Control Limits Review screen comes up.

4.2.3. Control Limits Review screen

4.2.3.1. A "Grubbs test complete" sign comes up, select OK

4.2.3.2. A minimum of 20 points are required. If points are below 20, select close form and increase the start and end date to no more than one year.

4.2.3.3. If there are at least 20 points, select "Control Limits Report". Right click on report and select print.

4.2.3.4. Select "Control Charts Report". Right click on report and select print.

4.2.3.5. This procedure demonstrates both "before" and "after" data sets used for control charts generation.

4.2.4. The following information must be present on the control charts or in an associated table:

4.2.4.1. Parameter, Analytical Method and preparation procedure

4.2.4.2. LCS Batch ID allowing cross-reference to LIMS containing all analytical information.

4.2.4.3. Matrix

4.2.4.4. Number of points used

4.2.4.5. Mean

4.2.4.6. Standard Deviation

4.2.4.7. Percent recoveries

4.2.4.8. Upper and Lower warning and Control limits

4.2.4.9. Chart generation date.

4.2.4.10. An example of the report is provided in **Appendix A**.

4.3. Evaluation of Control Charts

4.3.1. Criteria for an Out-of-Control Conditions

4.3.1.1. The causes for a shift or a trend in control charts could result from many reasons, including, but not limited to:
(1) incorrect preparation of a standard or a reagent,
(2) sample contamination,
(3) improper storage or preservation,
(4) incorrect instrument calibration,
(5) poor analytical technique, and
(6) deviation from the analytical method.

A measurement process for a particular analyte will be considered out-of-statistical-control when one of the following conditions occur:

4.3.1.1.1. A single point outside 3-sigma control limits

4.3.1.1.2. A series of eight consecutive points on the same side of the central line.

4.3.1.1.3. A series of three consecutive points between the warning limits and control limits.

4.3.1.1.4. A series of six consecutively increasing or decreasing points on the same side of the centerline.

4.3.1.1.5. A cyclic pattern of control values.

4.3.1.1.6. These conditions may indicate that the measurement system is out of statistical control. When this situation occurs, the data must be evaluated thoroughly to identify the most appropriate corrective action to be implemented. The problem and its solution may be documented through a Nonconformance Memo as appropriate. Exceeding warning limits will only require a close observation of the measurement system. In reviewing control charts, any significant changes in key analysts, instrumentation, standard reference materials, or processes must be kept in mind to explain potential out-of-control situations. After thorough evaluation of the data and documentation of corrective actions taken, the QA Department must determine if the defensiveness of analytical results generated during the out of control situation has been jeopardized. If it is determined that data defensiveness has been compromised, the client will be notified of the out of control situation.

4.4. On-Line Control Chart Generation

4.4.1. Laboratory group leaders or designees have access to the TraQar On-Line Control Chart program. This feature is used to view results in real time to determine trends or corrective actions.

4.4.2. From the Desktop, TraQAr double click the "Control limit " icon button.

4.4.3. Select "On-line Control Charts."

4.4.4. Select the QC Type and Group from the drop down menus.

4.4.5. The start and end date are automatically set for 30 days. The date can be changed as needed.

4.4.6. Select the appropriate Method from the list.

4.4.7. Select the appropriate QC code. In most cases, this will be 01. Then choose the appropriate spike list.

4.4.8. Press the Collect Data button.

4.4.9. A screen with Chart Options will appear. The default choices are All Analytes, All Instruments, and All Matrices. These choices may be modified as needed.

4.4.10. Select OK. Control charts will appear on the screen for each analyte and matrix. The report can be printed or viewed on line.

4.4.11. Refer to Section 4.3 for Control Chart Evaluation.

4.5. Setting Control Limits

4.5.1. The working control limits to be used by the laboratory are based on evaluation of the calculated laboratory statistical performance and available interlaboratory limits provided in the reference methods. Note that some SW-846 methods only supply single-operator or single-laboratory method performance data, which may not be appropriate.

Accuracy Evaluation:

Lower Limit Evaluation	Upper Limit Evaluation	Accuracy Decision
Laboratory-generated Lower Limit > Guidance Limit	Laboratory-generated Upper Limit > Guidance Limit	Use laboratory-gen. Lower Limit & Guidance Upper Limit
Laboratory-generated Lower Limit > Guidance Limit	Laboratory-generated Upper Limit < Guidance Limit	Use laboratory-gen. Lower Limit & laboratory-generated Upper Limit
Laboratory-generated Lower Limit < Guidance Limit	Laboratory-generated Upper Limit > Guidance limit	Use guidance Lower Limit & guidance Upper Limit
Laboratory-generated Lower Limit < Guidance Limit	Laboratory-generated Upper Limit < Guidance limit	Use guidance Lower Limit & laboratory-generated Upper Limit

Precision Evaluation:

Range Evaluation	Precision Decision
Laboratory-generated precision value > Guidance precision	Use guidance precision
Laboratory-generated precision < Guidance precision	Use laboratory-generated precision

Notes: If the decision is to use guidance limits from the method, the laboratory should investigate procedural improvements leading to better performance.

The following outlines other criteria:

Min/Max	Limit	Percentage	Inorganics	Organics
Minimum	LCL	10%	√	√
Maximum	LCL	90%	√	√
Minimum	UCL	110%	√	√
Maximum	UCL	199%	√	√
Minimum	RPD	20%	√	
Maximum	RPD	99%	√	√
Minimum	RPD	30%		√

5. DEFINITIONS

5.1. Control Chart - A graphical QC tool to monitor method performance over time and to establish acceptance limits.

5.2. Relative Percent Difference (RPD) - A measure of intra-lab precision based on a duplicate sample analyses.

5.3. Grubbs Test – Extension of sample sizes and percentage points for significant tests of outlying observations - a statistical outlier test.

5.4. Percent Recovery (%R) or Recovery - A measure of the accuracy (bias) of the measurement process based on a comparison of a measured value for a fortified (spiked) QC sample against the known spiked values.

5.5. Precision - A measure of mutual agreement (or variability) among individual measurements of the same property, usually under prescribed similar conditions.

5.6. Accuracy - The degree of agreement of a measurement (or an average of measurements of the same thing) with an accepted reference or true value. Accuracy is the measure of bias inherent in the system.

5.7. Bias - A systematic (consistent) error in test results. The difference between the population mean and the true or reference value, or as estimated from sample statistics; the difference between the sample average and the reference value.

5.8. X-chart – A control chart that plots a single measurement of a property (e.g., percent recovery) of quality control samples over time. The chart consists of a single line that is the mean of the statistic, warning limits at ± two standard deviations, and control limits at ± 3 sigma.

5.9. Assignable cause – A known reason for an outlying result (e.g., no spike added).

5.10. Duplicate – A second aliquot of a sample that is treated the same as the original sample in order to determine the precision of the method.

5.11. Laboratory Control Sample (LCS)

5.11.1. Organics - A LCS is a volume of deionized laboratory water (for water samples) or a suitable solid material (e.g., clean sand) (for soil/sediment samples) which is spiked with compounds of interest and subjected to the entire analytical procedure in order to estimate the accuracy of the method via percent spike recovery.

5.11.2. Inorganics - A well characterized liquid or solid sample which is prepared, digested or extracted along with each analytical batch of samples.

6. REFERENCES

6.1. STL Quality Management Plan (QMP), current revision.

6.2. STL Laboratory Quality Manual (LQM), current revision.

6.3. Test Methods for Evaluating Solid Waste, Third Edition, SW-846, US EPA, Final Update III, December 1996.

6.4. QA Policy, QA-003, current version.

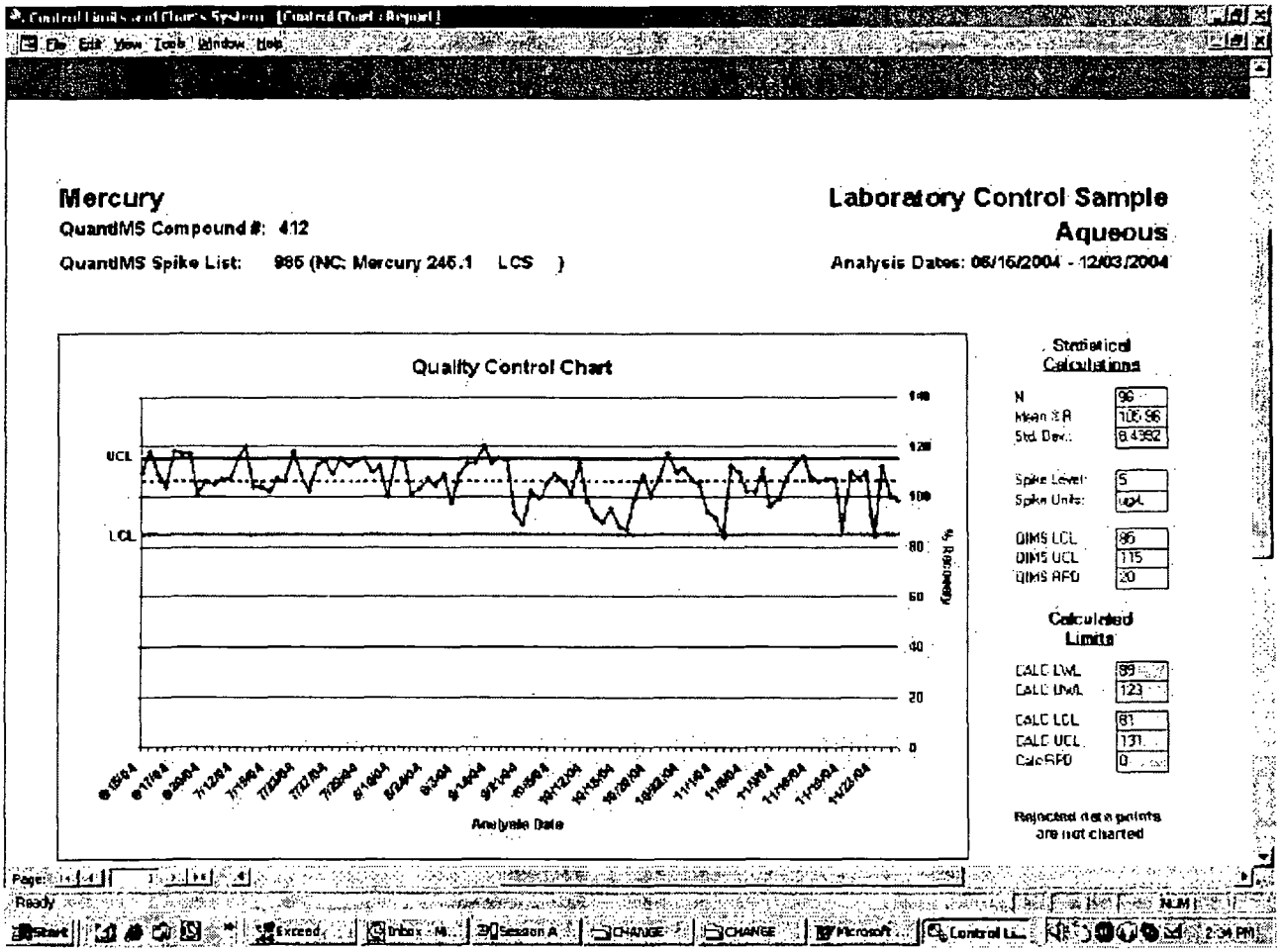
6.5. Supplemental Practices for DoD Project Work, NC-QA-0016, current version.

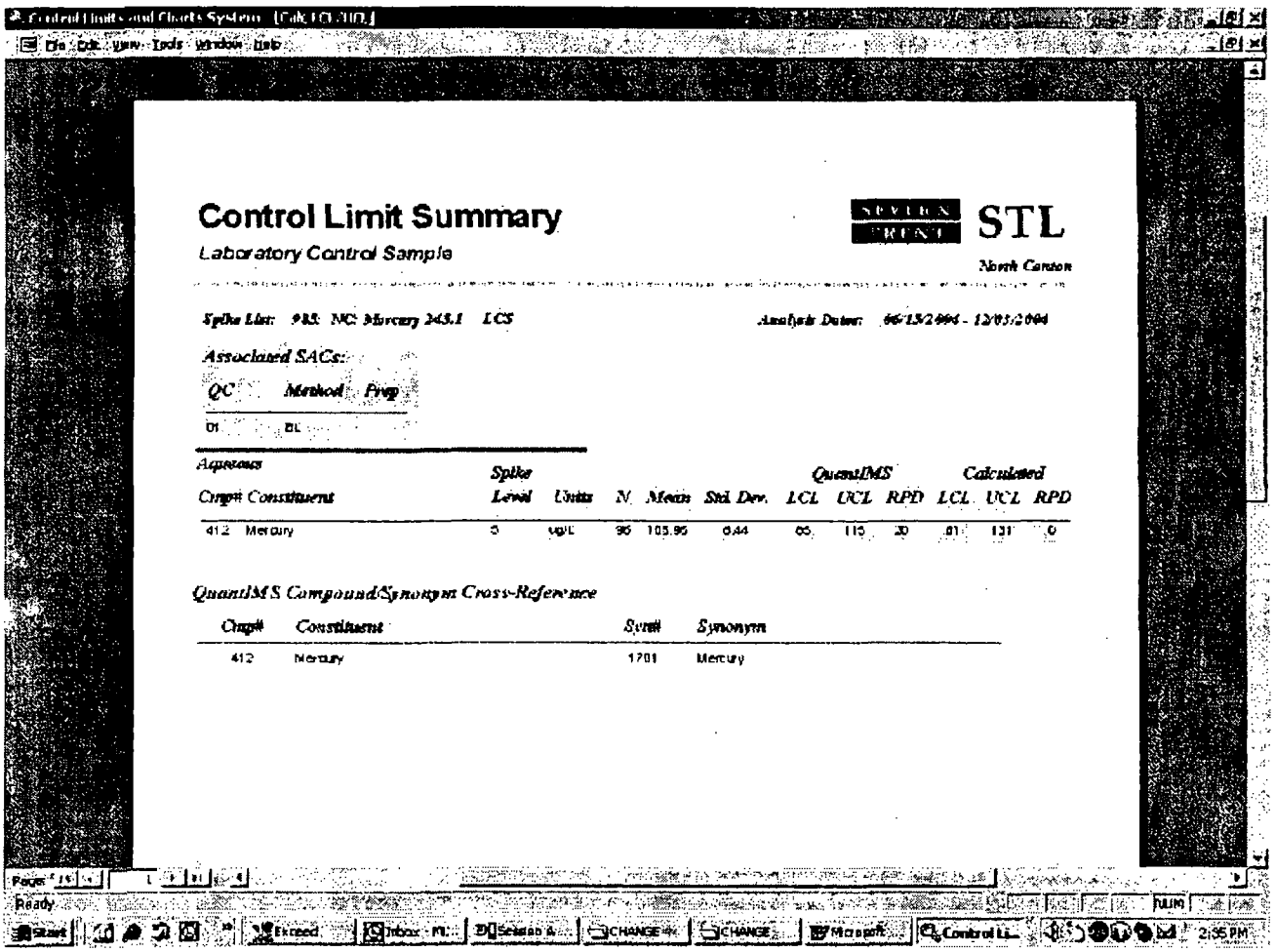
6.6. Dept. of Defense Quality Systems Manual for Environmental Laboratories, Final Version 3, January 2006 and future revisions.

6.7. Louisville Chemistry guideline (LCG), Version 5, June 2002.

APPENDIX A

Examples of Control Charts





Control Limit Summary

Laboratory Control Sample

STL North Canton

Spike List: 935 NC Mercury 245.1 LCS *Analysis Dates: 06/15/2006 - 12/05/2006*

Associated SACs:

QC	Method	Prep
DI	BL	

Aqueous Cmpd#	Constituent	Spike Level	Units	N	Mean	Std. Dev.	QuantIMS LCL	QuantIMS UCL	QuantIMS RPD	Calculated LCL	Calculated UCL	Calculated RPD
412	Mercury	5	ug/L	96	105.96	6.44	85	115	20	81	131	0

QuantIMS Compound/Synonym Cross-Reference

Cmpd#	Constituent	Synid	Synonym
412	Mercury	1701	Mercury

TestAmerica

THE LEADER IN ENVIRONMENTAL TESTING

TestAmerica North Canton

SOP No. CORP-MS-0002NC, Rev. 2.5
Effective Date: 04/03/07
Cover Page

Title: Determination of Volatile Organics by GC/MS
[Methods: 8260B, 8260A and 624 (Note: Update II and Update III are in one SOP)]

Approvals (Signature/Date):

Thomas E. Fuller 12/14/07
Technology Specialist Date

12-14-07
Health & Safety Coordinator Date

Dorothy J. Henson
Quality Assurance Manager Date

12/14/07
Laboratory Director Date

Mark E. Brace 12/14/07
Technical Director Date

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STL STANDARD OPERATING PROCEDURE

TITLE: DETERMINATION OF VOLATILE ORGANICS BY GC/MS BASED ON METHOD 8260B AND 8260A

(SUPERSEDES: REVISION 2.4, DATED 09/27/04)

Approved by:	Thomas E. Stelle	6/13/07
	Technology Specialist	Date
Approved by:	Dorothy J. Leeson	6/15/07
	Quality Assurance Manager	Date
Approved by:	William J. Gerbel	6-13-07
	Environmental Health and Safety Coordinator	Date
Approved by:		6/18/07
	Lab Manager	Date
Approved by:	Mark Bruce	6/14/07
	Technical Director	Date

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1.0 SCOPE AND APPLICATION

1.1. This method is applicable to the determination of Volatile Organic Compounds in waters, wastewater, soils, sludges and other solid matrices. Standard analytes are listed in Tables 5 and 6.

1.2. This SOP is applicable to method 8260B. It may also be used for analysis following method 8260A. The associated LIMS method codes are QK (8260B) and MZ (8260A). Ohio VAP projects are distinguished by Program Code 2J. The following Prep Codes are used: 15 (5 mL purge), 25 (low level 5mL purge), 4B (5035, Methanol preservation, EnCore™), 4D (5035, Sodium Bisulfate preservation, EnCore™), 4P (Frozen, EnCore™), M8 (5035A, Frozen Encore™), and 73 (5030A Methanol Prep).

1.3. This method can be used to quantify most volatile organic compounds that have boiling points below 200°C and are 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 because of poor purging efficiency.

1.4. The method is based upon a purge and trap, gas chromatograph/mass spectrometric (GC/MS) procedure. The approximate working range is 5 to 200 µg/L for 5 mL waters, 1 to 40 µg/L for low-level waters, 5 to 200 µg/kg for low-level soils, and 250 to 10,000 µg/kg for medium-level soils. Reporting limits are listed in Tables 1 and 3.

1.5. Method performance is monitored through the use of surrogate compounds, matrix spike/matrix spike duplicates, and laboratory control spike samples.

2.0 SUMMARY OF METHOD

2.1. Volatile compounds are introduced into the gas chromatograph by the purge and trap method. The components are separated via the chromatograph and detected using a mass spectrometer, which is used to provide both qualitative and quantitative information.

2.2. Aqueous samples are purged directly. Soils are preserved by extracting the volatile analytes into methanol. Soil samples may be preserved with sodium bisulfate or by freezing and purged directly.

2.3. In the purge and trap process, an inert gas is bubbled through the solution at ambient temperature or at 40°C (40°C required for low level soils) and the volatile components are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbant column where the volatile components are trapped. After purging is completed, the sorbant column (trap) is heated and backflushed with inert gas to desorb the components onto a gas chromatographic column. The gas chromatographic column is then heated to elute the components

which are detected with a mass spectrometer.

2.4. Qualitative identifications are confirmed by analyzing standards under the same conditions used for samples and comparing the resultant mass spectra and GC retention times. Each identified component is quantified by relating the MS response for an appropriate selected ion produced by that compound to the MS response for another ion produced by an internal standard.

3.0 DEFINITIONS

3.1. Batch

The batch is a set of up to 20 samples of the same matrix processed using the same procedures and reagents within the same time period. Using this method, each BFB analysis will normally start a new batch. Batches for medium level soils are defined at the sample preparation stage and may be analyzed on multiple instruments over multiple days, although reasonable effort should be made to keep the samples together.

3.1.1. The Quality Control batch must contain a matrix spike/spike duplicate (MS/MSD), a Laboratory Control Sample (LCS), and a method blank. Refer to the STL QC Program document (QA-003) for further details of the batch definition.

3.2. Method Blank

3.2.1. A method blank consisting of all reagents added to the samples must be analyzed with each batch of samples. The method blank is used to identify any background interference or contamination of the analytical system which may lead to the reporting of elevated concentration levels or false positive data.

3.3. Laboratory Control Sample (LCS)

3.3.1. Laboratory Control Samples are well characterized, laboratory generated samples used to monitor the laboratory's day-to-day performance of routine analytical methods. The LCS, spiked with a group of target compounds representative of the method analytes, is used to monitor the accuracy of the analytical process, independent of matrix effects. Ongoing monitoring of the LCS results provides evidence that the laboratory is performing the method within accepted QC guidelines for accuracy and precision.

3.4. Surrogates

3.4.1. Surrogates are organic compounds which are similar to the target analyte(s) in chemical composition and behavior in the analytical process, but which are not normally found in

environmental samples. Each sample, blank, LCS, and MS/MSD is spiked with surrogate standards. Surrogate spike recoveries must be evaluated by determining whether the concentration (measured as percent recovery) falls within the required recovery limits.

3.5. Matrix Spike/Matrix Spike Duplicate (MS/MSD)

3.5.1. A matrix spike is an environmental sample to which known concentrations of target analytes have been added. A matrix spike duplicate is a second aliquot of the same sample which is prepared and analyzed along with the sample and matrix spike. Matrix spikes and duplicates are used to evaluate accuracy and precision in the actual sample matrix.

3.6. Calibration Check Compound (CCC)

3.6.1. CCCs are a representative group of compounds which are used to evaluate initial calibrations and continuing calibrations. Relative percent difference for the initial calibration and % drift for the continuing calibration response factors are calculated and compared to the specified method criteria.

3.7. System Performance Check Compounds (SPCC)

3.7.1. SPCCs are compounds which are sensitive to system performance problems and are used to evaluate system performance and sensitivity. A response factor from the continuing calibration is calculated for the SPCC compounds and compared to the specified method criteria.

4. INTERFERENCES

4.1. Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus that lead to discrete artifacts. All of these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. The use of ultra high purity gases, pre-purged purified reagent water, and approved lots of purge and trap grade methanol will greatly reduce introduction of contaminants. In extreme cases the purging vessels may be pre-purged to isolate the instrument from laboratory air contaminated by solvents used in other parts of the laboratory.

4.2. Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride and fluorocarbons) into the sample through the septum seal during shipment and storage. A field blank prepared from reagent water and carried through the sampling and handling protocol can serve as a check on such contamination.

4.3. Matrix interferences may be caused by non-target contaminants that are coextracted from the

sample. The extent of matrix interferences will vary considerably from source to source depending upon the nature and diversity of the site being sampled.

4.4. Cross-contamination can occur whenever high-level and low-level samples are analyzed sequentially or in the same purge position on an autosampler. Whenever an unusually concentrated sample is analyzed, it should be followed by one or more blanks to check for cross-contamination. The purge and trap system may require extensive bake-out and cleaning after a high-level sample.

4.5. Some samples may foam when purged due to surfactants present in the sample. When this kind of sample is encountered, the sample is diluted.

5. SAFETY

5.1 Employees must abide by the policies and procedures in the Corporate Safety Manual and this document.

5.2. Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately. Cut resistant gloves MUST be worn when opening VOA vials and when doing any other task that presents a strong possibility of getting cut.

5.3. Primary Materials Used

5.3.1. The following is a list of the materials used in this method, which have a serious or significant hazard rating. NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table. A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Sodium bisulfate	Irritant	None	Causes mild to severe irritation to the eyes. Prolonged exposure may cause burn if not flushed with water. May cause mild irritation to skin. Prolonged exposure may cause burn if not flushed with water.

Hydrochloric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Methanol	Flammable Poison Irritant	200 ppm-TWA	A slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness and dizziness. Methyl alcohol is a defatting agent and may cause skin to become dry and cracked. Skin absorption can occur; symptoms may parallel inhalation exposure. Irritant to the eyes.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

5.4. Exposure to chemicals must be maintained **as low as reasonably achievable**, therefore, unless they are known to be non-hazardous, all samples should be opened, transferred, and prepared in a fume hood, or under other means of mechanical ventilation where possible. All samples with a sticker that reads "Caution/Use Hood!" **must** be opened in the hood. Contact the EH&S co-ordinator if this is not possible. Solvent and waste containers will be kept closed unless transfers are being made.

5.5. The preparation of standards and reagents will be conducted in a fume hood with the sash closed as far as the operations will permit.

5.6. All work must be stopped in the event of a known or potential compromise to the health and safety of a STL associate. The situation must be reported **immediately** to the EH&S coordinator and the laboratory group leader.

5.7. Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices outlined in the STL Health and Safety Manual. These employees must have training on the hazardous waste disposal practices initially upon assignment of these tasks, followed by an annual refresher training.

5.8. Specific Safety Concerns or Requirements

5.8.1. The gas chromatograph and mass spectrometer contain zones that have elevated temperatures. The analyst needs to be aware of the locations of those zones, and must cool them to room temperature prior to working on them.

5.8.2. The mass spectrometer is under deep vacuum. The mass spectrometer must be brought to atmospheric pressure prior to working on the source.

5.8.3. There are areas of high voltage in both the gas chromatograph and the mass spectrometer. Depending on the type of work involved, either turn the power to the instrument off, or disconnect it from its source of power.

5.8.4. Sodium bisulfate creates Sulfuric Acid when mixed with water.

6. EQUIPMENT AND SUPPLIES

6.1. Microsyringes: 10 µL and larger, 0.006 inch ID needle.

6.2. Syringe: 5 or 25 mL glass with luerlok tip, if applicable to the purging device.

6.3. Balance: Analytical, capable of accurately weighing 0.0001 g, and a top-loading balance capable of weighing 0.1 g

6.4. Glassware:

6.4.1. Vials: 20 mL with screw caps and Teflon liners.

6.4.2. Volumetric flasks: 10 mL and 100 mL, class A with ground-glass stoppers.

6.5. Spatula: Stainless steel.

6.6. Disposable pipettes: Pasteur, 5 ¾ in.

6.7. pH paper: Wide range, pH 0-14.

6.8. Gases:

6.8.1. Helium: Ultra high purity, gr. 5, 99.999%.

6.8.2. Nitrogen: Ultra high purity, from cylinders or gas generators, may be used as an

alternative to helium for purge gas.

6.9. Purge and Trap Device: The purge and trap device consists of the sample purger, the trap, and the desorber.

6.9.1. Sample Purger: The recommended purging chamber is designed to accept 5 mL samples with a water column at least 3 cm deep. The purge gas must pass through the water column as finely divided bubbles, each with a diameter of less than 3 mm at the origin. The purge gas must be introduced no more than 5 mm from the base of the water column. Alternative sample purge devices may be used provided equivalent performance is demonstrated. Low level soils are purged directly from a VOA vial.

6.9.2. Trap: A variety of traps may be used, depending on the target analytes required. One of the traps used is the Vocarb 3000 trap. Other traps such as the OI 10 may be used if the Quality Control criteria are met. Refer also to instrument operating manuals located within the laboratory.

6.9.3. Desorber: The desorber should be capable of rapidly heating the trap to 180°C. Many such devices are commercially available.

6.9.4. Sample Heater: A heater capable of maintaining the purge device at 40°C is necessary for low level soil analysis.

6.10. Gas Chromatograph/Mass Spectrometer System:

6.10.1. Gas Chromatograph: The gas chromatograph (GC) system must be capable of temperature programming.

6.10.2. Gas Chromatographic Columns: Capillary columns are used. Some typical columns are listed below:

6.10.2.1. Column 1: 20m x 0.18 ID DB-624 with 1 µm film thickness.

6.10.2.2. Mass Spectrometer: The mass spectrometer must be capable of scanning 35-300 AMU every two seconds or less, using 70 volts electron energy in the electron impact mode and capable of producing a mass spectrum that meets the required criteria when 50 ng of 4-Bromofluorobenzene (BFB) are injected onto the gas chromatograph column inlet.

6.10.3. GC/MS interface: In general direct introduction to the mass spectrometer is used but any interface that achieves all acceptance criteria may be used.

6.10.4. Data System: A computer system that allows the continuous acquisition and storage on machine readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that allows searching any GC/MS data file for ions of a specified mass and plotting such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundances in any EICP between the specified time or scan-number limits. Also, for the non-target compounds, software must be available that allows for the comparison of sample spectra against reference library spectra. The most recent release of the NIST/EPA mass spectral library should be used as the reference library. The computer system must also be capable of backing up data for long-term off-line storage.

7. REAGENTS AND STANDARDS

7.1. Reagents

7.1.1. Methanol: Purge and Trap Grade, High Purity

7.1.2. Reagent Water: High purity water that meets the requirements for a method blank when analyzed. (See section 9.4) Reagent water may be purchased as commercial distilled water and prepared by purging with an inert gas overnight. Other methods of preparing reagent water are acceptable.

7.1.3. Hydrochloric Acid – (1:1 v/v): Reagent grade or equivalent.

7.1.4. Sodium bisulfate: Reagent grade or equivalent.

7.2. Standards

7.2.1. Calibration Standard

7.2.1.1. Stock Solutions: Stock solutions may be purchased as certified solutions from commercial sources or prepared from pure standard materials as appropriate. These standards are prepared in methanol and stored in Teflon-sealed screw-cap bottles with minimal headspace at -10° to -20°C.

7.2.1.2. Working standards: A working solution containing the compounds of interest prepared from the stock solution(s) in methanol. These standards are stored in the freezer or as recommended by the manufacturer. Working standards are monitored by comparison to the initial calibration curve. If any of the calibration check compounds drift in response from the initial calibration by

more than 20% then corrective action is necessary. This may include steps such as instrument maintenance, preparing a new calibration verification standard or tuning the instrument. If the corrective actions do not correct the problem then a new initial calibration must be performed.

7.2.1.3. Aqueous Calibration Standards are prepared in reagent water using the secondary dilution standards. These aqueous standards must be prepared daily.

7.2.1.4. If stock or secondary dilution standards are purchased in sealed ampoules they may be used up to the manufacturers expiration date.

7.2.2. Internal Standards: Internal standards are added to all samples, standards, and blank analyses. Refer to Table 7 for internal standard components.

7.2.3. Surrogate Standards: Refer to Table 8 for surrogate standard components and spiking levels.

7.2.4. Laboratory Control Sample Spiking Solutions: Refer to Table 9 for LCS components and spiking levels.

7.2.5. Matrix Spiking Solutions: The matrix spike contains the same components as the LCS. Refer to Table 9.

7.2.6. Tuning Standard: A standard is made up that will deliver 50 ng on column upon injection. A recommended concentration of 50 ng/µL of 4-Bromofluorobenzene in methanol is prepared as described in Sections 7.2.1.1 and 7.2.1.2.

8. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1. Holding times for all volatile analysis are 14 days from sample collection.

8.2. Water samples are normally preserved at pH $\leq$ 2 with 1:1 hydrochloric acid.

8.3. Solid samples are field preserved with sodium bisulfate solution for low level analysis, or with methanol for medium level analysis. Soil samples can also be taken using the EnCore™ sampler and preserved in the lab within 48 hours of sampling. At specific client request, unpreserved soil samples may be accepted.

8.4. There are several methods of sampling soil. The recommended method, which provides the minimum of field difficulties, is to take an EnCore™ sample. (The 5 g or 25 g sampler can be used,

depending on client preference). Following shipment back to the lab the soil is preserved in methanol. This is the medium level procedure. If very low detection limits are needed (< 50 µg/kg for most analytes) then it will be necessary to use two additional 5 g EnCore™ samplers or to use field preservation.

8.5. Sample collection for medium level analysis using EnCore™ samplers.

8.5.1. Ship one 5 g (or 25 g) EnCore™ sampler per field sample position.

8.5.2. An additional 2 oz plastic bottle must be shipped for percent moisture determination.

8.5.3. When the samples are returned to the lab, extrude the (nominal) 5g (or 25 g) sample into a tared VOA vial containing 5 mL methanol (25 mL methanol for the 25 g sampler). Obtain the weight of the soil added to the vial and note on the label.

8.5.4. Add the correct amount of surrogate spiking mixture. (Add 25 µL of 2500 µg/mL solution for a nominal 25 g sample, 5 µL for a nominal 5 g sample.) Refer to Section 17.5 for Michigan project criteria.

8.5.5. Add the correct amount of matrix spiking solution to the matrix spike and matrix spike duplicate samples. (Add 500 µL of 50 µg/mL solution for a nominal 25 g sample, 100 µL for a nominal 5 g sample.) Reduce the volume of methanol added to ensure the final volume is 25 mL for nominal 25 g sample or 5 mL methanol for a nominal 5 g sample. Refer to Section 17.4 for Michigan project criteria.

8.5.6. Prepare an LCS for each batch by adding the correct amount of matrix spiking solution to clean methanol. (500 µL of spike to 25 mL methanol or 100 µL spike to 5 mL methanol). Refer to Section 17.4 for Michigan project criteria.

8.5.7. Shake the samples for two minutes to distribute the methanol throughout the soil.

8.6. Sample collection for medium level analysis using field methanol preservation

8.6.1. Prepare a 2 oz sample container by adding 25 mL purge and trap grade methanol. (If a 5 g sample is to be used, add 5 mL methanol to a 2 oz container or VOA vial).

8.6.2. Seal the bottle and attach a label.

8.6.3. Weigh the bottle to the nearest 0.01g and note the weight on the label.

8.6.4. Ship with appropriate sampling instructions.

8.6.5. Each sample will require an additional 2 oz plastic bottle with no preservative for percent moisture determination.

8.6.6. At client request, the methanol addition and weighing may also be performed in the field.

8.6.7. When the samples are returned to the lab, obtain the weight of the soil added to the vial and note on the label.

8.6.8. Add the correct amount of surrogate spiking mixture. (Add 25 µL of 2500 µg/mL solution for a nominal 25 g sample, 5 µL for a nominal 5 g sample.) Refer to Section 17.5 for Michigan project criteria.

8.6.9. Add the correct amount of matrix spiking solution to the matrix spike and matrix spike duplicate samples. (Add 500 µL of 50 µg/mL solution for a nominal 25 g sample, 100 µL for a nominal 5 g sample.) Reduce the volume of methanol added to ensure the final volume is 25 mL for nominal 25 g sample or 5 mL methanol for a nominal 5 g sample. Refer to Section 17.5 for Michigan project criteria.

8.6.10. Prepare an LCS for each batch by adding the correct amount of matrix spiking solution to clean methanol. (500 µL of spike to 25 mL methanol or 100 µL spike to 5 mL methanol). Refer to Section 17.5 for Michigan project criteria.

8.6.11. Shake the samples for two minutes to distribute the methanol throughout the soil.

8.7. Low level procedure

8.7.1. If low detection limits are required (typically < 50 µg/kg) sodium bisulfate preservation must be used. However, it is also necessary to take a sample for the medium level (field methanol preserved or using the EnCore™ sampler) procedure, in case the concentration of analytes in the soil is above the calibration range of the low level procedure.

8.7.2. A purge and trap autosampler capable of sampling from a sealed vial is required for analysis of samples collected using this method. (Varian Archon or O.I. 4552).

8.7.3. The soil sample is taken using a 5g EnCore™ sampling device and returned to the lab. It is recommended that two EnCore™ samplers be used for each field sample position, to allow for any reruns than may be necessary. A separate sample for % moisture determination is also necessary.

8.7.4. Prepare VOA vials by adding a magnetic stir bar, approximately 1 g of sodium bisulfate and 5 mL of reagent water.

8.7.5. Seal and label the vial. It is strongly recommended that the vial is labeled with an indelible marker rather than a paper label, since paper labels may cause the autosampler to bind and malfunction. The label absolutely must not cover the neck of the vial or the autosampler will malfunction.

8.7.6. Weigh the vial to the nearest 0.1g and note the weight on the label.

8.7.7. Extrude the soil sample from the EnCore™ sampler into the prepared VOA vial. Reweigh the vial to obtain the weight of soil and note on the label.

Note: Soils containing carbonates may effervesce when added to the sodium bisulfate solution. If this is the case at a specific site, add 5 mL of water instead, and freeze at <-10°C within 48 hours. The sample must be analyzed within 14 days after sampling and stored at a 45 degree angle in the freezer.

8.7.8. Alternatively the sodium bisulfate preservation may be performed in the field. This is not recommended because of the many problems that can occur in the field setting. Ship at least two vials per sample. The field samplers must determine the weight of soil sampled. Each sample will require an additional 2 oz plastic bottle with no preservative for percent moisture determination, and an additional VOA vial preserved with methanol for the medium level procedure. Depending on the type of soil it may also be necessary to ship vials with no or extra preservative.

8.8. Unpreserved soils

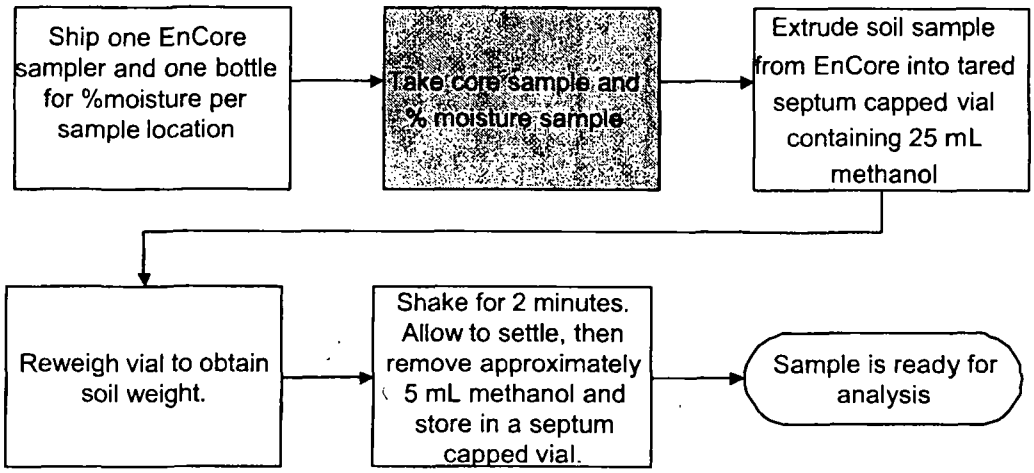
8.8.1. At specific client request, unpreserved soils packed into glass jars or brass tubes may be accepted and sub-sampled in the lab. This is the old procedure based on method 5030A and method 8260A. It is no longer included in SW846 and is likely to generate results that are biased low, possibly by more than an order of magnitude.

8.9. Aqueous samples are stored in glass containers with Teflon lined septa at 4°C +/- 2°C, with minimum headspace.

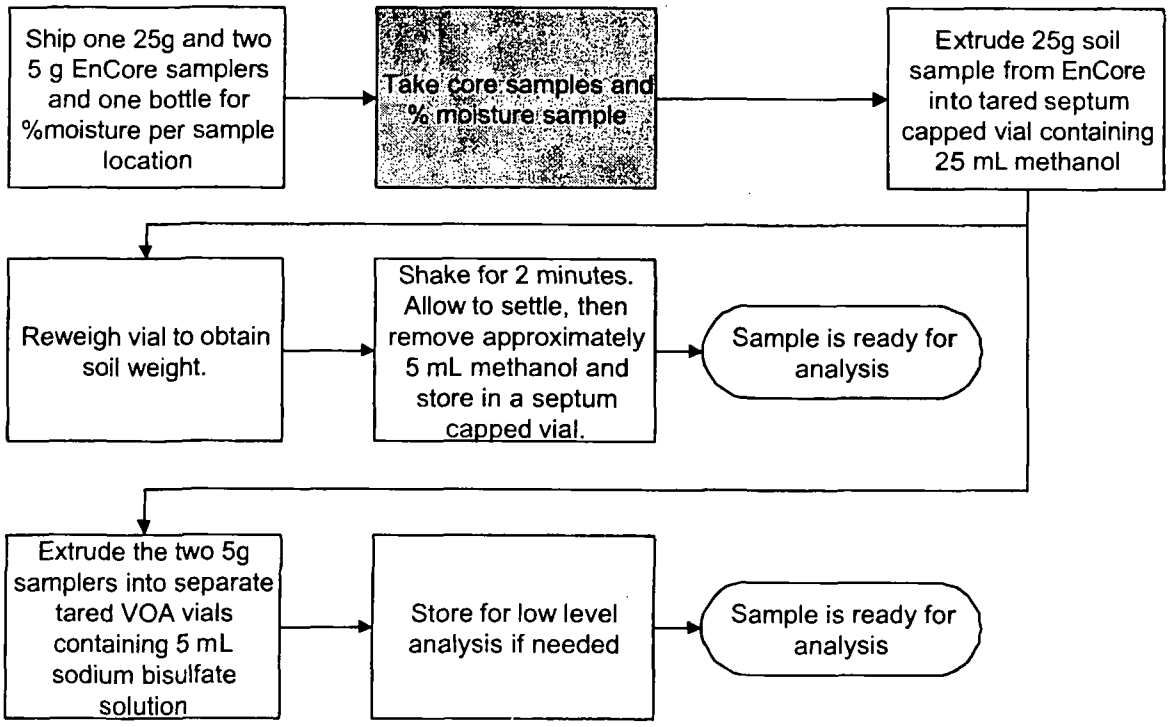
8.10. The maximum holding time is 14 days from sampling until the sample is analyzed. (Samples that are found to be unpreserved still have a 14 day holding time. However they should be analyzed as soon as possible. The lack of preservation should be addressed in the case narrative). Maximum holding time for the EnCore™ sampler (before the sample is added to methanol or sodium bisulfate) is 48 hours.

8.11. A holding blank is stored with the samples. This is analyzed weekly. It is replaced every seven days.

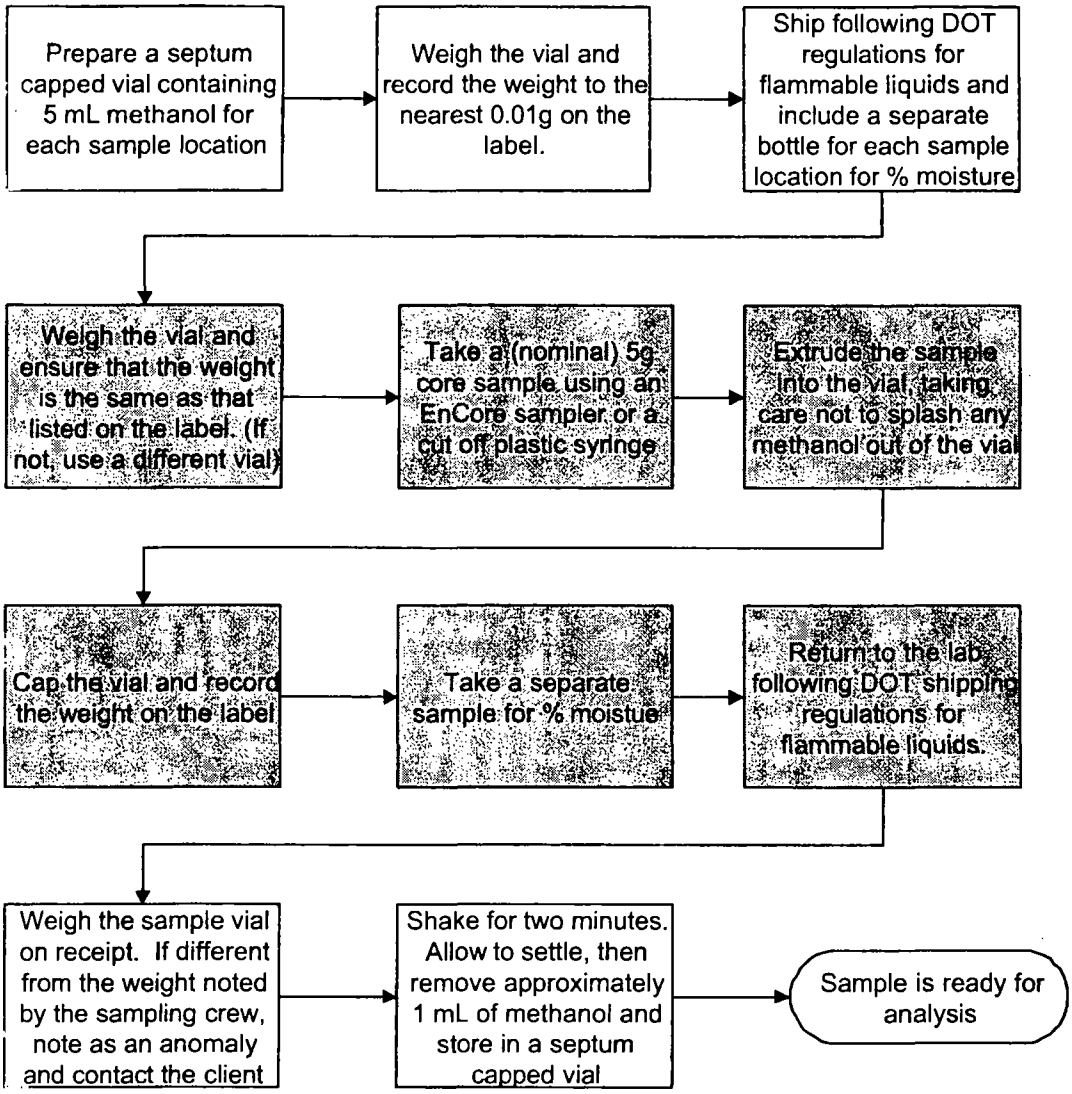
EnCore procedure when low level is not required (field steps in gray)



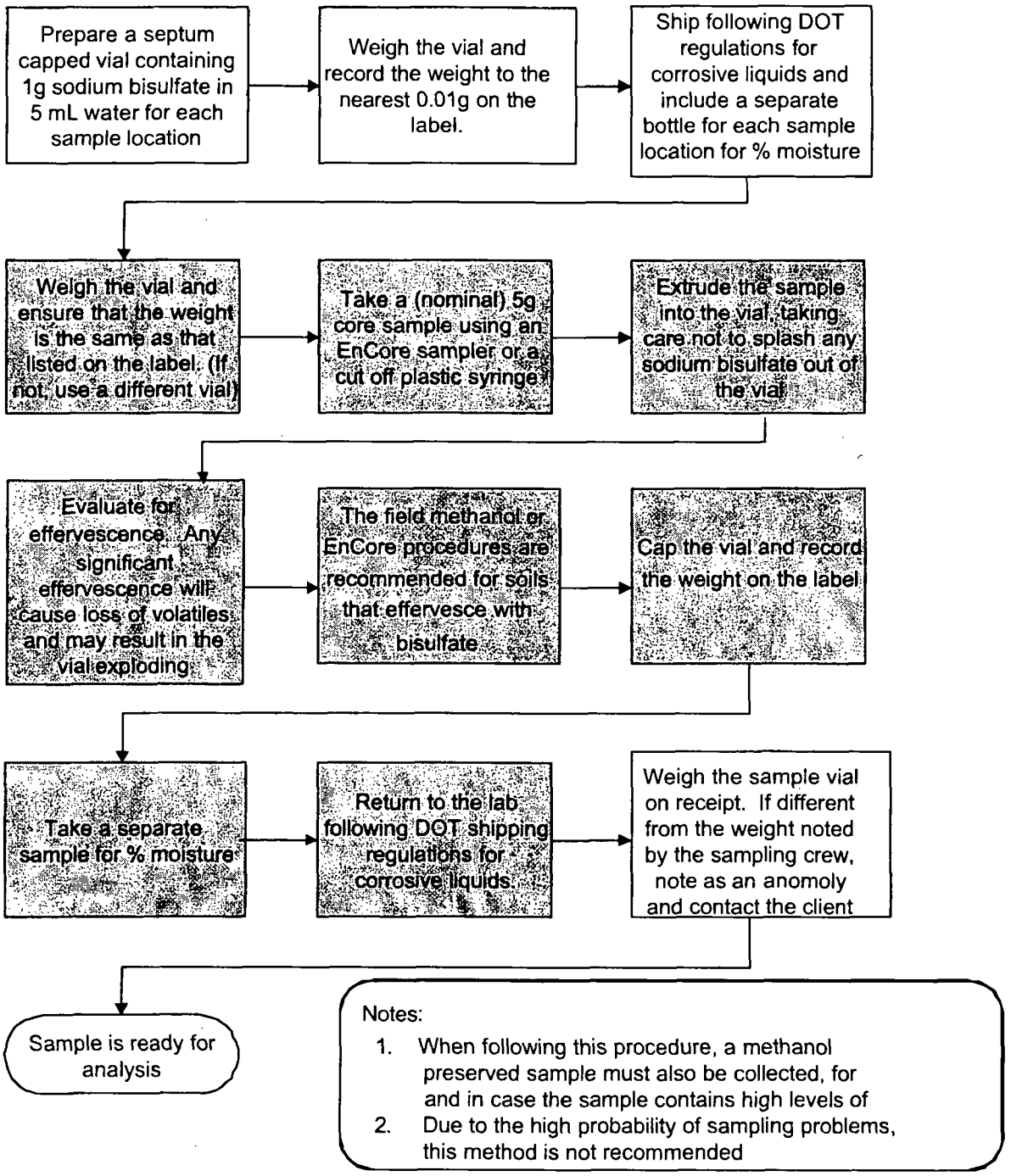
EnCore procedure when low level is required



Field methanol extraction procedure (field steps in gray)



Field bisulfate preservation procedure (field steps in gray)



9. QUALITY CONTROL

9.1. Control Limits

9.1.1. Control limits are established by the laboratory as described in SOP NC-QA-0018.

9.1.2. Laboratory control limits are internally generated and updated periodically unless method specified. Control limits are easily accessible via the LIMs (QC Browser program).

9.2. Surrogates

9.2.1. Every sample, blank, and QC sample is spiked with surrogates. Surrogate recoveries in samples, blanks, and QC samples must be assessed to ensure that recoveries are within established limits. The compounds included in the surrogate spiking solutions are listed in Table 8. If any surrogates are outside limits, the following corrective actions must take place (except for dilutions):

- Check all calculations for error.
- Ensure that instrument performance is acceptable.
- Recalculate the data and/or reanalyze if either of the above checks reveal a problem.
- Reprepare and reanalyze the sample if there is sufficient volume. If there is insufficient volume, the surrogate is narrated.

It is only necessary to reprepare/reanalyze a sample once to demonstrate that poor surrogate recovery is due to matrix effect, unless the analyst believes that the repeated out of control results are not due to matrix effect.

9.2.2. If the surrogates are out of control for the sample, matrix spike, and matrix spike duplicate, then matrix effect has been demonstrated for that sample and repreparation is not necessary. If the sample is out of control and the MS and/or MSD is in control, then reanalysis or flagging of the data is required.

9.2.3. Refer to the STL QC Program document (QA-003) for further details of the corrective actions.

9.3. Method Blanks

9.3.1. For each batch of samples, analyze a method blank. The method blank is analyzed after the calibration standards, normally before any samples. For low-level volatiles, the method

blank consists of reagent water. For medium-level volatiles, the method blank consists of the same volume of methanol that was used to prepare the samples. Surrogates are added and the method blank is carried through the entire analytical procedure. The method blank must not contain any analyte of interest at or above the reporting limit (except common laboratory contaminants, see below). The method blank is acceptable if any compound detected in the blank is present in the associated samples at 10 times the blank level.

- If the analyte is a common laboratory contaminant (methylene chloride, acetone, 2-butanone) the data may be reported with qualifiers if the concentration of the analyte is less than five times the reporting limit. Such action must be taken in consultation with the client.

- Reanalysis of samples associated with an unacceptable method blank is required when reportable concentrations are determined in the samples.

- If there is no target analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers.

9.3.2. The method blank must have acceptable surrogate recoveries. If surrogate recoveries are not acceptable, the data must be evaluated to determine if the method blank has served the purpose of demonstrating that the analysis is free of contamination. If surrogate recoveries are low and there are reportable analytes in the associated samples re-extraction of the blank and affected samples will normally be required. Consultation with the client should take place.

9.3.3. If reanalysis of the batch is not possible due to limited sample volume or other constraints, the method blank is reported, all associated samples are flagged with a "B," and appropriate comments may be made in a narrative to provide further documentation.

9.3.4. Refer to the STL QC Program document (QA-003) for further details of the corrective actions.

9.4. Laboratory Control Samples (LCS)

9.4.1. For each batch of samples, analyze a LCS. The LCS is analyzed after the calibration standard, and normally before any samples. The LCS contains a representative subset of the analytes of interest (See Table 9), and must contain the same analytes as the matrix spike. If any analyte or surrogate is outside established control limits, the system is out of control and corrective action must occur. Corrective action will normally be repreparation and reanalysis of the batch.

- If the batch is not re-extracted and reanalyzed, the reasons for accepting the batch must be clearly presented in the project records and the report.

- If re-extraction and reanalysis of the batch is not possible due to limited sample volume or other constraints, the LCS is reported, all associated samples are flagged, and appropriate comments are made in a narrative to provide further documentation.

9.4.2. Refer to the STL QC Program document (QA-003) for further details of the corrective action.

9.4.3. If full analyte spike lists are used at client request, it will be necessary to allow a percentage of the components to be outside control limits as this would be expected statistically. These requirements should be negotiated with the client. Refer to Section 17.2 for Ohio VAP specific analytes.

9.4.4. If full analyte spike lists are used at the client request, it is possible some compounds in the LCS may interfere with each other. In that case, the lab will quantitate those compounds in the LCS with a secondary ion which is free from interferences.

9.5. Matrix Spikes

9.5.1. For each QC batch, analyze a matrix spike and matrix spike duplicate. Spiking compounds and levels are given in Table 9. Compare the percent recovery and relative percent difference (RPD) to that in the laboratory specific historically generated limits. See Section 17.2 for Ohio VAP specific analytes.

- If any individual recovery or RPD falls outside the acceptable range, corrective action must occur. The initial corrective action will be to check the recovery of that analyte in the Laboratory Control Sample (LCS). Generally, if the recovery of the analyte in the LCS is within limits, then the laboratory operation is in control and analysis may proceed. The reasons for accepting the batch must be documented.

- If the recovery for any component is outside QC limits for both the matrix spike/ spike duplicate and the LCS, the laboratory is out of control and corrective action must be taken. Corrective action will normally include reanalysis of the batch.

- If a MS/MSD is not possible due to limited sample, then a LCS duplicate should be analyzed. RPD of the LCS and LCSD are compared to the matrix spike limits.

- The matrix spike/duplicate must be analyzed at the same dilution as the unspiked sample, even if the matrix spike compounds will be diluted out.

9.6. Non-Conformance and Corrective Action

9.6.1. Any deviations from QC procedures must be documented as a non-conformance, with applicable cause and corrective action approved by the facility QA Manager.

10. CALIBRATION AND STANDARDIZATION

10.1. Summary

10.1.1. Prior to the analysis of samples and blanks, each GC/MS system must be tuned and calibrated. Hardware tuning is checked through the analysis of the 4-Bromofluorobenzene (BFB) to establish that a given GC/MS system meets the standard mass spectral abundance criteria. The GC/MS system must be calibrated initially at a minimum of five concentrations (analyzed under the same BFB tune), to determine the linearity of the response utilizing target calibration standards. Once the system has been calibrated, the calibration must be verified each twelve hour time period for each GC/MS system.

10.1.2. General

Electron Energy:	70 volts (nominal)
Mass Range:	35–300 AMU
Scan Time:	to give at least 5 scans/peak, but not to exceed 2 second/scan
Injector Temperature:	200–250°C
Source Temperature:	According to manufacturer's specifications
Transfer Line	Temperature: 250–300°C
Purge Flow:	40 mL/minute
Carrier Gas	Flow: 15 mL/minute
Make-up Gas Flow:	25–30 mL/minute

10.2. Gas chromatograph suggested temperature program

10.2.1. BFB Analysis

Isothermal:	170°C

10.2.2. Sample Analysis

Initial Temperature:	40°C
Initial Hold Time:	4 minutes
Temperature Program:	8°C/minute
Final Temperature:	184°C
Second Temperature	Program: 40°C/minute
Final Temperature:	240°C
Final Hold Time:	2.6 minutes

10.3. Instrument Tuning

10.3.1. Each GC/MS system must be hardware-tuned to meet the abundance criteria listed in Table 10 for a maximum of a 50 ng injection or purging of BFB. Analysis must not begin until these criteria are met. These criteria must be met for each twelve-hour time period. The twelve-hour time period begins at the moment of injection of BFB.

10.4. Initial Calibration

10.4.1. A series of at least five initial calibration standards is prepared and analyzed for the target compounds and each surrogate compound. Six standards must be used for a quadratic least squares calibration. Suggested calibration levels for a 5 mL purge are: 5, 20, 50, 100, and 200 µg/L. Certain analytes are prepared at higher concentrations due to poor purge performance. Suggested calibration levels for a low level 5mL purge are 1, 5, 10, 20, and 40 µg/L. Again, some analytes are prepared at higher levels. Tables 2 and 4 list the calibration levels for each analyte. Other calibration levels and purge volumes may be used depending on the capabilities of the specific instrument. (For example, adequate sensitivity can be obtained on the Agilent 5973 instruments to use a 5 mL purge volume to reach the same reporting limits that once required a 25 mL purge. The calibration levels will still be the same 1, 5, 10, 20, 40µg/L.) However, the same purge volume must be used for calibration and sample analysis, and the low level standard must be at or below the reporting limit.

10.4.2. It may be necessary to analyze more than one set of calibration standards to encompass all of the analytes required for same tests. For example, the Appendix IX list requires the Primary standard (Table 5) and the Appendix IX standard (Table 6).

10.4.3. Internal standard calibration is used. The internal standards are listed in Table 7. Target compounds should reference the nearest internal standard. Each calibration standard is analyzed and the response factor (RF) for each compound is calculated using the area response of the characteristic ions against the concentration for each compound and internal standard. See equation 1, Section 12, for calculation of response factor.

10.4.4. The % RSD of the calibration check compounds (CCC) must be less than 30%. Refer to Table 12 for the CCCs.

10.4.4.1. If none of the CCCs are required analytes, project specific calibration specifications must be agreed with the client.

10.4.5. The average RF must be calculated for each compound. A system performance check is made prior to using the calibration curve. The five system performance check compounds

(SPCC) are checked for a minimum average response factor. Refer to Table 11 for the SPCC compounds and required minimum response factors.

10.4.6. For any analyte with %RSD >15%, linear or quadratic curve fits may be used. The analyst should consider instrument maintenance to improve the linearity of response. If the % RSD is > 15%, the analyst may drop the low or high in the ICAL , as long as a minimum of 5 points are maintained (6 points for quadratic) and the quantitation range is adjusted accordingly. Otherwise the coefficient of determination, r^2 must be $\geq$ 0.990.

10.4.6.1. Refer to Section 17.2 for specific Ohio VAP criteria.

10.4.7. Weighting of data points

10.4.7.1. In a linear or quadratic calibration fit, the points at the lower end of the calibration curve have less weight in determining the curve generated than points at the high concentration end of the curve. However, in environmental analysis, accuracy at the low end of the curve is very important. For this reason it is preferable to increase the weighting of the lower concentration points. $1/Concentration^2$ weighting (often called $1/X^2$ weighting) will improve accuracy at the low end of the curve and should be used if the data system has this capability. The Y-intercept is evaluated to determine calibration acceptability.

10.4.8. If time remains in the 12-hour period initiated by the BFB injection before the initial calibration, samples may be analyzed. Otherwise, proceed to continuing calibration.

10.4.9. The calibration standards for the initial 5-point calibration for low level soils that are not preserved in sodium bisulfate (i.e. are preserved by freezing, or not preserved) must be heated to 40°C for purging. Using this calibration curve for water samples is acceptable as long as all calibration, QC, and samples are also heated to 40°C. A separate five point calibration must be prepared for analysis of low level soils that are preserved with sodium bisulfate. Low level soils analysis requires the use of a closed vial autosampler such as the Varian Archon, O.I. 4552 or Tekmar Precept. Each standard for analysis of sodium bisulfate preserved samples is prepared by spiking the methanolic standard solution through the septum of a VOA vial containing 5 mL of water and 1 g sodium bisulfate. The standards are heated to 40°C for purging. All low-level soil samples, standards, and blanks must also be heated to 40°C for purging.

10.4.10. Non-standard analytes are sometimes requested. For these analytes, it is acceptable to analyze a single standard at the reporting limit with each continuing calibration rather than a five point initial calibration. If the analyte is detected in any of the samples, a five point initial calibration must be generated and the sample(s) reanalyzed for quantitation. However, if the analyte is not detected, the non-detect may be reported and no further action is necessary.

Note: This procedure may not be used for Ohio VAP samples.

10.4.11. Calibration accuracy is verified by analyzing a second source standard (ICV) immediately after the initial calibration. The recovery for CCC compounds must be ≤ 20%. The recovery for non-CCC compounds must be ≤ 50% with an allowance of up to six compounds > 50%.

10.5. Continuing Calibration: The initial calibration must be verified every twelve hours.

10.5.1. Continuing calibration begins with analysis of BFB as described in Section 10.3. If the system tune is acceptable, the continuing calibration standard(s) are analyzed. A midpoint calibration standard is used as the continuing calibration.

10.5.2. The RF data from the standards are compared with the average RF from the initial five-point calibration to determine the percent drift of the CCC compounds. The calculation is given in equation 4, Section 12.3.4.

10.5.3. The % drift of the CCCs must be ≤ 20% for the continuing calibration to be valid. The SPCCs are also monitored. The SPCCs must meet the criteria described in Table 11. In addition, the % drift of all analytes must be ≤ 50% with allowance for up to six target analytes to have % drift > 50%.

10.5.3.1. If none of the CCCs are required analytes, project specific calibration specifications must be agreed with the client.

10.5.3.2. Refer to Table 12 for specific Ohio VAP analytes.

10.5.4. If the CCCs and or the SPCCs do not meet the criteria in Sections 10.5.3 and 10.5.4, the system must be evaluated and corrective action must be taken. The BFB tune and continuing calibration must be acceptable before analysis begins. Extensive corrective action such as a different type of column will require a new initial calibration.

10.5.5. Once the above criteria have been met, sample analysis may begin. **Initial calibration average RFs (or the calibration curve) will be used for sample quantitation, not the continuing calibration RFs.** Analysis may proceed until 12 hours from the injection of the BFB have passed. (A sample *desorbed* less than or equal to 12 hours after the BFB is acceptable.)

11. PROCEDURE

11.1. Procedural Variations

11.1.1. One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation shall be completely documented using a Non-Conformance Memo and approved by a Supervisor or Group Leader and QA Manager. If contractually required, the client shall be notified. The Non-Conformance Memo shall be filed in the project file.

11.1.2. Any unauthorized deviations from this procedure must also be documented as a non-conformance, with a cause and corrective action described.

11.2. Preliminary Evaluation

11.2.1. Where possible, samples are screened by headspace or GC/MS off-tune analysis to determine the correct aliquot for analysis. Alternatively, an appropriate aliquot can be determined from sample histories.

11.2.2. Dilutions should be done just prior to the GC/MS analysis of the sample. Dilutions are made in a Luerlok syringe. Calculate the volume of reagent water required for the dilution. Fill the syringe with reagent water, compress the water to vent any residual air and adjust the water volume to the desired amount. Adjust the plunger to the mark and inject the proper aliquot of sample into the syringe. If the dilution required would use less than 1 µL of sample then serial dilutions must be made in volumetric flasks.

11.2.2.1. The diluted concentration is to be estimated to be in the upper half of the calibration range.

11.3. Sample Analysis Procedure

11.3.1. All analysis conditions for samples must be the same as for the continuing calibration standards (including purge time and flow, desorb time and temperature, column temperatures, multiplier setting etc.).

11.3.2. All samples must be analyzed as part of a batch. The batch is a set of up to 20 samples of the same matrix processed using the same procedures and reagents within the same time period. The batch also must contain a MS/MSD, a LCS, and a method blank.

11.3.2.1. If there is insufficient time in the 12-hour tune period to analyze 20 samples, the batch may be continued into the next tune period. However, if any re-tuning of the instrument is necessary, or if a period of greater than 24 hours from the preceding BFB tune has passed, a new batch must be started. For medium level soils the batch is defined at the sample preparation stage.

11.3.2.2. It is not necessary to reanalyze batch QC with reanalyses of samples. However, any reruns must be as part of a valid batch.

11.4. Water Samples

11.4.1. All samples and standard solutions must be at ambient temperature before analysis.

11.4.2. Fill a syringe with the sample. If a dilution is necessary it may be made in the syringe if the sample aliquot is $\geq$ 5 µL. Check and document the pH of the remaining sample.

11.4.3. Add 250 ng of each internal and surrogate standard (5 µL of a 50 µg/mL solution, refer to Tables 7and 8). The internal standards and the surrogate standards may be mixed and added as one spiking solution (this results in a 50 µg/L solution for a 5 mL sample, and a 10 µg/L solution for a 25 mL sample). Inject the sample into the purging chamber.

11.4.3.1. For TCLP samples use 1 mL of TCLP leachate with 4 mL reagent water. (Note that TCLP reporting limits will be 5 times higher than the corresponding aqueous limits).

11.4.4. Purge the sample for eleven minutes (the trap must be below 35°C).

11.4.5. After purging is complete, desorb the sample, start the GC temperature program, and begin data acquisition. After desorption, bake the trap for approximately 3-10 minutes to condition it for the next analysis. When the trap is cool, it is ready for the next sample.

11.4.6. Desorb and bake time and temperature are optimized for the type of trap in use. The same conditions must be used for samples and standards.

11.5. Methanol Extract Soils

11.5.1. Rinse a gas-tight syringe with organic free water. Fill the syringe with the same volume of organic free water as used in the calibrations. Add no more than 2% (v/v) (100 µL for a 5 mL purge) methanolic extract (from Section 8.5 or 8.6) to the syringe. Add internal standard (if used). Load the sample onto the purge and trap device and analyze as for aqueous samples. If less than 1µL of methanolic extract is to be added to the water, dilute the methanolic extract such that a volume greater than 1µL will be added to the water in the syringe. Refer to Section 17.5 for Michigan project requirements.

11.6. Liquid wastes that are soluble in methanol and insoluble in water.

11.6.1. Pipet 1 mL of the sample into a tared vial. Use a top-loading balance. Record the weight to the nearest 0.1 gram.

11.6.2. Quickly add 4 mL of methanol, then add 5µL of a 2500 µg/mL surrogate spiking solution to bring the final volume to 5 mL. Cap the vial and shake for 2 minutes to mix thoroughly. For a MS/MSD or LCS, 4.9 mL of methanol, 5µL of a 2500 µg/mL surrogate spiking solution, and 0.1 mL of matrix spike solution is used.

11.6.3. Rinse a gas-tight syringe with organic free water. Fill the syringe with the same volume of organic free water as used in the calibrations. Add no more than 2% (v/v) (100 µL for a 5 mL purge) methanolic extract (from Section 8.5 or 8.6) to the syringe. Add internal standard (if used). Load the sample onto the purge and trap device and analyze as for aqueous samples. If less than 5µL of methanolic extract is to be added to the water, dilute the methanolic extract such that a volume greater than 1µL will be added to the water in the syringe.

11.7. Aqueous and Low level Soil Sample Analysis (Purge and Trap units that sample directly from the VOA vial)

11.7.1. Units which sample from the VOA vial should be equipped with a module which automatically adds surrogate and internal standard solution to the sample prior to purging the sample.

11.7.2. If the autosampler uses automatic IS/SS injection, no further preparation of the VOA vial is needed. Otherwise the internal and surrogate standards must be added to the vial. *Note:* Aqueous samples with high amounts of sediment present in the vial may not be suitable for analysis on this instrumentation, or they may need to analyzed as soils.

11.7.3. Soil samples, which are preserved with sodium bisulfate, must be quantitated against a curve prepared with standards containing about the same amount of sodium bisulfate as the samples (1 g in 5 mL).

11.7.4. Soil samples, which are preserved by freezing, must be allowed to thaw completely before sample analysis begins.

11.7.5. Sample remaining in the vial after sampling with one of these mechanisms is no longer valid for further analysis. A fresh VOA vial must be used for further sample analysis.

11.8. Low-Level Solids Analysis using discrete autosamplers, Method 8260A, 5030A.

Note: This technique may seriously underestimate analyte concentration and must not be used except at specific client request for the purpose of comparability with previous data. It is no longer part of SW-846.

This method is based on purging a heated soil/sediment sample mixed with reagent water containing the surrogates and internal standards. Analyze all reagent blanks and standards under the same conditions as the samples (e.g., heated). The calibration curve is also heated during analysis. Purge temperature is 40°C.

11.8.1. Do not discard any supernatant liquids. Mix the contents of the container with a narrow metal spatula.

11.8.2. Weigh out 5 g (or other appropriate aliquot) of sample into a disposable culture tube or other purge vessel. Record the weight to the nearest 0.1 g. If method sensitivity is demonstrated, a smaller aliquot may be used. Do not use aliquots less than 0.5 g. If the sample is contaminated with analytes such that a purge amount less than 0.5 g is appropriate, use the medium level method. For the medium level method, add 5g soil to 5 mL methanol containing the surrogates, mix for two minutes, allow to settle then remove a portion of the methanol and store in a clean Teflon capped vial at 4°C until analysis. Analyze as described in section 11.5.

11.8.3. Connect the purge vessel to the purge and trap device.

11.8.4. Rinse a 5 mL gas-tight syringe with organic free water, and fill. Compress to 5 mL. Add surrogate/internal standard (and matrix spike solutions if required.). Add directly to the sample from 11.5.1.

11.8.5. The above steps should be performed rapidly and without interruption to avoid loss of volatile organics.

11.8.6. Add the heater jacket or other heating device and start the purge and trap unit.

11.8.7. Soil samples that have low IS recovery when analyzed (<50%) should be reanalyzed once to confirm matrix effect.

11.9. Medium-Level Soil/Sediment and Waste Samples

11.9.1. Sediments/soils and waste that are insoluble in methanol.

11.9.1.1. Sediments/soils and waste that are insoluble in methanol.

11.9.1.1.1. Gently mix the contents of the sample container with a narrow metal or wood spatula. Weigh 5 g (wet weight) into a tared vial. Use a top-loading balance. Record the weight to 0.1 gram. Do not discard any supernatant liquids.

11.9.1.1.2. Quickly add 5 mL of methanol, and 5µL of 2500 µg/mL

surrogate spiking solution to bring the final volume of methanol to 5 mL. For an LCS or MS/MSD sample add 4.9 mL of methanol, 5µL of surrogate spike solution, and 0.1 mL of matrix spike solution. Cap the vial and shake or vortex to mix thoroughly.

Note: Sections 11.9.1.1.1 and 11.9.1.1.2 must be performed rapidly and without interruption to avoid the loss of volatile organics.

11.10. Initial review and corrective actions

11.10.1. If the retention time for any internal standard in the continuing calibration changes by more than 0.5 minutes from the mid-level initial calibration standard, the chromatographic system must be inspected for malfunctions and corrected. Reanalysis of samples analyzed while the system was malfunctioning is required.

11.10.2. If the internal standard response in the continuing calibration is more than 200% or less than 50% of the response in the mid-level of the initial calibration standard, the chromatographic system must be inspected for malfunctions and corrected. Reanalysis of samples analyzed while the system was malfunctioning is required.

11.10.2.1. Any samples that do not meet the internal standard criteria for the continuing calibration must be evaluated for validity. If the change in sensitivity is a matrix effect, the sample is reanalyzed to confirm. If the change in sensitivity is due to instrumental problems all affected samples must be reanalyzed after the problem is corrected.

11.10.3. The surrogate standard recoveries are evaluated to ensure that they are within limits. Corrective action for surrogates out of control will normally be to reanalyze the affected samples. However, if the surrogate standard response is out high and there are no target analytes or tentatively identified compounds, reanalysis may not be necessary. Out of control surrogate standard response may be a matrix effect. It is only necessary to reanalyze a sample once, at the same dilution as the original run, to demonstrate matrix effect, but reanalysis at a dilution could be considered for severe matrix effect.

11.11. Dilutions

11.11.1 If the response for any compound exceeds the working range of the GC/MS system, a dilution of the extract is prepared and analyzed. An appropriate dilution should be in the upper half of the calibration range. Samples may be screened to determine the appropriate dilution for the initial run. If the initial diluted run has no hits or hits below 20% of the calibration range and the matrix allows for analysis at a lesser dilution, then the sample must be reanalyzed at a dilution targeted to bring the largest hit above 50% of the calibration range.

11.11.2Guidance for Dilutions Due to Matrix

11.11.2.1 If the sample is initially run at a dilution and the baseline rise is less than half the height of the internal standards, or if individual non target peaks are less than twice the height of the internal standards, then the sample should be reanalyzed at a more concentrated dilution. This requirement is approximate and subject to analyst judgement.

11.11.3Reporting Dilutions

11.11.3.1 The most concentrated dilution with no target compounds above the calibration range will be reported. Other dilutions will only be reported at client request.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Qualitative identification

12.1.1 An analyte is identified by retention time and by comparison of the sample mass spectrum with the mass spectrum of a standard of the suspected compound (standard reference spectrum). Mass spectra for standard reference may be obtained on the user's GC/MS by analysis of the calibration standards or from the NIST Library. Two criteria must be satisfied to verify identification: (1) elution of sample component at the same GC retention time as the standard component; and (2) correspondence of the sample component and the standard component characteristic ions. (Note: Care must be taken to ensure that spectral distortion due to co-elution is evaluated.)

- The sample component retention time must compare to within ± 0.2 min. of the retention time of the standard component. For reference, the standard must be run within the same twelve hours as the sample.

- The relative intensities of ions should agree to within ±30% between the standard and sample spectra. (Example: For an ion with an abundance of 50% in the standard spectra, the corresponding sample abundance must be between 20 and 80 percent.)

12.1.2 If a compound cannot be verified by all the above criteria, but in the technical judgment of the analyst, the identification is correct, then the analyst shall report that identification and proceed with quantitation.

12.2. Tentatively Identified Compounds (TICs)

12.2.1. If the client requests components not associated with the calibration standards, a search of

the NIST library may be made for the purpose of tentative identification. Guidelines are:

12.2.1.1. Relative intensities of major ions in the reference spectrum (ions > 10% of the most abundant ion) should be present in the sample spectrum.

12.2.1.2. The relative intensities of the major ions should agree to within 20%. (Example: If an ion shows an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30% and 70%).

12.2.1.3. Molecular ions present in the reference spectrum should be present in the sample spectrum.

12.2.1.4. Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.

12.2.1.5. Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the spectrum because of background contamination or coeluting peaks. (Data system reduction programs can sometimes create these discrepancies.)

12.2.1.6. Computer-generated library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other. Only after visual inspection of the sample with the nearest library searches should the analyst assign a tentative identification.

12.3. Calculations

12.3.1. Response factor (RF)

Equation 1

$$RF = \frac{A_x C_{is}}{A_{is} C_x}$$

Where:

A_x = Area of the characteristic ion for the compound to be measured

A_{is} = Area of the characteristic ion for the specific internal standard

C_{is} = Concentration of the specific internal standard, ng

C_x = Concentration of the compound being measured, ng

12.3.2. Standard deviation (SD):

Equation 2

$$SD = \sqrt{\sum_{i=1}^{N} \frac{(Xi - X)^2}{N - 1}}$$

Where:

X_i = Value of X at i through N

N = Number of points

X = Average value of X_I

12.3.3. Percent relative standard deviation (%RSD):

Equation 3

$$\%RSD = \frac{\textbf{Standard Deviation}}{\overline{RF_i}} \times 100$$

$\overline{RF_i}$ **= Mean of RF values in the curve**

12.3.4. Percent drift between the initial calibration and the continuing calibration:

Equation 4

$$\%\ \text{Drift} = \frac{C_{\text{expecte}} - C_{\text{found}}}{C_{\text{expecte}}} \times 100$$

Where:

$C_{expecte}$ = Known concentration in standard

C_{found} = Measured concentration using selected quantitation method

12.3.5. Target compound and surrogate concentrations:

12.3.5.1 Concentrations in the sample may be determined from linear or second order (quadratic) curve fitted to the initial calibration points, or from the average response factor of the initial calibration points. Average response factor may only be used when the % RSD of the response factors in the initial calibration is $\leq$ 15%.

12.3.5.2 Calculation of concentration using Average Response Factors:

Equation 5

$$\textbf{Concentration } \mu\text{g / L} = \frac{x}{RF}$$

12.3.5.3 Calculation of concentration using Linear fit:

Equation 6

$$\textbf{Concentration } \mu\text{g / L} = A + Bx$$

12.3.5.3. Calculation of concentration using Quadratic fit:

Equation 7

$$\textbf{Concentration } \mu\text{g / L} = A + Bx + Cx^2$$

x is defined in equations 8, 9 and 10
A is a constant defined by the intercept
B is the slope of the curve
C is the curvature

12.3.5.4. Calculation of x for Water and water-miscible waste:

Equation 8

$$x = \frac{(A_x)(I_s)(D_f)}{(A_{is})(V_o)}$$

Where:

X = ug/L

$\mathbf{A_x}$ = Area of characteristic ion for the compound being measured (secondary ion quantitation is allowed only when there are sample interferences with the primary ion)

$\mathbf{A_{is}}$ = Area of the characteristic ion for the internal standard

$\mathbf{I_s}$ = Amount of internal standard added in ng

$$\text{Dilution Factor} = D_f = \frac{\text{Total volume purged (mL)}}{\text{Volume of original sample used (mL)}}$$

$\mathbf{V_o}$ = Volume of water purged, mL

12.3.5.5. Calculation of x for Medium level soils:

Equation 9

$$x = \frac{(A_x)(I_s)(V_t)(1000)(D_f)}{(A_{is})(V_a)(W_s)(D)}$$

Where:

X = ug/kg

$\mathbf{A_x}$, $\mathbf{I_s}$, $\mathbf{D_f}$, $\mathbf{A_{is}}$, same as for water.

$\mathbf{V_t}$ = Volume of total extract, mL (Typically 25 mL)

$\mathbf{V_a}$ = Volume of extract added for purging, µL

$\mathbf{W_s}$ = Weight of sample extracted, g

$$\mathbf{D} = \frac{100 - \%\text{moisture}}{100}$$

12.3.5.6. Calculation of x for Low level soils:

Equation 10

$$x = \frac{(A_x)(I_s)}{(A_{is})(W_s)(D)}$$

Where:

X = ug/kg

$\mathbf{A_x}$, $\mathbf{I_s}$, $\mathbf{A_{is}}$, same as for water.

D is as for medium level soils

$\mathbf{W_s}$ = Weight of sample added to the purge vessel, g

12.3.5.7. Calculation of TICs: The calculation of TICs (tentatively identified compounds) is identical to the above calculations with the following exceptions:

$\mathbf{A_x}$ = Area in the total ion chromatogram for the compound being measured

$\mathbf{A_{is}}$ = Area of the total ion chromatogram for the nearest internal standard without interference

RF = 1

In other words, the concentration is equal to x as defined in equations 8, 9 and 10.

12.3.6. MS/MSD Recovery

Equation 11

$$\textbf{Matrix Spike Recovery, \%} = \frac{SSR - SR}{SA} \times 100$$

SSR = Spike sample result
SR = Sample result
SA = Spike added

12.3.7. Relative % Difference calculation for the MS/MSD:

Equation 12

$$\textbf{RPD} = \frac{|\textbf{MSR - MSDR}|}{\frac{1}{2}(\textbf{MSR + MSDR})} \times 100$$

Where:

RPD = Relative percent difference

MSR = Matrix spike result

MSDR = Matrix spike duplicate result

13. METHOD PERFORMANCE

13.1. Method Detection Limit

13.1.1. Generally, each laboratory must generate a valid method detection limit for each analyte of interest. The MDL must be below the reporting limit for each analyte. The procedure for determination of the method detection limit is given in 40 CFR Part 136, Appendix B, and further defined in QA Policy #: S-Q-003 and NC-QA-0021. When non-standard compounds are analyzed at client request, lesser requirements are possible with client agreement. At a minimum, a standard at the reporting limit must be analyzed to demonstrate the capability of the method. The non-standard compound must be detected in the reporting limit standard to be acceptable.

13.1.2. For non-standard analytes, a MDL study must be performed and calibration curve generated before analyzing any samples, unless lesser requirements are previously agreed to with the client. In any event, the minimum initial demonstration required is analysis of a standard at the reporting limit and a single point calibration.

13.2. Initial Demonstration

13.2.1. Each laboratory must have initial demonstration of performance data on file and corresponding method detection limit files.

13.3. Training Qualification

13.3.1. The Group/Team Leader has the responsibility to ensure that this procedure is performed by an analyst who has been properly trained in its use and has the required experience.

13.3.2. Method validation information (where applicable) in the form of laboratory demonstrations of capabilities is maintained for this method in the laboratory QA files.

14. POLLUTION PREVENTION

14.1. This method does not contain any specific modifications that serve to minimize or prevent pollution.

15. WASTE MANAGEMENT

15.1. Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices of STL. They must have training on the hazardous waste disposal practices upon initial assignment to these tasks, followed by an annual refresher training.

15.2. All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

15.3. The following waste streams are produced when this method is carried out.

15.3.1. **Acidic material from the auto-sampler**: Waste stream must be collected and neutralized before discharge to a sewer system if the pH is less than 4.

15.3.2. **Methanol waste from rinses and standards:** Methanol waste is discarded as a

flammable liquid in a solvent waste container identified as "Flammable Liquid Waste."

15.3.3. **All samples including purged and extracted soils and waters:** Samples are collected in boxes and removed from the lab to storage. The waste coordinator handles crushing the vials and proper disposal.

15.3.4. **Solid samples** - Stirbars are removed from the sample. The contents of the vial are poured into a beaker and the soil allowed to settle out. The soil is disposed of in the solid waste container.

16. REFERENCES

16.1. References

16.1.1. SW846, *Test Methods for Evaluating Solid Waste,* Third Edition, Gas Chromatography/Mass Spectrometry for Volatile Organics, Method 8260B, Update III, December 1996

16.1.2. SW846, *Test Methods for Evaluating Solid Waste,* Third Edition, Gas Chromatography/Mass Spectrometry for Volatile Organics, Method 8260A, Update II, September 1994.

16.1.3. SW846, *Test Methods for Evaluating Solid Waste,* Third Edition, Purge-and-Trap for Aqueous Samples, Method 5030B, Rev 2, December 1996.

16.1.4. SW846, *Test Methods for Evaluating Solid Waste,* Third Edition, Closed System Purge-and-Trap and Extraction for Volatile Organics in Soil and Waste Samples, Method 5035, Rev 0, December 1996.

16.1.5. Corporate Quality Management Plan (QMP), current version.

16.1.6. STL Laboratory Quality Manual (LQM), current version.

16.1.7. STL Corporate Safety Manual, M-E-0001 and STL North Canton Facility Addendum and Contingency Plan, current version.

16.2. Associated SOPs and Policies, latest version

16.2.1. QA Policy, QA-003

16.2.2. Glassware Washing, NC-QA-0014

16.2.3. Statistical Evaluation of Data and Development of Control Charts, NC-QA-0018

16.2.4. Method Detection Limits and Instrument Detection Limits, S-Q-003 and NC-QA-0021

16.2.5. Supplemental Practices for DoD Project Work, NC-QA-0016

16.2.6. Standards and Reagents, NC-QA-0017

16.2.7. Laboratory Holding Blanks, NC-QA-0020

17. MISCELLANEOUS

17.1. Modifications from the reference method

17.1.1. A retention time window of 0.2 minutes is used for all components, since some data systems do not have the capability of using the relative retention time units specified in the reference method.

17.1.2. The quantitation and qualifier ions for some compounds have been changed from those recommended in SW-846 in order to improve the reliability of qualitative identification.

17.2. The following are protocols that must be followed when analyzing OhioVAP samples:

- Sections 9.4 and 9.5: n-Hexane must be spiked and reported for both the LCS and MS/MSD.
- Sections 10.4.6: All analytes must have a %RSDs $\leq$ 15%. Corrective action must be completed for any compounds failing the <15% requirement.
- Section 11.1 is not to be performed.
- Section 11.10.2: For OhioVAP projects, the laboratory will reanalyze any sample where the internal standard fails and there is no evidence of matrix interference.

17.3. The following are protocols that must be followed when analyzing BP Oil – Lima Refinery RFI work plan.

- Section 8.1 STL will continue to follow the 14 day holding time specified in the Corporate SOP.
- Delete for this project Section 8.3 At specific client request, unpreserved soil samples may be accepted.
- Delete for this project Section 8.8.1 At specific client request unpreserved soils packed into

glass jars or brass tubes may be accepted and subsampled in the lab. This is the old procedure based on method 5030A. It is no longer included and is likely to generate results that are biased low, possibly by more than an order of magnitude.

- Modify Section 8.5 For the purpose of this project, the soil/methanol mixture may be stored for two days prior to analysis.

- Modify Section 8. For the purpose of this project, the soil/methanol mixture may be stored for two days prior to analysis.

- Modify (per discussion with Region V representative) to Section 10.4.6 Compounds with %RSD >15% are to be calibrated using an alternate calibration technique (e.g. linear or quadratic calibration curve). For poor responders, the alternate calibration technique requirements may not be met either. This sentence is added for those cases.If the correlation coefficient is < 0.990, then any hit for these compounds must be flagged as estimated.

- Modify Section 10.4.2 It is necessary to analyze the Appendix IX standard separately from the primary standard due to the presence of xylene solvent in the Appendix IX standard. Alternatively, STL will purchase the Appendix IX standard in a solvent other than xylene.

- Modify Section 10.4.9 For this project, this section will be modified to comply with the requirement of adding methanol to the calibration standards so that those standards contain the same amount of methanol as the diluted soil extracts.

- Modify Table 6

- For the project specific SOP, acetonitrile will be removed from table 6, page 49 and appended onto table 5, page 48. Acetonitrile will be calibrated as part of the STL primary standard, using a separate acetonitrile standard. This will ensure that the calibration curve for acetonitrile will be done free from any interference from allyl chloride.

17.4. The following are protocols that must be followed to achieve the lower reporting limits required when analyzing Michigan projects.

17.4.1. Modify Section 8.5.4 and 8.6.8 (add 25 uL of 2500 ug/mL surrogate solution for a nominal 25 g sample).

17.4.2. Modify Section 8.5.5 and 8.6.9 (add 500 uL of 50 ug/mL spike solution for a nominal 25 g sample).

17.4.3. Modify Section 8.5.6 and 8.6.10 (add 100 uL of 50 ug/mL spike solution for a nominal 25g sample).

17.4.4. Michigan reporting limits for methanol preserved soils are achieved by injecting 100 uL of the methanol extract in a 5 mL purge. The instrument is calibrated using the recommended

calibration levels in water of 0.5 ug/L, 1 ug/L, 5 ug/L, 10 ug/L, 20 ug/L, and 50 ug/L. Some analytes are prepared at higher concentrations.

17.4.5. Samples for Michigan projects frequently require calibration for 2-Methylnaphthalene. Recommended calibration levels for this compounds are 2 ug/L, 10 ug/L, 20 ug/L, 40 ug/L and 80 ug/L.

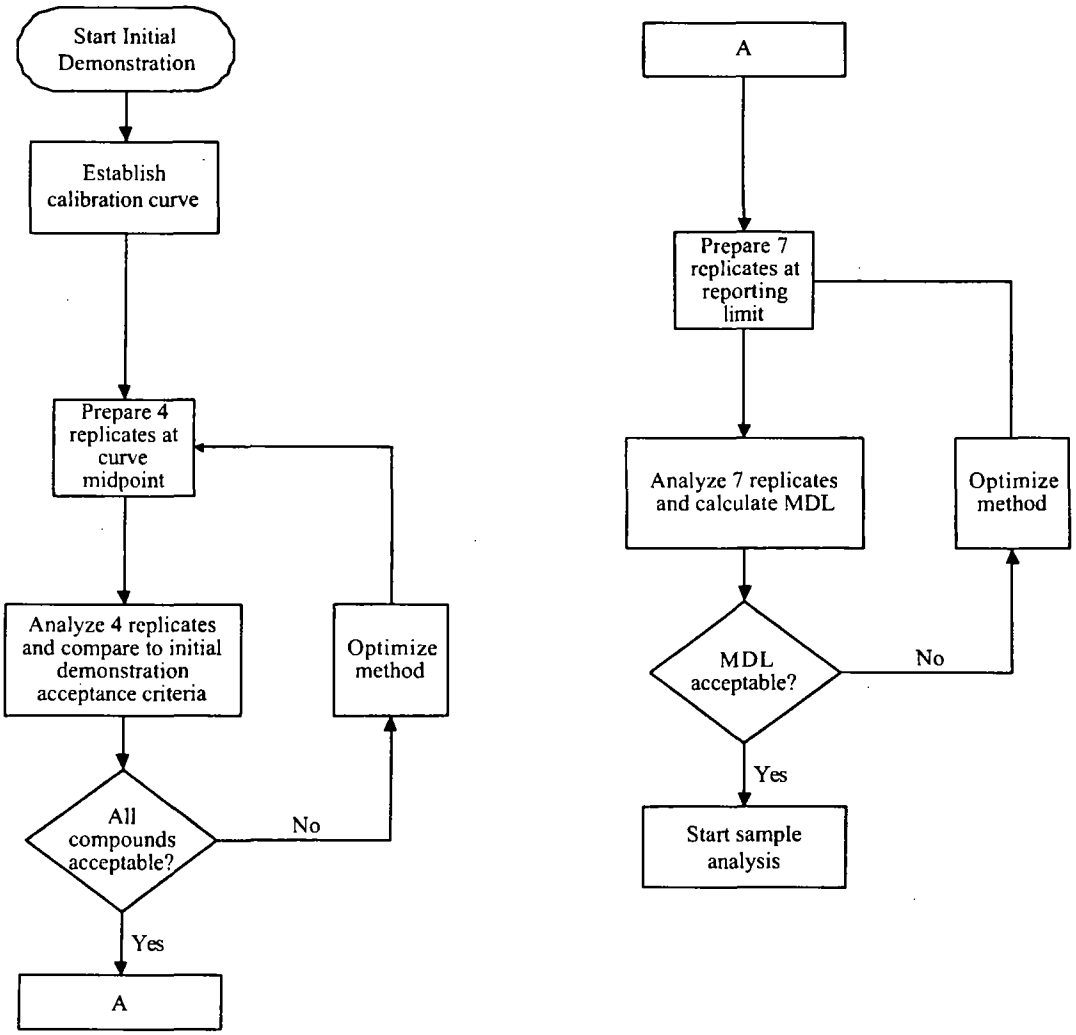


Table 1 - STL Primary Standard and Reporting Limits

Compound	CAS Number	Reporting Limits[1]				
		5 mL Water µg/L	Low Level 5 mL water µg/L	Low soil µg/kg	8260B/ 5035 Soil ug/kg	8260A 5030A Med Level Soil µg/kg
Dichlorodifluoromethane	75-71-8	5	1	5	250	1200
Chloromethane	74-87-3	5	1	5	250	1200
Bromomethane	74-83-9	5	1	5	250	1200
Vinyl chloride	75-01-4	5	1	5	250	1200
Chloroethane	75-00-3	5	1	5	250	1200
Trichlorofluoromethane	75-69-4	5	1	5	250	1200
Acrolein	107-02-8	100	20	100	5000	12000
Acetone	67-64-1	20	10	20	1000	2500
Trichlorotrifluoroethane	76-13-1	5	1	5	250	620
Iodomethane	74-88-4	5	1	5	250	620
Carbon disulfide	75-15-0	5	1	5	250	620
Methylene chloride	75-09-2	5	1	5	250	620
tert-Butyl alcohol	75-65-0	200	50	200	10,000	25000
1,1-Dichloroethene	75-35-4	5	1	5	250	620
1,1-Dichloroethane	75-34-3	5	1	5	250	620
trans-1,2-Dichlorocthene	156-60-5	5.0	1.0	5.0	250	310
Acrylonitrile	107-13-1	100	20	100	5000	12000
Methyl *tert*-butyl ether (MTBE)	1634-04-4	20	5	20	1000	2500
Hexane	110-54-3	5	1	5	250	620
cis-1,2-Dichloroethene	156-59-2	5	1	5	250	620
1,2-Dichloroethene (Total)	540-59-0	10	2	10	500	620
Tetrahydrofuran	109-99-9	20	5	20	1000	2500
Chloroform	67-66-3	5	1	5	250	620
1,2-Dichloroethane	107-06-2	5	1	5	250	620
Dibromomethane	74-95-3	5	1	5	250	620
2-Butanone	78-93-3	20	5	20	1000	2500
1,4-Dioxane	123-91-1	500	200	500	25000	62000
1,1,1-Trichloroethane	71-55-6	5	1	5	250	620
Carbon tetrachloride	56-23-5	5	1	5	250	620
Bromodichloromethane	75-27-4	5	1	5	250	620
1,2-Dichloropropane	78-87-5	5	1	5	250	620
cis-1,3-Dichloropropene	10061-01-5	5	1	5	250	620
Trichloroethene	79-01-6	5	1	5	250	620

Table 1 - STL Primary Standard and Reporting Limits

Compound	CAS Number	Reporting Limits[1]				
		5 mL Water µg/L	Low Level 5 mL water µg/L	Low soil µg/kg	8260B/ 5035 Soil ug/kg	8260A 5030A Med Level Soil µg/kg
Dibromochloromethane	124-48-1	5	1	5	250	620
1,2-Dibromoethane	106-93-4	5	1	5	250	620
1,2,3-Trichloropropane	96-18-4	5	1	5	250	620
1,1,2-Trichloroethane	79-00-5	5	1	5	250	620
Benzene	71-43-2	5	1	5	250	620
Ethylmethacrylate	97-63-2	5	1	5	250	620
trans-1,3-Dichloropropene	10061-02-6	5	1	5	250	620
Bromoform	75-25-2	5	1	5	250	620
4-Methyl-2-pentanone	108-10-1	20	5	20	1000	2500
2-Hexanone	591-78-6	20	5	20	1000	2500
Tetrachloroethene	127-18-4	5	1	5	250	620
Toluene	108-88-3	5	1	5	250	620
1,1,2,2-Tetrachloroethane	79-34-5	5	1	5	250	620
2-Chloroethyl vinyl ether	110-75-8	N/A[2]	N/A	50	1000	6200
Vinyl acetate	108-05-4	10	2	10	500	1200
Chlorobenzene	108-90-7	5	1	5	250	620
Ethylbenzene	100-41-4	5	1	5	250	620
Styrene	100-42-5	5	1	5	250	620
t-1,4-Dichloro-2-butene	110-57-6	5	1	5	250	620
m and p Xylenes		10	2	10	500	1200
o-xylene	95-47-6	5.0	1	5	250	620
Total xylenes	1330-20-7	10	2	10	500	1200
1,3-Dichlorobenzene	541-73-1	5	1	5	250	620
1,4-Dichlorobenzene	106-46-7	5	1	5	250	620
1,2-Dichlorobenzene	95-50-1	5	1	5	250	620
2,2-Dichloropropane	590-20-7	5	1	5	250	
Bromochloromethane	74-97-5	5	1	5	250	
1,1-Dichloropropene	563-58-6	5	1	5	250	
Bromodichloromethane	75-27-4	5	1	5	250	
1,2-Dichloropropane	78-87-5	5	1	5	250	
1,3-Dichloropropane	142-28-9	5	1	5	250	
Isopropylbenzene	98-82-8	5	1	5	250	
Bromobenzene	108-86-1	5	1	5	250	
n-Propylbenzene	103-65-1	5	1	5	250	
2-Chlorotoluene	95-49-8	5	1	5	250	

Table 1 - STL Primary Standard and Reporting Limits

Compound	CAS Number	Reporting Limits[1]				
		5 mL Water µg/L	Low Level 5 mL water µg/L	Low soil µg/kg	8260B/ 5035 Soil ug/kg	8260A 5030A Med Level Soil µg/kg
4-Chlorotoluene	106-43-4	5	1	5	250	
1,3,5-Trimethylbenzene	108-67-8	5	1	5	250	
Tert-Butylbenzene	98-06-6	5	1	5	250	
1,2,4-Trimethylbenzene	95-63-6	5	1	5	250	
Sec-butylbenzene	135-98-8	5	1	5	250	
4-Isopropyltoluene	99-87-6	5	1	5	250	
n-Butylbenzene	104-51-8	5	1	5	250	
1,2,4-Trichlorobenzene	120-82-1	5	1	5	250	
Napthalene	91-20-3	5	1	5	250	
Hexachlorobutadiene	87-68-3	5	1	5	250	
1,2,3-Trichlorobenzene	87-61-6	5	1	5	250	
Acetonitrile	75-05-8	100	20	100	5000	
Cyclohexane	110-82-7	10	1	10	500	
Methyl Acetate	79-20-9	10	10	10	500	
Methyl cyclohexane	108-87-2	10	1	10	500	

[1] Reporting limits listed for soil/sediment are based on wet weight. The reporting limits calculated by the laboratory for soil/sediment, calculated on dry weight basis, will be higher.

[2] 2-Chloroethyl vinyl ether cannot be reliably recovered from acid preserved samples

Table 2 - STL Primary Standard Calibration Levels, 5 mL purge

Compound	Calibration Level ug/L				
	Level 1	Level 2	Level 3	Level 4	Level 5
1,2-Dichloroethane-d4 (Surrogate)	5	20	50	100	200
Toluene-d8 (Surrogate)	5	20	50	100	200
4-Bromofluorobenzene (Surrogate)	5	20	50	100	200
Dichlorodifluoromethane	5	20	50	100	200
Chloromethane	5	20	50	100	200
Bromomethane	5	20	50	100	200
Vinyl chloride	5	20	50	100	200
Chloroethane	5	20	50	100	200
Trichlorofluoromethane	5	20	50	100	200
Acrolein	50	200	500	1000	2000
Acetone	5	20	50	100	200
Trichlorotrifluoroethane	5	20	50	100	200
Iodomethane	5	20	50	100	200
Carbon disulfide	5	20	50	100	200
Methylene chloride	5	20	50	100	200
tert-Butyl alcohol	100	400	1,000	2,000	4,000
1,1-Dichloroethene	5	20	50	100	200
1,1-Dichloroethane	5	20	50	100	200
trans-1,2-Dichloroethene	5	20	50	100	200
Acrylonitrile	50	200	500	1,000	2,000
Methyl *tert*-butyl ether (MTBE)	5	20	50	100	200
Hexane	5	20	50	100	200
cis-1,2-Dichloroethene	5	20	50	100	200
Tetrahydrofuran	5	20	50	100	200
Chloroform	5	20	50	100	200
1,2-Dichloroethane	5	20	50	100	200
Dibromomethane	5	20	50	100	200
2-Butanone	5	20	50	100	200
1,4-Dioxane	250	1000	2,500	5,000	10,000
1,1,1-Trichloroethane	5	20	50	100	200
Carbon tetrachloride	5	20	50	100	200
Bromodichloromethane	5	20	50	100	200
1,2-Dichloropropane	5	20	50	100	200
cis-1,3-Dichloropropene	5	20	50	100	200
Trichloroethene	5	20	50	100	200
Dibromochloromethane	5	20	50	100	200

Table 2 - STL Primary Standard Calibration Levels, 5 mL purge

Compound	Calibration Level ug/L				
	Level 1	Level 2	Level 3	Level 4	Level 5
1,2-Dibromoethane	5	20	50	100	200
1,2,3-Trichloropropane	5	20	50	100	200
Acetonitrile	50	200	500	1000	2000
1,1,2-Trichloroethane	5	20	50	100	200
Benzene	5	20	50	100	200
Ethylmethacrylate	5	20	50	100	200
trans-1,3-Dichloropropene	5	20	50	100	200
Bromoform	5	20	50	100	200
4-Methyl-2-pentanone	5	20	50	100	200
2-Hexanone	5	20	50	100	200
Tetrachloroethene	5	20	50	100	200
Toluene	5	20	50	100	200
1,1,2,2-Tetrachloroethane	5	20	50	100	200
2-Chloroethyl vinyl ether	10	40	100	200	400
Vinyl acetate	5	20	50	100	200
Chlorobenzene	5	20	50	100	200
Ethylbenzene	5	20	50	100	200
Styrene	5	20	50	100	200
t-1,4-Dichloro-2-butene	5	20	50	100	200
m and p Xylenes	10	40	100	200	400
o-xylene	5	20	50	100	200
1,3-Dichlorobenzene	5	20	50	100	200
1,4-Dichlorobenzene	5	20	50	100	200
1,2-Dichlorobenzene	5	20	50	100	200
2,2-Dichloropropane	5	20	50	100	200
Bromochloromethane	5	20	50	100	200
1,1-Dichloropropene	5	20	50	100	200
Bromodichloromethane	5	20	50	100	200
1,2-Dichloropropane	5	20	50	100	200
1,3-Dichloropropane	5	20	50	100	200
Isopropylbenzene	5	20	50	100	200
Bromobenzene	5	20	50	100	200
n-Propylbenzene	5	20	50	100	200
2-Chlorotoluene	5	20	50	100	200
4-Chlorotoluene	5	20	50	100	200
1,3,5-Trimethylbenzene	5	20	50	100	200
tert-Butylbenzene	5	20	50	100	200
1,2,4-Trimethylbenzene	5	20	50	100	200
sec-butylbenzene	5	20	50	100	200
4-Isopropyltoluene	5	20	50	100	200

Table 2 - STL Primary Standard Calibration Levels, 5 mL purge

Compound	Calibration Level ug/L				
	Level 1	Level 2	Level 3	Level 4	Level 5
n-Butylbenzene	5	20	50	100	200
1,2,4-Trichlorobenzene	5	20	50	100	200
Napthalene	5	20	50	100	200
Hexachlorobutadiene	5	20	50	100	200
1,2,3-Trichlorobenzene	5	20	50	100	200

Table 2A - STL Primary Standard Calibration Levels, Low Level [1]

Compound	Calibration Level ug/L				
	Level 1	Level 2	Level 3	Level 4	Level 5
Dibromofluoromethane (Surrogate)	1	5	10	20	40
1,2-Dichloroethane-d4 (Surrogate)	1	5	10	20	40
Toluene-d8 (Surrogate)	1	5	10	20	40
Bromofluorobenzene (Surrogate)	1	5	10	20	40
Dichlorodifluoromethane	1	5	10	20	40
Chloromethane	1	5	10	20	40
Vinyl Chloride	1	5	10	20	40
Bromomethane	1	5	10	20	40
Chloroethane	1	5	10	20	40
Trichlorofluoromethane	1	5	10	20	40
Acrolein	10	50	100	200	400
Acetone	2	10	20	40	80
1,1-Dichloroethene	1	5	10	20	40
Trichlorotrifluoroethane	1	5	10	20	40
Iodomethane	1	5	10	20	40
Carbon Disulfide	1	5	10	20	40
Methylene Chloride	1	5	10	20	40
Acetonitrile	10	50	100	200	400
Acrylonitrile	10	50	100	200	400
Methyl tert-butyl ether	1	5	10	20	40
trans-1,2-Dichloroethene	1	5	10	20	40
Hexane	1	5	10	20	40
Vinyl acetate	1	5	10	20	40
1,1-Dichloroethane	1	5	10	20	40
tert-Butyl Alcohol	20	100	200	400	800
2-Butanone	2	10	20	40	80
cis-1,2-dichloroethene	1	5	10	20	40
2,2-Dichloropropane	1	5	10	20	40
Bromochloromethane	1	5	10	20	40
Chloroform	1	5	10	20	40
Tetrahydrofuran	1	5	10	20	40
1,1,1-Trichloroethane	1	5	10	20	40
1,1-Dichloropropene	1	5	10	20	40
Carbon Tetrachloride	1	5	10	20	40
1,2-Dichloroethane	1	5	10	20	40
Benzene	1	5	10	20	40
Trichloroethene	1	5	10	20	40
1,2-Dichloropropane	1	5	10	20	40
1,4-Dioxane	50	250	500	1000	2000

Table 2A - STL Primary Standard Calibration Levels, Low Level [1]

Compound	Calibration Level ug/L				
	Level 1	Level 2	Level 3	Level 4	Level 5
Dibromomethane	1	5	10	20	40
Bromodichloromethane	1	5	10	20	40
2-Chloroethyl vinyl ether	2	10	20	40	80
cis-1,3-Dichloropropene	1	5	10	20	40
4-Methyl-2-pentanone	2	10	20	40	80
Toluene	1	5	10	20	40
trans-1,3-Dichloropropene	1	5	10	20	40
Ethyl Methacrylate	1	5	10	20	40
1,1,2-Trichloroethane	1	5	10	20	40
1,3-Dichloropropane	1	5	10	20	40
Tetrachloroethene	1	5	10	20	40
2-Hexanone	2	10	20	40	80
Dibromochloromethane	1	5	10	20	40
1,2-Dibromoethane	1	5	10	20	40
Chlorobenzene	1	5	10	20	40
1,1,1,2-Tetrachloroethane	1	5	10	20	40
Ethylbenzene	1	5	10	20	40
m + p-Xylene	2	10	20	40	80
Xylene-o	1	5	10	20	40
Styrene	1	5	10	20	40
Bromoform	1	5	10	20	40
Isopropylbenzene	1	5	10	20	40
1,1,2,2-Tetrachloroethane	1	5	10	20	40
1,4-Dichloro-2-butene	1	5	10	20	40
1,2,3-Trichloropropane	1	5	10	20	40
Bromobenzene	1	5	10	20	40
n-Propylbenzene	1	5	10	20	40
2-Chlorotoluene	1	5	10	20	40
1,3,5-Trimethylbenzene	1	5	10	20	40
4-Chlorotoluene	1	5	10	20	40
tert-Butylbenzene	1	5	10	20	40
1,2,4-Trimethylbenzene	1	5	10	20	40
sec-Butylbenzene	1	5	10	20	40
4-Isopropyltoluene	1	5	10	20	40
1,3-Dichlorobenzene	1	5	10	20	40
1,4-Dichlorobenzene	1	5	10	20	40
n-Butylbenzene	1	5	10	20	40
1,2-Dichlorobenzene	1	5	10	20	40
1,2-Dibromo-3-chloropropane	1	5	10	20	40
1,2,4-Trichlorobenzene	1	5	10	20	40

Table 2A - STL Primary Standard Calibration Levels, Low Level [1]

Compound	Calibration Level ug/L				
	Level 1	Level 2	Level 3	Level 4	Level 5
Hexachlorobutadiene	1	5	10	20	40
Naphthalene	1	5	10	20	40
1,2,3-Trichlorobenzene	1	5	10	20	40
Cyclohexane	1	5	10	20	40
Methyl Acetate	2	10	20	40	80
Methylcyclohexane	1	5	10	20	40
1,3,5-Trichlorobenzene	1	5	10	20	40

[1] 25 mL purge samples analyzed at 5 mL purge on more sensitive equipment.

Table 3 - STL Appendix IX Standard and Reporting Limits, 5 mL purge

Compound	CAS Number	Reporting Limits			
		5 mL Water µg/L	Low Level 5mL purge water µg/L	Low Soil µg/kg	Medium Soil µg/mL
Allyl Chloride	107-05-1	10	2	10	500
Dichlorofluoromethane	75-43-4	10	2	10	500
Isopropyl ether	108-20-3	10	2	10	500
Chloroprene	126-99-8	5	2	5	250
n-Butanol	71-36-3	200	50	200	10,000
Propionitrile	107-12-0	20	4	20	1000
Methacrylonitrile	126-98-7	5	2	5	250
Isobutanol	78-83-1	200	50	200	10,000
Methyl methacrylate	80-62-6	5	2	5	250
1,1,1,2-Tetrachloroethane	630-20-6	5	1	5	250
1,2-Dibromo-3-chloropropane	96-12-8	10	2	10	500
Ethyl ether	60-29-7	10	2	10	500
Ethyl Acetate	141-78-6	20	4	20	1,000
2-Nitropropane	79-46-9	10	4	10	500
Cyclohexanone	108-94-1	50	20	50	2500
Isopropylbenzene	98-82-8	5	1	5	250
2-Methylnaphthalene (Michigan only)	91-57-6	NA	5	NA	330

Table 4

Recommended/STL Appendix IX Standard Calibration Levels, µg/L

Compound	Level 1	Level 2	Level 3	Level 4	Level 5
Allyl Chloride	5	20	50	100	200
Dichlorofluoromethane	5	20	50	100	200
Isopropyl ether	5	20	50	100	200
Chloroprene	5	20	50	100	200
n-Butanol	100	400	1,000	2,000	4,000
Propionitrile	10	40	100	200	400
Methacrylonitrile	5	20	50	100	200
Isobutanol	100	400	1,000	2,000	4,000
Methyl methacrylate	5	20	50	100	200
1,1,1,2-Tetrachloroethane	5	20	50	100	200
1,2-Dibromo-3-chloropropane	10	40	100	200	400
Ethyl ether	5	20	50	100	200
Ethyl Acetate	10	40	100	200	400
2-Nitropropane	10	40	100	200	400
Cyclohexanone	50	200	500	1,000	2,000
2-Methylnaphthalene (Michigan only)	2	10	20	40	80

Table 5 - Reportable Analytes for STL Standard Tests, Primary Standard

Compound	CAS Number	STL Standard List	TCLP	TCL	Appendix IX
Dichlorodifluoromethane	75-71-8			X	X
Chloromethane	74-87-3	X		X	X
Bromomethane	74-83-9	X		X	X
Vinyl chloride	75-01-4	X	X	X	X
Chloroethane	75-00-3	X		X	X
Trichlorofluoromethane	75-69-4			X	X
Acrolein	107-02-8				X
Acetone	67-64-1	X		X	X
Trichlorotrifluoroethane	76-13-1				
Iodomethane	74-88-4				X
Carbon disulfide	75-15-0	X		X	X
Methylene chloride	75-09-2	X		X	X
tert-Butyl alcohol	75-65-0				
1,1-Dichloroethene	75-35-4	X	X	X	X
1,1-Dichloroethane	75-34-3	X		X	X
trans-1,2-Dichloroethene	156-60-5	X		X	X
Total 1,2-Dichloroethene		X		X	X
Acrylonitrile	107-13-1				X
Methyl *tert*-butyl ether (MTBE)	1634-04-4			X	
Hexane	110-54-3				
cis-1,2-Dichloroethene	156-59-2	X		X	
Tetrahydrofuran	109-99-9				
Chloroform	67-66-3	X	X	X	X
1,2-Dichloroethane	107-06-2	X	X	X	X
Dibromomethane	74-95-3				X
2-Butanone	78-93-3	X	X	X	X
1,4-Dioxane	123-91-1				X
1,1,1-Trichloroethane	71-55-6	X		X	X
Carbon tetrachloride	56-23-5	X	X	X	X
Bromodichloromethane	75-27-4	X		X	X
1,2-Dichloropropane	78-87-5	X		X	X
cis-1,3-Dichloropropene	10061-01-5	X		X	X
Trichloroethene	79-01-6	X	X	X	X
Dibromochloromethane	124-48-1	X		X	X
1,2-Dibromoethane	106-93-4			X	X
1,2,3-Trichloropropane	96-18-4				X
1,1,2-Trichloroethane	79-00-5	X		X	X
Benzene	71-43-2	X	X	X	X
Ethylmethacrylate	97-63-2				X
trans-1,3-Dichloropropene	10061-02-6	X		X	X

Table 5 - Reportable Analytes for STL Standard Tests, Primary Standard

Compound	CAS Number	STL Standard List	TCLP	TCL	Appendix IX
Bromoform	75-25-2	X		X	X
4-Methyl-2-pentanone	108-10-1	X		X	X
2-Hexanone	591-78-6	X		X	X
Tetrachloroethene	127-18-4	X	X	X	X
Toluene	108-88-3	X		X	X
1,1,2,2-Tetrachloroethane	79-34-5	X		X	X
2-Chloroethyl vinyl ether	110-75-8				
Vinyl acetate	108-05-4				X
Chlorobenzene	108-90-7	X	X	X	X
Ethylbenzene	100-41-4	X		X	X
Styrene	100-42-5	X		X	X
t-1,4-Dichloro-2-butene	110-57-6				X
m and p Xylenes		X		X	X
o-xylene	95-47-6	X		X	X
Total xylenes	1330-20-7	X		X	X
1,3-Dichlorobenzene	541-73-1	X		X	
1,4-Dichlorobenzene	106-46-7	X		X	
1,2-Dichlorobenzene	95-50-1	X		X	
Cyclohexane	110-82-7	X		X	
Methyl Acetate	79-20-9	X		X	
Methyl cyclohexane	108-87-2	X		X	
Isopropylbenzene	98-82-8			X	
1,2-Dibromo-3-chloropropane	96-12-8			X	X
1,2,4-Trichlorobenzene	120-82-1			X	
Acetonitrile	75-05-8				X
1,1,1,2-Tetrachloroethane	630-20-6				X
2,2-Dichloropropene	594-20-7				
Bromochloromethane	74-97-5				
1,1-Dichloropropene	563-58-6				
1,3-Dichloropropane	142-28-9				
Bromobenzene	108-86-1				
n-Propylbenzene	103-65-1				
2-Chlorotoluene	95-49-8				
1,3,5-Trimethylbenzene	108-67-8				
4-Chlorotoluene	106-43-4				
tert-Butylbenzene	98-06-6				
1,2,4-Trimethylbenzene	95-63-6				
sec-Butylbenzene	135-98-8				
4-Isopropyltoluene	99-87-6				
n-Butylbenzene	104-51-8				

Table 5 - Reportable Analytes for STL Standard Tests, Primary Standard

Compound	CAS Number	STL Standard List	TCLP	TCL	Appendix IX
Hexachlorobutadiene	87-68-3				
Naphthalene	91-20-3				
1,2,3-Trichlorobenzene	87-61-6				
1,3,5-Trichlorobenzene	108-70-3				

Table 6

Reportable Analytes for STL Standard Tests, Appendix IX standard

Compound	Number	Appendix IX
Allyl Chloride	107-05-1	X
Dichlorofluoromethane	75-43-4	
Isopropyl ether	108-20-3	
Chloroprene	126-99-8	X
n-Butanol	71-36-3	
Propionitrile	107-12-0	X
Methacrylonitrile	126-98-7	X
Isobutanol	78-83-1	X
Methyl methacrylate	80-62-6	X
Ethyl ether	60-29-7	
Ethyl Acetate	141-78-6	
2-Nitropropane	79-46-9	
Cyclohexanone	108-94-1	

Table 7 - Internal Standards

Compound	Standard Concentration µg/mL	Quantitation ion (5 mL purge)
Fluorobenzene	50	96
Chlorobenzene-d5	50	117
1,4-Dichlorobenzene-d4	50	152

Notes:

1) Except for medium level soils, the surrogate and internal standards may be combined in one solution.

Table 8 - Surrogate Standards

Surrogate Compounds	Standard Concentration µg/mL
1,2-Dichloroethane-d_4	50
Dibromofluoromethane	50
Toluene-d_8	50
4-Bromofluorobenzene	50

Notes:

1) Except for medium level soils, the surrogate and internal standards may be combined in one solution.

2) Recovery limits for surrogates are generated from historical data and are maintained by the QA Dept.

Table 9 - Matrix Spike / LCS Control Compounds

Compound	Standard Concentration µg /mL
1,1,1-Trichloroethane	50
1,1,2,2-Tetrachloroethane	50
1,1,2-Trichloro-1,2,2-trifluoroethane	50
1,1,2-Trichloroethane	50
1,1-Dichloroethane	50
1,1-Dichloroethene	**50**
1,1-Dichloropropene	50
1,2,3-Trichlorobenzene	50
1,2,3-Trichloropropane	50
1,2,4-Trichlorobenzene	50
1,2,4-Trimethylbenzene	50
1,2-Dibromo-3-chloropropane	50
1,2-Dibromoethane	50
1,2-Dichlorobenzene	50
1,2-Dichloroethane	50
1,2-Dichloroethene (total)	100
1,2-Dichloropropane	50
1,3,5-Trimethylbenzene	50
1,3-Dichlorobenzene	50
1,3-Dichloropropane	50
1,4-Dichlorobenzene	50
2,2-Dichloropropane	50
2-Butanone	50
2-Chloroethyl Vinyl Ether	100
2-Chlorotoluene	50
2-Hexanone	50
4-Chlorotoluene	50
4-Methyl-2-pentanone	50
Acetone	50
Acetonitrile	500
Acrolein	500
Acrylonitrile	500
Benzene	**50**
Bromobenzene	50
Bromochloromethane	50
Bromodichloromethane	50
Bromoform	50
Bromomethane	50
Carbon disulfide	50
Carbon tetrachloride	50
Chlorobenzene	**50**

Table 9 - Matrix Spike / LCS Control Compounds

Compound	Standard Concentration µg/mL
Chloroethane	50
Chloroform	50
Chloromethane	50
cis-1,2-Dichloroethene	50
cis-1,3-Dichloropropene	50
Cyclohexane	50
Dibromochloromethane	50
Dibromomethane	50
Dichlorodifluoromethane	50
Ethylbenzene	50
Hexachlorobutadiene	50
Iodomethane	50
Isopropylbenzene	50
Isopropylether	50
Methyl acetate	50
Methyl tert-butyl ether (MTBE)	50
Methylcyclohexane	50
Methylene chloride	50
Naphthalene	50
n-Butylbenzene	50
n-Hexane (Ohio VAP only)	50
n-Propylbenzene	50
p-Isopropyltoluene	50
sec-Butylbenzene	50
Styrene	50
tert-Butylbenzene	50
Tetrachloroethene	50
Toluene	**50**
trans-1,2-Dichloroethene	50
trans-1,2-Dichloroethene	50
trans-1,3-Dichloropropene	50
Trichloroethene	**50**
Trichlorofluoromethane	50
Vinyl Acetate	50
Vinyl chloride	50
Xylenes (total)	150

Notes: 1) 5 µL of the standard is added to the LCS or matrix spiked sample. This results in a concentration of each spike analyte in the sample of 50µg/L for a 5 mL purge or 10 µg/L for a 25 mL purge.

2) Recovery and precision limits for LCS and MS/MSD are generated from historical data and are maintained by QA Dept.

3) Analytes in **BOLD** denote control analytes.

Table 10 - BFB Key Ion Abundance Criteria

Mass	Ion Abundance Criteria
50	15% to 40% of Mass 95
75	30% to 60% of Mass 95
95	Base Peak, 100% Relative Abundance
96	5% to 9% of Mass 95
173	Less Than 2% of Mass 174
174	Greater Than 50% of Mass 95
175	5% to 9% of Mass 174
176	Greater Than 95%, But Less Than 101% of Mass 174
177	5% to 9% of Mass 176

Table 11 - SPCC Compounds and Minimum Response Factors

Compound	8260B, 8260A Min. RF
Chloromethane	0.100
1,1-Dichloroethane	0.100
Bromoform	0.100
1,1,2,2-Tetrachloroethane	0.300
Chlorobenzene	0.300

Table 12 - CCC compounds

Compound	Max. %RSD from Initial Calibration	Max. %D for continuing calibration
Vinyl Chloride	<30.0	<20.0
1,1-Dichloroethene	<30.0	<20.0
Chloroform	<30.0	<20.0
1,2-Dichloropropane	<30.0	<20.0
Toluene	<30.0	<20.0
Ethylbenzene	<30.0	<20.0
n-Hexane (Ohio VAP only)	<30.0	<20.0

Table 13 - Characteristic Ions

Compound	Primary*	Secondary	Tertiary
1,2-Dichloroethane-d_4 (Surrogate)	65	102	
Dichlorodifluoromethane	85	87	50, 101,103
Chloromethane	50	52	49
Vinyl chloride	62	64	61
Bromomethane	94	96	79
Chloroethane	64	66	49
Trichlorofluoromethane	101	103	66
1,1-Dichloroethene	96	61	98
Acrolein	56	55	58
Iodomethane	142	127	141
Carbon disulfide	76	78	
Trichlorotrifluoroethane	151	101	153
Acetone	43	58	
Methylene chloride	84	49	51, 86
tert-Butyl alcohol	59	74	
trans-1,2-Dichloroethene	96	61	98
Acrylonitrile	53	52	51
Methyl *tert* butyl ether	73		
Hexane	57	43	
1,1-Dichloroethane	63	65	83
cis-1,2-Dichloroethene	96	61	98
2-Butanone	43	72**	

Table 13 - Characteristic Ions

Compound	Primary*	Secondary	Tertiary
Tetrahydrofuran	42	71	
Chloroform	83	85	47
1,2-Dichloroethane	62	64	98
Dibromomethane	93	174	95, 172, 176
1,4-Dioxane	88	58	
Vinyl acetate	43	86	
1,1,1-Trichloroethane	97	99	117
Carbon tetrachloride	117	119	121
Benzene	78	52	77
Trichloroethene	130	95	97, 132
1,2-Dichloropropane	63	65	41
Bromodichloromethane	83	85	129
2-Chloroethyl vinyl ether	63	65	106
cis-1,3-Dichloropropene	75	77	39
trans-1,3-Dichloropropene	75	77	39
1,1,2-Trichloroethane	97	83	85, 99
Chlorodibromomethane	129	127	131
Bromoform	173	171	175, 252
1,2,3-Trichloropropane	75	110	77, 112, 97
Toluene-d_8 (Surrogate)	98	70	100
4-Bromofluorobenzene (Surrogate)	95	174	176
Toluene	91	92	65
4-Methyl-2-pentanone	43	58	57, 100
Tetrachloroethene	164	166	131
Ethyl methacrylate	69	41	99, 86, 114
2-Hexanone	43	58	57, 100
Chlorobenzene	112	114	77
Ethylbenzene	106	91	
Xylenes	106	91	
Styrene	104	103	78, 51, 77
Dichlorobenzene (all isomers)	146	148	111
trans 1,4-Dichloro-2-butene	53	75	89, 77, 124
1,1,2,2-Tetrachloroethane	83	85	131, 133
Allyl Chloride	76	41	78
Acetonitrile	40	41	
Dichlorofluoromethane	67	69	
Isopropyl ether	87	59	45
Chloroprene	53	88	90
n-Butanol	56	41	42
Propionitrile	54	52	55
Methacrylonitrile	41	67	52

Table 13 - Characteristic Ions

Compound	Primary*	Secondary	Tertiary
Isobutanol	41	43	74
Methyl methacrylate	41	69	100
1,1,1,2-Tetrachloroethane	131	133	119
1,2-Dibromo-3-chloropropane	157	155	75
Ethyl ether	59	74	
Ethyl Acetate	43	88	61
2-Nitropropane	41	43	46
Cyclohexanone	55	42	98
Isopropylbenzene	105	120	
Cyclohexane	56	69	84
Methyl Acetate	43	74	
Methyl cyclohexane	83	55	98

* The primary ion should be used for quantitation unless interferences are present, in which case a secondary ion may be used.

** m/z 43 may be used for quantitation of 2-Butanone, but m/z 72 must be present for positive identification.

TestAmerica

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TestAmerica North Canton

SOP No. CORP-OP-0001NC, Rev. 4.2
Effective Date: 01/30/06
Cover Page

Title: Extraction and Cleanup of Organic Compounds From Waters and Soils

[Methods: UPDATE III SW846 3500-Ser., 3600-Ser., 8151A, & 600-Ser.]

Approvals (Signature/Date):

Technology Specialist	Date	Health & Safety Coordinator	Date
Quality Assurance Manager	Date	Laboratory Director	Date
Technical Director	Date		

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Implementation Date: 2-1-06

SOP No: CORP-OP-0001NC
Revision No: 4.2
Revision Date: 01/30/06
Page 1 of 34

STL NORTH CANTON STANDARD OPERATING PROCEDURE

TITLE: **EXTRACTION OF ORGANIC COMPOUNDS FROM WATERS AND SOILS, BASED ON SW-846 3500 SERIES, 3600 SERIES, AND 600 SERIES METHODS.**

(SUPERSEDES: Revision 4.1, Dated 10/07/03)

Reviewed by: _____ 2-1-06
Date

Approved by: Quality Assurance Manager _____ 2/1/06
Date

Approved by: Environmental Health and Safety Coordinator _____ 2-1-06
Date

Approved by: Laboratory Director _____ 2/1/06
Date

Approved by: Technical Director _____ 2/1/06
Date

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1. SCOPE AND APPLICATION

This SOP describes procedures for preparation (extraction) of semivolatile organic analytes in aqueous, TCLP leachate, and soil matrices for analysis by Gas Chromatography (GC) and Gas Chromatography / Mass Spectrometry (GC/MS). The procedures are based on SW-846 and 600 series methodology and are applicable for measurements made to comply with the Resource Conservation and Recovery Act (RCRA) and for wastewater testing.

1.1. Extraction procedures for the following determinative methods are covered:
8081A, 8082, 8141A, 8270C, 8310, 8015B, 608, 610, and 625

1.2. The extraction procedures here may be appropriate for other determinative methods when appropriate spiking mixtures are used.

1.3. Other extraction procedures (PFE, SPE, etc.) may be used but are not currently covered in this SOP.

1.4. The applicable LIMS method codes are: P2 (8141A), QJ (8081A), QL (8270C), SG (8310), DM (608), VT (610), DP (625), KI (8015B)

2. SUMMARY OF METHOD

2.1. Separatory Funnel Extraction

A measured volume of sample, typically 1 liter, is adjusted, if necessary, to a specified pH and serially extracted with methylene chloride using a separatory funnel.

2.2. Continuous Liquid/Liquid Extraction

A measured volume of sample, typically 1 liter, is placed into a continuous liquid/liquid extractor, adjusted, if necessary, to a specific pH and extracted with the appropriate solvent for 18-24 hours.

2.3. Sonication Extraction

A measured weight of sample, typically 30 g, is mixed with anhydrous sodium sulfate to form a free flowing powder. This is solvent extracted three times using an ultrasonic horn.

2.4. Soxhlet Extraction (Accelerated and Traditional)

A 30 g sample is mixed with anhydrous sodium sulfate to form a free flowing powder. This is extracted with refluxing solvent.

2.5. Concentration

Procedures are presented for drying and concentration of the extract to final volume for analysis.

3. DEFINITIONS

3.1. Definitions of terms used in this SOP may be found in the glossary of the STL North Canton Laboratory Quality Manual (LQM), current version .

4. INTERFERENCES

4.1. Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus. All these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. Specific selection of reagents may be required to avoid introduction of contaminants.

4.2. Visual interferences or anomalies (such as foaming, emulsions, odor, etc.) must be documented.

5. SAFETY

5.1. Employees must abide by the policies and procedures in the Corporate Safety Manual, Lab Specific Addendum to the CSM, and this document.

5.2. Eye protection that protects against splash, laboratory coat and appropriate gloves must be worn while samples, standards, solvents and reagents are being handled. Disposable gloves that have become contaminated will be removed and discarded, other gloves will be cleaned immediately.

5.3. The following analytes have been tentatively classified as known or suspected, human or mammalian carcinogens: benzo(a)anthracene, benzidine, 3,3'dichlorobenzindine, benzo(a)pyrene, alpha-BHC, beta-BHC, gamma-BHC, delta-BHC, dibenz(a,h)anthracene, N-nitrosodimethylamine, 4,4'-DDT, and polychlorinated biphenyl compounds. Primary standards of these toxic compounds should be prepared in hood.

5.4. The following is a list of the materials used in this method, which have a serious or significant hazard rating. NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table. A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Methylene Chloride	Carcinogen Irritant	25 ppm-TWA 125 ppm-STEL	Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. May be absorbed through skin.
Sodium Hydroxide	Corrosive Poison	2 ppm, 5 mg/m^3 2 Mg/M3-Ceiling	This material will cause burns if comes into contact with the skin or eyes. Severe irritant. Effects from inhalation of dust or mist vary from mild irritation to serious damage of the upper respiratory tract, depending on severity of exposure. Symptoms may include sneezing, sore throat or runny nose. Contact with skin can cause irritation or severe burns and scarring with greater exposures. Causes irritation of eyes, and with greater exposures it can cause burns that may result in permanent impairment of vision, even blindness.
Sulfuric Acid (1)	Corrosive Oxidizer Dehydrator Poison Carcinogen	1 mg/m^3	This material will cause burns if comes into contact with the skin or eyes. Inhalation of vapors will cause irritation of the nasal and respiratory system. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain, and severe tissue burns. Can cause blindness.
Acetone	Flammable	1000 ppm-TWA	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.
Acetonitrile	Flammable Poison	40 ppm-TWA	Early symptoms may include nose and throat irritation, flushing of the face, and chest tightness. Prolonged exposure to high levels of vapors may cause formation of cyanide anions in the body.
Hexane	Flammable Irritant	500 ppm-TWA	Inhalation of vapors irritates the respiratory tract. Overexposure may cause lightheadedness, nausea, headache, and blurred vision. Vapors may cause irritation to the skin and eyes.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

5.5. Exposure to hazardous chemicals must be maintained **as low as reasonably achievable**, therefore, unless they are known to be non-hazardous, all samples should be opened,

transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

5.6. The preparation of standards and reagents and glassware cleaning procedures that involve solvents such as methylene chloride will be conducted in a fume hood with the sash closed as far as the operations will permit. If more than 500 mL of Methylene chloride is spilled, evacuate the area until the area has been cleaned by EH&S.

5.7. All work must be stopped in the event of a known or potential compromise to the health and safety of a STL North Canton associate. The situation must be reported **immediately** to a laboratory supervisor.

5.8. During Kuderna-Danish (KD) concentration, do not allow the extract to boil to dryness. The solvent vapors remaining in the KD apparatus may superheat and create an explosion or fire hazard. The KD apparatus and glass separatory funnels have ground glass joints which can become stuck. Technicians must use Kevlar or other cut/puncture resistant gloves when separating stuck joints.

5.9. 3510 Separatory Funnel

5.9.1. The use of separatory funnels to extract aqueous samples with Methylene Chloride creates excessive pressure very rapidly. Initial venting should be done immediately after the sample container has been sealed and inverted, periodic venting may be necessary during the extraction. Vent the funnel into the hood away from people and other samples. This is considered a high-risk activity, the use of a face shield over safety glasses or goggles is recommended. Keep the sash on the fume hood as low as reasonably possible.

5.10. 3520 Extraction Cont Liq/Liq

5.10.1. All personnel are to ensure liquid-liquid area is clear of unnecessary items. Heating mantles used with liquid- liquid extractions generate temperatures that could ignite some materials that come in contact with the heating mantles.

5.10.2. Ensure all solvents are away from liquid-liquid extractor. Increased temperatures near solvents can cause the pressure in the containers to increase.

5.10.3. Ensure all boiling flasks have cooled to room temperature before disconnecting liquid-liquid bodies from boiling flasks to prevent any burns.

6. EQUIPMENT AND SUPPLIES

6.1. Glassware should be cleaned per Glassware Washing, SOP NC-QA-0014.

6.2. Equipment and supplies for extraction procedures

EQUIPMENT AND SUPPLIES	Sep fun.	CLLE	Soni	Sox	Conc
Separatory Funnel: 2 L	√				
Separatory Funnel Rack	√				
Balance: >1400 g capacity, accurate ±1 g	√	√	√	√	
pH indicator paper, wide-range: covers extraction pH	√	√			
Graduated cylinder: 1 liter. (other sizes may be used as needed)	√	√			
Erlenmeyer Flask: 125 & 300 mL (other sizes optional)	√	√	√		√
Centrifuge	√				
Methylene Chloride Collection Tank	√	√			
Initial Volume Template	√	√			
Solvent Dispenser Pump or 100 mL Graduated Cylinder	√	√	√	√	√
Continuous Liquid/Liquid Extractor		√			
Round or flat Bottom: 250, 500 mL or 1 L		√		√	
Boiling Chips: Contaminant free, approximately 10/40 mesh (Teflon® PTFE, carbide or equivalent).		√		√	√
Cooling Condensers		√		√	
Heating Mantle: Rheostat controlled		√		√	
Auto-timer for heating mantle		√		√	
Beakers: 250 & 400 mL, graduated	√	√	√		√
450mL wide-mouth glass jars			√		
Balance: >100 g capacity, accurate ±0.1 g	√	√	√	√	√
Soxhlet Extractor				√	
Cellulose and Glass Thimbles				√	
Accelerated Soxhlet Extractor (Soxtherm-trade name)				√	
Sonicator (at least 300 watts)			√		
Sonicator horn, 3/4 inch			√		
Kuderna-Danish (K-D) Apparatus: 500 mL					√
Concentrator Tube: 10 mL, attached to K-D with clips					√
Snyder Column: Three-ball macro					√
Water Bath: Heated, with concentric ring cover, capable of temperature control (± 5°C) up to 95°C. The bath must be used in a hood or with a solvent recovery system.					√
Vials: Glass, 2 mL, 4 mL, and 10 mL capacity with Teflon®-lined screw-cap					√

EQUIPMENT AND SUPPLIES	Sep fun.	CLLE	Soni	Sox	Conc
Nitrogen Blowdown Apparatus					√
Nitrogen: reagent grade.					√
Culture tubes: 10 mL, 16 mmx100 mm					√
Syringe: 1 mL	√	√	√	√	
Glass Wool	√	√	√	√	
Glass Funnel: 75 X 75 mm	√	√	√	√	√
Disposable Pipets	√	√	√	√	√
Aluminum foil	√	√	√	√	√
Paper Towels	√	√	√	√	√

7. REAGENTS AND STANDARDS

7.1. Reagents for Extraction Procedures

All reagents must be ACS reagent grade or better unless otherwise specified.

REAGENTS	Sep fun.	CLLE	Soni	Sox	Conc
Sodium hydroxide (NaOH), Pellets: Reagent Grade	√	√			
Sodium hydroxide solution, 10 N: Dissolve 40 g of NaOH in reagent water and dilute to 100 mL.	√	√			
Sulfuric acid (H_2SO_4), Concentrated: Reagent Grade	√	√			
Sulfuric acid (1:1): Carefully add 500 mL of H_2SO_4 to 500 mL of reagent water. Mix well.	√	√			
Hydrochloric Acid (HCl)			√		
Organic free reagent water.	√	√			
Sodium sulfate (Na_2SO_4), Granular, Anhydrous: Purify by heating at 400°C a minimum of two hours.	√	√	√	√	√
Extraction/Exchange Solvents: Methylene chloride, hexane, acetonitrile, acetone, pesticide quality or equivalent	√	√	√	√	√
Acetone, Methylene Chloride: Used for cleaning	√	√	√	√	√

7.2. Standards

7.2.1. Stock Standards

Stock standards are purchased as certified solutions or prepared from neats. Semivolatile stock standards are stored at $\leq$ 6°C. All stock standards must be protected from light. Stock standard solutions must be replaced after one year (from the time of preparation, if prepared in house, or from the time the ampoule is opened if purchased.) Standards must be allowed to come to room temperature before use.

7.2.2. Surrogate Spiking Standards

Prepare or purchase surrogate spiking standards at the concentrations listed in Table 5. Surrogate spiking standards are purchased or prepared as dilutions of the stock standards. Surrogate spiking solutions must be refrigerated and protected from light. The standards must be replaced at least every six months or sooner if there is reason to believe that the standard has degraded or concentrated.

7.3.3. Matrix Spiking and Laboratory Control Spiking Standards.

The same spiking solution is used for the matrix spike and the Laboratory Control Sample. Prepare MS/LCS spiking standards at the concentrations listed in Table 6. Spiking standards are purchased or prepared as dilutions of the stock standards. Spiking solutions must be refrigerated and protected from light. The standards must be replaced at least every six months or sooner if there is reason to believe that the standard has degraded or concentrated.

8. SAMPLE COLLECTION PRESERVATION AND STORAGE

8.1. Samples are not chemically preserved.

8.2. Samples are stored at 4°C ± 2°C in glass containers with Teflon®-lined caps.

8.3. Holding Times

8.3.1 Extraction is initiated within 7 days of the sampling date for aqueous samples, 14 days for solid and waste samples.

8.3.2 For TCLP leachates, extraction is initiated within seven days from when the TCLP Leach tumbling has been completed, excluding the filtration step. If the filtration step requires extended times, this time counts as part of the seven day holding time.

8.3.3. Analysis of the extracts is completed within forty days of extraction.

9. QUALITY CONTROL

9.1. Quality Control Batch

9.1.1. The batch is a set of up to 20 samples that are of the same matrix and are processed together using the same procedures and reagents. The batch must contain a method blank, an LCS and a matrix spike / matrix spike duplicate. (In some cases, at client request, it may be appropriate to process a matrix spike and sample duplicate in place of the MS / MSD). If clients specify specific samples for MS/MSD, the batch may contain multiple MS/MSD. See policy QA-003 for further definition of the batch.

9.2. Insufficient Sample

9.2.1. If insufficient sample is available to process a MS/MSD, then a second LCS must be processed. The LCS pair is then evaluated according to the LCS/LCSD criteria. Use of a LCS pair in place of a MS/MSD must be documented.

9.3. Sample count

9.3.1. Laboratory generated QC samples (method blanks, LCS, MS/MSD) are not included in the sample count. Field samples are included. Additional MS/MSD sets are included in the sample count.

9.4. Method Blank

9.4.1. A method blank consisting of all reagents added to the samples must be prepared and analyzed with each batch of samples. Surrogates are spiked into the method blank at the same level as the samples. The method blank is used to identify any background interference or contamination of the analytical system which may lead to the reporting of elevated concentration levels or false positive data.

9.4.2. Aqueous Method Blanks use 1000 mL of reagent water spiked with the surrogates. The method blank goes through the entire analytical procedure.

9.4.3. Solid method blanks use approximately 30 g of sodium sulfate spiked with the surrogates. The method blank goes through the entire analytical procedure.

9.4.4. TCLP method blanks use 250 mL of leachate fluid spiked with the surrogates. SPLP method blanks use 1000 mL of leachate fluid spiked with the surrogates The leachate may optionally be diluted to 1000 mL with reagent water. The method blank goes through the entire analytical procedure.

9.5. Laboratory Control Sample (LCS)

9.5.1. Laboratory Control Samples are well-characterized, laboratory generated samples used to monitor the laboratory's day to day performance of routine analytical methods. The LCS, spiked with a group of target compounds representative of the method analytes, is used to monitor the accuracy of the analytical process, independent of matrix effects. On-going monitoring of the LCS results provides evidence that the laboratory is performing the method

within accepted QC guidelines for accuracy and precision. The LCS goes through the entire analytical procedure.

9.5.2. The LCS is made up in the same way as the method blank (See sections 9.4.1 - 9.4.4) but spiked with the LCS standard and the surrogates.

9.6. Surrogates

9.6.1. Surrogates are organic compounds which are similar to the target analyte(s) in chemical composition and behavior in the analytical process, but which are not normally found in environmental samples.

9.6.2. Each applicable sample, blank, LCS and MS/MSD is spiked with surrogate standards. Surrogate spike recoveries must be evaluated by determining whether the concentration (measured as percent recovery) falls within the required recovery limits.

9.7. Matrix Spike/Matrix Spike Duplicate (MS/MSD)

9.7.1. A matrix spike is an environmental sample to which known concentrations of target analytes have been added. A matrix spike duplicate is a second spiked aliquot of the same sample which is prepared and analyzed along with the sample and matrix spike.

9.8. Initial Demonstration of Capability

9.8.1. The initial demonstration and method detection limit studies described in section 13 must be acceptable before analysis of samples may begin.

10. CALIBRATION AND STANDARDIZATION

10.1. On a weekly basis, measure the appropriate volume of solvent into an autovial using a gastight syringe that is manufactured to a certified volume delivery tolerance of ±0.01 mL. The "standard" autovial is sealed and the meniscus are marked by etching a line on the bottle. The autovials containing the sample extracts are then compared against the "standard" vial to ensure that the final volume is consistently 1.0 ± 0.01 mL. If a new box of autovials are used, then the steps are repeated to further ensure that variations due to vial size and shape are minimized. A log is kept of the lot number of the vials and the day the vials were prepared.

11. PROCEDURE

Procedures for separatory funnel liquid/liquid extraction (11.2), continuous liquid/liquid extraction (11.3), sonication extraction (11.4), soxhlet extraction (11.5), accelerated soxhlet

(11.6), waste dilution (11.7), and extract concentration (11.8).

11.1. Procedural Variations

Procedural variations are allowed only if deemed necessary in the professional judgment of the supervisor to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance memo and approved by a supervisor and QA/QC manager. If contractually required, the client will be notified. The Nonconformance memo will be filed in the project file.

Any deviations from this procedure identified after the work has been completed must be documented as a nonconformance, with a cause and corrective action described. A Nonconformance memo shall be used for this documentation.

11.2. Separatory Funnel Liquid/Liquid Extraction of Water Samples.

11.2.1. Remove surrogate and matrix spiking solutions from refrigerator and allow to return to room temperature.

11.2.2. Measure the initial sample pH with wide-range pH paper and record on the extraction benchsheet. If sample is a leachate (e.g. TCLP), compare the current pH against leachate log, note on the benchsheet if there is any discrepancy.

11.2.3. Measure the initial volume using using the volume template. Place the template next to the sample bottle and read the volume marking from the template. Record this volume on the benchsheet. The normal sample volume is 1 liter. Other sample volumes may be used to obtain specific reporting limits, and reduced sample volumes, diluted to 1 liter with reagent water, may be used for very dirty samples.

11.2.4. Prepare a method blank, LCS and MS/MSD for each batch as specified in section 9 of this SOP. Use 1 L of reagent water for method blanks and LCS. The LCS and MS/MSD are spiked with the surrogate and matrix spike solutions, the method blank only with the surrogates.

11.2.5. Use 250 mL of leachate for TCLP pesticides and TCLP semivolatiles, measured in a beaker.

11.2.6. For a TCLP method blank, LCS and LCS Dup measure 250 mL of the buffer solution used in the leaching procedure and transfer to the separatory funnel. Add 60 mL of methylene chloride to the separatory funnel. The TCLP leachate may be diluted to approximately 1 liter before extraction if desired.

11.2.7. Adjust sample pH as indicated in Table 1 for the initial extraction. Use the minimum amount of 1:1 H_2SO_4 or 10 N NaOH necessary. Recheck the sample with pH paper. Record adjusted pH, spiking volumes and standard numbers on the benchsheet. Return spiking solutions to the refrigerator as soon as possible.

11.2.8. Seal and shake or rotate the separatory funnel vigorously for 2 minutes with periodic venting to release excess pressure. An autoshaker may be used to shake and rotate the separatory funnel.

Warning: Dichloromethane creates excessive pressure very rapidly! Therefore, initial venting should be done immediately after the separatory funnel has been sealed and inverted. Vent into hood away from analysts and other samples.

11.2.9. Allow the organic layer to separate from the water phase until complete visible separation has been achieved. 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, filtration of the emulsion through glass wool, centrifugation, or other physical methods. If the emulsion cannot be broken (recovery of <80% of the methylene chloride*), transfer the sample, solvent, and emulsion into the extraction chamber of a continuous extractor and proceed as described in continuous liquid-liquid extraction (Section 11.3.). If this is done, the sample must be extracted as part of a valid CLLE batch.

*Note: 15 - 20 mL of methylene chloride is expected to dissolve in 1 L of water. Thus, solvent recovery could be as low as 35 mL from the first shake and still be acceptable. Subsequent shakes should recover at least 50 mL of solvent.

11.2.10. Fill a funnel with of anhydrous sodium sulfate. The funnel is plugged with glass wool to hold the sodium sulfate. Drain the solvent extract from the separatory funnel through the prepared filtration funnel into a clean glass container. The extract may be drained directly into the KD flask. Close the stopcock just before the water level begins draining out of the separatory funnel. If the sodium sulfate becomes saturated with water add more to the funnel or replace the existing sodium sulfate with fresh drying agent.

11.2.11. Repeat the extraction process two more times using fresh 60 mL portions of solvent, combining the three solvent extracts in the collection container.

11.2.12. If extraction at a secondary pH is required, pour the sample into a clean separatory funnel and adjust the pH of the sample in the separatory funnel to the pH indicated in Table 1 with a minimum amount of 10 N NaOH or 1:1 H_2SO_4. Measure with pH paper and record the adjusted pH on the benchsheet. Serially extract with three 60 mL portions of methylene chloride, as outlined in Steps 11.2.7 to 11.2.9. Collect these three extracts in the same container used for the

previous fraction.

11.2.13. Rinse the extract residue from the sodium sulfate by pouring 20-30 mL of clean methylene chloride through the funnel and into the collection container.

11.2.14. Dispose of solvent and water remaining in the extractor into the appropriate waste container.

11.2.15. Cover with aluminum foil if the extract is not concentrated immediately. Refer to Section 11.8 for concentration.

11.3. Continuous Liquid/Liquid Extraction from Water Samples.

11.3.1. Remove surrogate and matrix spiking solutions from refrigerator and allow to return to room temperature.

11.3.2. Assemble the apparatus. Add 250-400mL of methylene chloride to the extractor body. Add 3 to 5 boiling chips to the round-bottom distilling flask.

11.3.3. Measure the initial sample pH with wide-range pH paper and record on the extraction benchsheet. If sample is a leachate (e.g. TCLP), compare the current pH against leachate log, note on the benchsheet if there is any discrepancy.

11.3.4. Measure the initial volume using using the volume template. Place the template next to the sample bottle and read the volume marking from the template. Record this volume on the benchsheet. If the entire sample bottle will not be used, transfer the aliquot to the extractor, then add the spiking solutions to the sample in the extractor. Prepare a method blank, LCS and MS/MSD for each batch as specified in Section 9 of this SOP. Use 1 L of reagent water for method blanks and LCS. The method blank is spiked with the surrogates, the LCS and matrix spikes with the surrogates and matrix spiking solutions.

11.3.5. Use 250mL of leachate for TCLP for TCLP semivolatiles and TCLP pesticides. Use 1000 mL of leachate for SPLP semivolatiles and SPLP pesticides. Dilute to about 1 liter with reagent water.

11.3.6. For a TCLP method blank, LCS and LCS Dup measure 250 mL of the buffer solution used in the leaching procedure and transfer to the separatory funnel. Dilute to about 1 liter with reagent water. For an SPLP method blank, LCS and LCS Dup measure 1000 mL of the buffer solution used in the leaching procedure and transfer to the separatory funnel. No dilution with reagent water is required.

11.3.7. Less than one liter of sample may be used, for highly contaminated samples, or if the reporting limit can be achieved with less than one liter of sample. In this event, dilute the sample to about 1 liter with reagent water.This must be documented with a Non-Conformance Memo.

11.3.8. Adjust sample pH as indicated in Table 1 for the initial extraction. Use the minimum amount of 1:1 H_2SO_4 or 10 N NaOH necessary. Recheck the sample with pH paper. Record adjusted pH, spiking volumes and standard numbers on the benchsheet. Return spiking solutions to the refrigerator as soon as possible.

11.3.9. Add reagent water to the extractor body until approximately 250 mL of methylene chloride is pushed over into the round-bottomed flask to ensure proper operation and solvent cycling. Attach cold condenser (about 10°C). Turn on heating mantle. Inspect joints for leaks once solvent has begun cycling. Extract for 18-24 hours. (24 hours required for 600 series)

11.3.10. If extraction at a secondary pH is required, (see Table 1) turn off the heating mantle and allow the extractor to cool. Detach the condenser and adjust the pH of the sample in the extractor body to the pH indicated in Table 1 with a minimum amount of 10 N NaOH or 1:1 H_2SO_4. Measure with pH paper and record the adjusted pH on the benchsheet. Reattach the condenser and turn on heating mantle. Extract for 18-24 hours.

11.3.11. Turn off the heating mantle and allow the extractor to cool.

11.3.12. Place a funnel containing 10-20 g of anhydrous sodium sulfate on the Kuderna-Danish (K-D) apparatus or other glass container. The funnel can be plugged with glass wool enabling it to hold the granular anhydrous sodium sulfate.

11.3.13. Dry the extract in the round bottom flask by filtering it through the sodium sulfate filled funnel. Note that it is not necessary or advisable to attempt to add the solvent remaining in the continuous extractor body to the extract.

11.3.14. Collect the dried extract in a K-D or other glass container. Rinse the funnel with 20-30 mL of methylene chloride to complete the quantitative transfer. Dispose of solvent and water remaining in the extractor in the appropriate waste container.

11.3.15. Cover with aluminum foil if the extract is not concentrated immediately. Refer to Section 11.8 for concentration.

11.4. Sonication

11.4.1. Remove surrogate and matrix spiking solutions from refrigerator and allow to warm to room temperature.

11.4.2. Decant and discard any water layer on a sediment/soil sample, unless there are specific instructions not to decant the water. Record and document if a water layer was discarded on the benchsheet. Homogenize the sample by mixing it thoroughly in the container. If this is not possible place the sample in clean beaker and homogenize. Upon completion of homogenization in beaker return sample to original container. Discard foreign objects such as sticks, leaves and rocks, unless extraction of this material is required by client. If the sample consists primarily of foreign materials consult with the client (via the Project Manager or Administrator).

11.4.3. Weigh 30 g of sample ± 0.2g into a 250 or 400 mL beaker or wide-mouth jar. Record the weight to the nearest 0.01 g in the appropriate column on the benchsheet.

11.4.4. Mix weighed sample with a spatula adding enough anhydrous sodium sulfate (approximately 30 g) to be free flowing. (If the sample is not free flowing extraction efficiency may be reduced)

11.4.5. Prepare a method blank, LCS and MS/MSD for each batch as specified in Section 9 of this SOP. Use 30 g of sodium sulfate for the method blank. Use 30 g ± 0.2g of parent sample for the MS and MSD samples.

11.4.6. Add appropriate volume of matrix spiking solution to any matrix spike / matrix spike duplicate samples (See Table 4) Add the appropriate volume of the surrogate spiking solution to each sample, method blank, Laboratory Control Sample (LCS), and matrix spikes (see Table 3 for appropriate amounts). Refer to Table 6 for details of the surrogate spiking solutions. Add 1 mL of the appropriate matrix spiking solution to each Matrix Spike/Matrix Spike Duplicate (MS/MSD) and LCS. Refer to Tables 3 and 5 for details of the spiking solutions. Record spiking volumes and standard numbers on the benchsheet. Return spiking solutions promptly to refrigerator.

11.4.7. Immediately add a minimum of 100 mL of solvent to the beaker.

Solvents:

Semivolatile GC/MS, TPH, Organochlorine pesticides and PCBs	1:1 Methylene Chloride / Acetone

Note: Steps 11.4.5 - 11.4.9 should be performed rapidly to avoid loss of the more volatile extractables.

11.4.8. Place the bottom surface of the appropriate disrupter horn tip approximately ½ inch below the surface of the solvent, but above the sediment layer.

11.4.9. Sonicate for 3 minutes, making sure the entire sample is agitated.
Note: Do ***not*** use ***Microtip*** probe.

11.4.10. Loosely plug the stem of a 75 mm x 75 mm glass funnel with glass wool. Add 10-20 g of anhydrous sodium sulfate to the funnel cup.

11.4.11. Place the prepared funnel on a collection apparatus (beaker or K-D Apparatus).

11.4.12. Decant and filter extracts through the prepared funnel into a clean beaker or K-D Apparatus.

11.4.13. Repeat the extraction two more times with additional 100 mL minimum portions of solvent each time. Decant off extraction solvent after each sonication. On the final sonication pour the entire sample (sediment and solvent) into the funnel and rinse with an additional 10 mL-20 mL of the methylene chloride/acetone appropriate solvent (Refer to Table in 11.4.7).

Note: Alternatively, the three extracts may be collected together and then filtered through the sodium sulfate.

11.4.14. Cover with aluminum foil if the extract is not concentrated immediately. Refer to Section 11.8 for concentration

11.4.15. Sonicator Tuning: Tune the sonicator according to manufacturer's instructions. The sonicator must be tuned quarterly and if a new horn is installed.

11.5. Soxhlet

11.5.1. Remove surrogate and matrix spiking solutions from refrigerator and allow to warm to room temperature.

11.5.2. Decant and discard any water layer on a sediment/soil sample, unless there are specific instructions not to decant. Record and document if a water layer was discarded on the benchsheet. Homogenize the sample by mixing it thoroughly in the container. If this is not possible, place the sample in a clean beaker and homogenize. Upon completion of homogenization in the beaker, return the sample to original container. Discard foreign objects such as sticks, leaves, and rocks, unless extraction of this material is required by the client. If the sample consists primarily of foreign materials, consult with the client (via the Project manager or Administrator).

11.5.3. Weigh 30 g of sample ± 0.2g into a thimble in a beaker, recording the weight to the nearest 0.01 g on the benchsheet.. Use enough sodium sulfate for the method blank and LCS to cover the bottom of the container. Add anhydrous sodium sulfate and mix well. The mixture should have a free flowing texture. If not, add more sodium sulfate. Add the sample/sodium sulfate mixture to a soxhlet extractor thimble, but do not pack the thimble tightly. The Soxhlet extractor or extraction thimble must drain freely for the duration of the extraction period. A glass wool plug below the sample in the soxhlet extractor is an acceptable alternative for the thimble.

11.5.4. Add the appropriate amount of surrogate and matrix spiking solution as indicated in

Tables 3, 4, 5, and 6.

11.5.5. Sample weights less than 30 g but over 5 g may be used if the appropriate reporting limits can be met.

11.5.6. Prepare a method blank, LCS and MS/MSD for each batch as specified in Section 9 of this SOP, using sodium sulfate as the matrix for the LCS. The parent sample is used for the MS/MSD. The weight of sodium sulfate used should be approximately the weight of soil used in each sample.

11.5.7. Place approximately 200mL of solvent into a 250 mL flat bottom flask containing one or two clean boiling chips. Attach the flask to the extractor and extract the sample for 16-24 hours at 4-6 cycles per hour. Check the system for leaks at the ground glass joints after it has warmed up.

NOTE: If a reduced quantity of sample is extracted, it is usually necessary to increase the amount of sodium sulfate added or increase the solvent boiling rate to properly set the cycling rate.

Solvents:

Semivolatile GC/MS, OPP, PAH, TPH Organochlorine pesticides and PCBs	1:1 Methylene Chloride / Acetone

11.5.8. Allow the extract to cool after the extraction is complete, then disassemble by gently twisting the soxhlet from the flask.

11.5.9. The sample is now ready for the concentration step. (Section 11.8)

11.5.10. Cover with aluminum foil if the extract is not concentrated immediately. Refer to Section 11.8 for concentration.

11.6. Accelerated Soxhlet (Soxtherm Trade Name)

11.6.1. Remove surrogate and matrix spiking solutions from refrigerator and allow to return to room temperature.

11.6.2. Decant and discard any water layer on a sediment/soil sample, unless there are specific instructions not to decant. Record and document if a water layer was discarded on the benchsheet. Homogenize the sample by mixing it thoroughly in the container. If this is not possible, place the sample in clean beaker and homogenize. Upon completion of homogenization in beaker, return sample to original container. Discard foreign objects such as sticks, leaves and rocks, unless extraction of this material is required by client. If the sample consists primarily of foreign materials, consult with the client (via the Project Manager or Administrator).

11.6.3. Weigh 30 g of sample ± 0.2 g into a beaker, recording the weight to the nearest

0.01 g on the benchsheet. Use 30 g of sodium sulfate for the method blank and LCS. Add 30 g of anhydrous sodium sulfate and mix well. The mixture should have a free flowing texture. If not, add more sodium sulfate. Add the sample/sodium sulfate mixture to an accelerated soxhlet thimble, but do not pack the thimble tightly. The extraction thimble must drain freely for the duration of the extraction period. A glass wool plug below the sample in the thimble is required.

11.6.4. Add the appropriate amount of surrogate and matrix spiking solution as indicated in Tables 3, 4, 5, and 6.

11.6.5. Sample weights less than 30 g, but over 5 g may be used if the appropriate reporting limits can be met.

11.6.6. Prepare a method blank, LCS and MS/MSD for each batch as specified in Section 9 of this SOP, using sodium sulfate as the matrix. The weight of sodium sulfate used should be approximately the weight of soil used in each sample.

11.6.7. Place thimble in the extract beaker containing at least 6 clean boiling chips and add approximately 140 mL of solvent. Place beakers into positions on the accelerated soxhlet unit. Run appropriate program for the extraction solvent. Check the system for leaks at the joints periodically.

Solvents:

Semivolatile MS, PAH, TPH	1:1 Methylene Chloride / Acetone
Semivolatile GC PCB, PEST, OPP	1:1 Hexane/Acetone

11.6.8. Upon completion of the program, remove the extract beaker from the unit and dispose of the extracted sample. Dry the extract in the flask by filtering it through a sodium sulfate filled funnel.

11.6.9. Transfer extract into a culture tube, rinsing the extract beaker to complete the quantitative transfer. Rinse the extractor beaker which contained the solvent extract with 10-15 mL of the appropriate solvent and pour it through the funnel. Rinse the funnel with 10-15 mL of methylene chloride to complete the quantitative transfer.

11.6.10. Cover with aluminum foil if the extract is not concentrated immediately. Refer to Section 11.8 for concentration.

11.7. Waste Dilution

11.7.1. Label the vial with the sample number. Tare the vial, then transfer approximately 1g of sample to the vial. Record the weight to the nearest ±0.01 g.

11.7.2. For the blank and LCS/LCSD, add a small amount of the appropriate solvent to the vial. Add appropriate volume of surrogate and spike solutions (Table 3).Dilute to

10mL with the appropriate solvent.

11.7.3. Dilute to 10 mL with the appropriate solvent. (Methylene Chloride for GC/MS Semi and GCS TPH. Add 10 mL of appropriate solvent (Hexane) for GCS pesticide and/or PCB analysis.

11.7.4. Cap and shake or vortex each extract. TPH samples are then placed on the nitrogen evaporation unit and reduced to a 2 mL final volume.

11.7.5. Label the sample, which is now ready for cleanup or analysis.

11.8. Concentration

According to the type of sample and any cleanup procedures needed, different solvents and final volumes will be required. Refer to Table 2 for the appropriate final volumes and concentrations.

11.8.1. Kuderna-Danish (KD) Method:

11.8.1.1. Assemble a Kuderna-Danish concentrator by attaching a 10 mL concentrator tube to the 500 mL KD flask. Transfer the sample to the labeled K-D flask, filtering Continuous Liquid/Liquid and Soxhlet samples through funnels filled with sodium sulfate.

11.8.1.2. Add one or two clean boiling chips and the extract to be concentrated to the KD flask and attach a three-ball Snyder Column. Add approximately 1 mL of clean methylene chloride to the top of the Snyder column. (This is important to ensure that the balls are not stuck, and the column will work properly).

11.8.1.3. Place the KD apparatus on a water bath (90-98°C) so that the tip of the concentrator tube is submerged. The water level should not reach the joint between the concentrator and the KD flask. At the proper rate of distillation, the balls will actively chatter but the chambers should not flood.

11.8.1.4. Concentrate to 15-20 mL. If the determinative method requires a solvent exchange add the appropriate exchange solvent to the top of the Snyder Column, and then continue the water bath concentration back down to 5-8 mL. Refer to Table 2 for details of exchange solvents and final volumes. The Snyder column may be insulated if necessary to maintain the correct rate of distillation.

Note: For Method 8310 replace the macro Snyder column and KD flask with a micro Snyder column, concentrate to approximately 1 mL, add the

appropriate solvent, and concentrate back down to 1 mL. The extract must be cool before the macro Snyder assembly is removed.

Note: It is very important not to concentrate to dryness as analytes will be lost.

11.8.1.5. Remove the KD apparatus from the water bath and allow to cool for a minimum of 10 minutes. If the level of the extract is above the level of the concentrator tube joint, continue to distill the solvent as necessary. Again, allow the KD flask to cool for a minimum of 10 minutes.

11.9. Nitrogen Evaporation to Final Concentration

11.9.1. Transfer the CT to the evaporation apparatus

11.9.2. Place the tube in a warm water bath that is at least 5°C below the boiling temperature of the solvent being evaporated and evaporate the solvent using a gentle stream of nitrogen. The nitrogen flow will form a slight depression on the surface of the solvent, but should not create splattering of the extract.

Boiling points of commonly used solvents are:

Methylene chloride	40°C
Acetone	56°C
Hexane	69°C
Acetonitrile	82°C
Toluene	111°C

11.9.3. An alternative technique is to follow the previous steps concentrating the solvent to slightly below the required final volume and then drawing the extract into a syringe. Rinse the evaporation tube with a small amount of solvent and draw additional solvent into the syringe to make up the accurate final volume.

Note: It is very important not to concentrate to dryness as analytes will be lost.

11.4.1. *Note:* The final concentration and volume measurement steps are critical. Use care when concentrating and make certain that the final volume measurement is accurate.

12. DATA ANALYSIS AND CALCULATIONS

Not applicable

13. METHOD PERFORMANCE

13.1. Method Detection Limit

13.1.1. Each laboratory must generate a valid method detection limit for each analyte of interest. The procedure for the determination of the method detection limit is given in STL North Canton QA Policy #: S-Q-003.

13.2. Initial Demonstration

13.2.1. Each laboratory must make an initial demonstration of capability for each individual method. This requires analysis of four QC Check samples. The QC check sample is a well-characterized laboratory generated sample used to monitor method performance, which should contain all the analytes of interest. The spiking level should be equivalent to a mid-level calibration. (For certain tests more than one set of QC check samples may be necessary in order to demonstrate capability for the full analyte list.)

13.2.2. Four aliquots of the QC check sample are analyzed using the same procedures used to analyze samples, including sample preparation.

13.2.3. Calculations and acceptance criteria for the QC check samples are given in the determinative SOPs.

13.3. Training Qualification

13.3.1. The group/team leader has the responsibility to ensure that this procedure is performed by an analyst who has been properly trained in its use and has the required experience.

14. POLLUTION PREVENTION

14.1. Within the constraints of following the methodology in this SOP, use of organic solvents should be minimized.

15. WASTE MANAGEMENT

15.1. All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

15.2. The following waste streams are produced when this method is carried out:

15.2.1. Extracted aqueous samples contaminated with methylene chloride. This tank is

then periodically rolled to the tank room where the DCM emptied a larger tank using tubing attached to the bottom of the tank. The remaining water is neutralized with sodium bicarbonate, the pH verified and the water discharged to the POTW.

15.2.2. **Used sodium sulfate and glass wool or filter paper contaminated with methylene chloride/acetone or acetone/hexane from the extract drying step.** These materials are disposed of in the solid waste and debris in a red container located in the extractions lab.

15.2.3. **Assorted flammable solvent waste from various rinses**. These wastes are put into the halogenated/non-halogenated 25 gallon solvent waste container located under the fume hood in extractions.

15.2.4. **Methylene chloride waste from various rinses:** These wastes are disposed of in the liquid-liquid separation unit.

15.2.5. **Hexane- Hexane waste:** These samples are to be disposed in the flammable waste.

15.2.6. **Waste Hexane in vials.** These vials are placed in the vial waste located in the GC prep laboratory.

15.2.7. **Waste Methylene Chloride sample vials**. These vials are placed in the vial waste located in the GC prep laboratory.

15.2.8. **Extracted solid samples contaminated with methylene chloride/acetone or acetone/hexane.** These materials are disposed of in the solid waste and debris in a red container located in the extractions lab.

15.2.9. Samples, standards, and all extraction materials contaminated with high levels (>50ppm) of PCB's must be segregated into their own waste stream. PCB wastes are collected in one of three waste streams, solid PCB, liquid PCB and PCB vial waste.

15. REFERENCES

15.1. References

15.1.1. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW846, 3rd Edition, Final Update III (December 1996). Sections 3500B, 3510C, 3520C, 3540C, 3550B, 3600C, 3610B, 3620B, 3640A, 3650B, 3660B, AND 3665A.

15.1.2. Corporate Quality Management Plan (QMP), current version.

15.1.3. STL Laboratory Quality Manual (LQM), current version.

15.2. Associated SOPs and Policies, latest version

15.2.1. QA Policy, QA-003

15.2.2. Glassware Washing, NC-QA-0014

15.2.3. Statistical Evaluation of Data and Development of Control Charts, NC-QA-0018, current version.

15.2.4. Method Detection Limits and Instrument Detection Limits, NC-QA-0021, current version.

15.2.5. Navy/Army SOP, NC-QA-0016

15.2.6. Hazardous Waste Management SOP, NC-HS-0001.

15.2.7. Method Detection Limit Studies, S-Q-003, current version.

15.2.8. CORP-GC-0001NC, Gas Chromatographic Analysis based on Method 8000B, 8021B, 8081A, 8082, 8151A, 8310, 8141A, 8015B, and 615, current version.

15.2.9. CORP-MS-0001NC, GC/MS Analysis based on Method 8270C, current version.

15.2.10. NC-LC-0001, Polynuclear Aromatic Hydrocarbons by High Performance Liquid Chromatography Method 8310, current version.

15.2.11. NC-GC-0007, Analysis of Pesticides and PCBs by EPA Method 608, current version.

15.2.12. NC-MS-0003, GC/MS Semivolatile Organic Compounds Capillary Column Technique Based on EPA Method 625, current version.

17. MISCELLANEOUS

17.1. Modifications from Reference method

17.1.1. Some surrogate spiking concentrations are modified from those recommended in SW-846, in order to make the concentrations more consistent with the calibration levels in the determinative methods.

17.1.2. Spiking levels for method 608 have been reduced by a factor of ten to bring the levels within the normal calibration range of the instrument.

17.2. Tables

Table 1
Liquid /Liquid Extraction Conditions

Determinative Method	Initial Ext. pH	Secondary Ext. pH
BNA: 8270C[1]	1-2 (acid first) or 11-12 (base first)	11-12 (base first) or 1-2 (acid first)
625	11-12 (base first) or 1-2 (acid first)	1-2 (acid first) or 11-12 (base first)
Pest/PCB: 8081A, 8082 & 608	5-9	None
OPP: 8141A	as received	None
Hydrocarbons: 8015B	as received	None
PAH: 8310, & 610	as received	None

[1] If the laboratory has validated acid only 8270 extraction for the target compound list required then the base extraction step may be omitted. The required validation consists of a 4 replicate initial demonstration of capability and a method detection limit study. (See section 13). Additionally, either of the base or acid fractions of Method 8270 can be run first.

Table 2
Exchange Solvents and Final Volumes

Final Volumes and Exchange Solvents if no cleanup is used		
Type	Exchange Solvent for Analysis	Final Volume for Analysis in mL
Semivolatiles	N/A	2.0 mL
PCB	18 mL Hexane – water 36 mL Hexane - solid	10.0 for solids 5.0 for H2O 2.0 for H2O*
Pesticides	18 mL Hexane	10.0 for solids 5.0 for H2O
Pesticides/TCLP	18 mL Hexane	3.0 mL
PAH by HPLC	4mL Acetonitrile	1.0 mL
BNA – SIM	N/A	2.0 mL - Solids & H2O
TPH	N/A	1.0
OPP	20mL Hexane/Acetone	2.0

* Michigan work requires a final volume of 2 mL.

Note: Different final volumes may be necessary to meet special client reporting limit requirements.

.Table 3		
Surrogate Spiking Solutions		
Analyte Group	Surrogate Spike Solution ID	Volume (mL)
BNA	100/150 ppm BNA	0.2
BNA / SIM	100/150 ppm BNA	.2 / 0.02
BNA Waste Dilution	100/150 ppm BNA	0.5
PEST	0.2 ppm DCB/TCX	1.0
TPH	40ng C9	1.0
PCB	0.2 ppm DCB/TCX	1.0
PAH	1.0 ug/mL p-Terphenyl-d14 5.0 ug/mL Benzo(e)pyrene	1.0
OPP	10 ug/mL Triphenyl Phosphate	1.0

Table 4

Matrix Spike and LCS Solutions

Analyte Group	Matrix Spike Solution ID	Volume (mL)
BNA	100 ppm BNA All-Analyte Spike & Restek Spike	0.2
BNA / SIM	100 ppm BNA All-Analyte Spike & Restek Spike	0.2 / 0.02
PEST	Pest NPDES Spike	1.0
PEST TCLP	Pest TCLP Spike	1.0
PCB	10 ppm PCB Spike	1.0
PAH	See Spike List – Table 6	1.0
TPH	See Spike List – Table 6	1.0
OPP	See Spike List – Table 6	1.0

Table 5 Surrogate Spike Components		
Compounds	Solvent	Conc. (µg/mL)
2-Fluorobiphenyl	Methanol	100
Nitrobenzene-d5		100
p-Terphenyl-d14		100
2-Fluorophenol		150
Phenol-d6		150
2,4,6-Tribromophenol		150
1,2-Dichlorobenzene-d4		100
2-Chlorophenol-d4		150
Decachlorobiphenyl	MethanolAcetone	0.2
Tetrachloro-m-xylene		0.2
Nonane (C9)	Methanol	40.0
p-Terphenyl-d-14	CH3CN	1.0
Benzo(e)pyrene		5.0
Triphenylphosphate	Acetone	10.0

Table 6

Matrix Spike Components

Compounds	Solvent	Conc. (µg/mL)
Acenaphthene	Methanol	100
4-Chloro-3-Methylphenol		150
2-Chlorophenol		150
1,4-Dichlorobenzene		100
2,4-Dinitrotoluene		100
4-Nitrophenol		150
N-Nitroso-Di-n-Propylamine		100
Pentachlorophenol		150
Phenol		150
Pyrene		100
1,2,4-Trichlorobenzene		100
1,4-Dichlorobenzene	Methanol	100
2,4-Dinitrotoluene		100
Hexachlorobenzene		100
Hexachlorobutadiene		100
Hexachloroethane		100
2-Methylphenol		100
3-Methylphenol		100
4-Methylphenol		100
Nitrobenzene		100
Pentachlorophenol		100
Pyridine		100
2,4,5-Trichlorophenol		100
2,4,6-Trichlorophenol		100

Table 6

Matrix Spike Components

Compounds	Solvent	Conc. (µg/mL)
	Methanol	
Acenaphthene		100
Acenaphthylene		100
Anthracene		100
Benzo(a)anthracene		100
Benzo(b)fluoranthene	Methanol	100
Benzo(k)fluoranthene		100
Benzo(a)pyrene		100
Benzo(ghi)perylene		100
Benzyl butyl phthalate		100
Bis(2-chloroethyl)ether		100
Bis(2-chloroethoxy)methane		100
Bis(2-ethylhexyl)phthalate		100
Bis(2-chloroisopropyl)ether		100
4-Bromophenyl phenyl ether		100
2-Chloronaphthalene		100
4-Chlorophenyl phenyl ether		100
Chrysene		100
Dibenzo(a,h)anthracene		100
Di-n-butylphthalate		100
1,3-Dichlorobenzene		100
1,2-Dichlorobenzene		100
1,4-Dichlorobenzene		100
3,3'-Dichlorobenzidine		100
Diethyl phthalate		100

Table 6

Matrix Spike Components

Compounds	Solvent	Conc. (µg/mL)
Dimethyl phthalate		100
2,4-Dinitrotoluene		100
2,6-Dinitrotoluene		100
Di-n-octylphthalate		100
Fluoranthene		100
Fluorene		100
Hexachlorobenzene		100
Hexachlorobutadiene		100
Hexachloroethane		100
Indeno(1,2,3-cd)pyrene		100
Isophorone		100
Naphthalene		100
Nitrobenzene		100
N-Nitrosodi-n-propylamine		100
Phenanthrene		100
Pyrene		100
1,2,4-Trichlorobenzene		100
4-Chloro-3-methylphenol		100
2-Chlorophenol		100
2,4-Dichlorophenol		100
2,4-Dimethylphenol		100
2,4-Dinitrophenol		100
2-Methyl-4,6-dinitrophenol		100
2-Nitrophenol		100
4-Nitrophenol		100

Table 6

Matrix Spike Components

Compounds	Solvent	Conc. (µg/mL)
Pentachlorophenol		100
Phenol		100
2,4,6-Trichlorophenol		100
Acetophenone		100
Atrazine		100
Caprolactum		100
Benzaldehyde		100
1,1′-Biphenyl		100
Safrole		100
1,4-Dioxane		100
Pronamide		100
p-Chlorobenzilate		100
Phenacetin		100
Ethyl methanesulfonate		100
2-Picoline		100
Phorate		100
Quinoline		100

Type	Compounds	Solvent	Conc. (µg/mL)
Pest TCLP	Heptachlor	Methanol Acetone	0.5
	Heptachlor epoxide		0.5
	Lindane		0.5
	Endrin		0.5
	Methoxychlor		1.0
Pest NPDES/Pest	Alrin	Methanol Acetone	1.0
	Alpha-BHC		1.0
	beta-BHC		1.0
	delta-BHC		1.0
	gamma-BHC (Lindane)		1.0
	4,4'-DDD		1.0
	4,4'-DDE		1.0
	4,4'-DDT		1.0
	Dieldrin		1.0
	alpha-Endosulfan		1.0
	beta-Endosulfan		1.0
	Endosulfan Sulfate		1.0
	Endrin		1.0
	Heptachlor		1.0
	Heptachlor Epoxide		1.0

Diesel Range Organics (8015B) Spike	
Compound	**Final Concentration**
n-decane	50 µg/ml
n-dodecane	50 µg/ml
n-tetradecane	50 µg/ml
n-hexadecane	50 µg/ml
n-octadecane	50 µg/ml
n-eicosane	50 µg/ml
n-docosane	50 µg/ml
n-tetracosane	50 µg/ml

n-hexacosane	50 µg/ml
n-octacosane	50 µg/ml
Organophorphorous Pesticides (8141A)	
Compound	**Final Concentration**
dimethoate	20 µg/mL
disulfoton	20 µg/mL
famphur	20 µg/mL
methyl parathion	20 µg/mL
parathion (ethyl)	20 µg/mL
phorate	20 µg/mL
sulfotepp	20 µg/mL
thionazin	20 µg/mL
o,o,o-triethyl phosphorothioate	20 µg/mL
triphenylphosphate (surrogate)	20 µg/mL

Polynuclear Aromatic Hydrocarbons (8310)	
Compound	**Final Concentration**
Acenaphthylene	10 µg/mL
Carbazole	10 µg/mL
Naphthalene	10 µg/mL
1-Methylnaphthalene	10 µg/mL
2-Methylnaphthalene	10 µg/mL
Acenaphthene	10 µg/mL
Fluorene	2 µg/mL
Phenanthrene	2 µg/mL
Anthracene	2 µg/mL
Fluoranthene	2 µg/mL
Pyrene	2 µg/mL
Benzo(a)anthracene	2 µg/mL
Chrysene	2 µg/mL
Benzo(a)pyrene	2 µg/mL
Benzo(k)fluoranthene	2 µg/mL
Benzo(a)pyrenek)fluoranthene	2 µg/mL
Dibenzo(a,h)anthracene	2 µg/mL
Benzo(g,h,I)perylene	2 µg/mL
Indeno(1,2,3-cd)pyrene	2 µg/mL

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TestAmerica North Canton

SOP No. CORP-MS-0001NC, Rev. 2.12
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Title: GC/MS Analysis Based
[Method: **Method 8270C - UPDATE III**]

Approvals (Signature/Date):

Tom Hulz 12/14/07
Technology Specialist Date

12-14-07
Health & Safety Coordinator Date

Dorothy J. Lucon 12/13/07
Quality Assurance Manager Date

12/14/07
Laboratory Director Date

Mark Bauer 12/14/07
Technical Director Date

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STL NORTH CANTON STANDARD OPERATING PROCEDURE

TITLE: GC/MS ANALYSIS BASED ON METHODS 8270C

(SUPERSEDES: Revision 2.11, Dated 02/03/06)

Reviewed by: _____ 5/10/07
Technology Specialist — Date

Approved by: _____ 5/22/07
Quality Assurance Manager — Date

Approved by: _____ 5-7-07
Environmental Health and Safety — Date

Approved by: _____ 5/20/07
Laboratory Director — Date

Approved by: _____ 5/16/07
Technical Director — Date

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1. SCOPE AND APPLICATION

1.1 This method is based upon SW846 8270C, and is applicable to the determination of the concentration of semivolatile organic compounds in extracts prepared from solid and aqueous matrices. Direct injection of a sample may be used in limited applications. Refer to Tables 1, 2, 3 and 4 for the list of compounds applicable for this method. Note that the compounds are listed in approximate retention time order. Additional compounds may be amenable to this method. If non-standard analytes are required, they must be validated by the procedures described in Section 13 before sample analysis.

1.2 The following compounds may require special treatment when being determined by this method:

- Benzidine can be subject to oxidative losses during solvent concentration and exhibits poor chromatography. Neutral extraction should be performed if this compound is expected.
- Hexachlorocyclopentadiene is subject to thermal decomposition in the inlet of the gas chromatograph, chemical reaction in acetone solution, and photochemical decomposition.
- N-Nitrosodiphenylamine decomposes in the gas chromatographic inlet and cannot be distinguished from diphenylamine.
- Pentachlorophenol, 2,4-dinitrophenol, 4-nitrophenol, 4,6-dinitro-2-methylphenol, 4-chloro-3-methylphenol, benzoic acid, 2-nitroaniline, 3-nitroaniline, 4-chloroaniline, and benzyl alcohol are subject to erratic chromatographic behavior, especially if the GC system is contaminated with high boiling material.
- Hexachlorophene is not amenable to analysis by this method.
- 3-Methylphenol cannot be separated from 4-methylphenol by the conditions specified in this method.

1.3 The standard reporting limit of this method for determining an individual compound is approximately 0.33 mg/kg (wet weight) for soil/sediment samples, 1 - 200 mg/kg for wastes (dependent on matrix and method of preparation), and 10 µg/L for groundwater samples. Some compounds have higher reporting limits. Refer to Tables 1 and 2 for specific SRLs. Reporting limits will be proportionately higher for sample extracts that require dilution.

1.4 The associated LIMS code is QL (8270C).

2. SUMMARY OF METHOD

2.1 Aqueous samples are extracted with methylene chloride using a separatory funnel, and/or a continuous extractor. Solid samples are extracted with methylene chloride / acetone using sonication, soxhlet, accelerated soxhlet or pressurized fluid extraction. The extract is dried, concentrated to a final volume of 2 mL for waters and soils, and analyzed by GC/MS. Extraction procedures are detailed in SOP# CORP-OP-0001NC. Qualitative identification of the parameters in the extract is performed using the retention time and the relative abundance of characteristic ions. Quantitative analysis is performed using the internal standard technique with a

single characteristic ion.

3. DEFINITIONS

3.1 CCC (Calibration Check Compounds) - A subset of target compounds used to evaluate the calibration stability of the GC/MS system. A maximum percent deviation of the CCC's is specified for calibration acceptance.

3.2 SPCC (System Performance Check Compounds) - Target compounds designated to monitor chromatographic performance, sensitivity, and compound instability or degradation on active sites. Minimum response factors are specified for acceptable performance.

3.3 Batch - The batch is a set of up to 20 samples of the same matrix processed using the same procedures and reagents within the same time period. The Quality Control batch must contain a matrix spike / spike duplicate (MS/MSD), a Laboratory Control Sample (LCS), and a method blank. Batches are defined at the sample preparation stage. Batches should be kept together through the whole analytical process to the extent possible, but it is not mandatory to analyze prepared extracts on the same instrument or in the same sequence. Refer to the STL North Canton QC Program document (QA-003) for further details of the batch definition.

3.4 Method Blank - An analytical control consisting of all reagents, internal standards and surrogate standards, that is carried through the entire analytical procedure. The method blank is used to define the level of laboratory background and reagent contamination.

3.5 LCS (Laboratory Control Sample) - A blank spiked with the parameters of interest that is carried through the entire analytical procedure. Analysis of this sample with acceptable recoveries of the spiked materials demonstrates that the laboratory techniques for this method are acceptable.

3.6 MS (Matrix Spike)- aliquot of a matrix (water or soil) fortified (spiked) with known quantities of specific compounds and subjected to the entire analytical procedure in order to indicate the appropriateness of the method for the matrix by measuring recovery.

3.7 MSD (Matrix Spike Duplicate)- a second aliquot of the same sample as the matrix spike (above) that is spiked in order to determine the precision of the method for the matrix by measuring relative percent difference.

4. INTERFERENCES

4.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus that lead to discrete artifacts. All of these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. Raw GC/MS data from all blanks, samples, and spikes must be evaluated for interferences. If an interference is detected it is necessary to determine if the source of interference is in the preparation and/or cleanup of the samples; then take corrective action to eliminate the problem.

4.2 The use of high purity reagents, solvents, and gases helps to minimize interference problems.

4.3 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 sample.

4.4 Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed with solvent between samples. Whenever an unusually concentrated sample is encountered, it should be followed by the analysis of solvent to check for cross contamination.

4.5 Phthalate contamination is commonly observed in this analysis and its occurrence should be carefully evaluated as an indicator of a contamination problem in the sample preparation step of the analysis.

5 SAFETY PRECAUTIONS

5.1 Employees must abide by the policies and procedures in the Corporate Safety Manual and this document.

5.2 Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents and reagents are being handled. Disposable gloves that have become contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.3 Chemicals that have been classified as carcinogens, or potential carcinogens, under OSHA include: Benzo(a)anthracene, benzidine, 3,3'-dichlorobenzidine, benzo(a)pyrene, dibenzo(a,h)anthracene, and n-nitrosodimethylamine.

5.4 The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Methylene Chloride	Carcinogen Irritant	25 ppm-TWA 125 ppm-STEL	Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. May be absorbed through skin.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

5.5 Exposure to chemicals must be maintained as low as reasonably achievable; therefore, unless they are known to be non-hazardous, all samples should be opened, transferred, and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers should be kept closed unless transfers are being made.

5.6 The preparation of standards and reagents will be conducted in a fume hood with the sash closed as far as the operation will permit.

5.7 It is recommended that neat standards be purchased only as a last resort. The preparation of standards from neat materials and reagents should be conducted in a fume hood with the sash closed as far as the operations will permit.

5.8 Standards in solution may be diluted in the open laboratory when syringes and the like are utilized.

5.9 All work must be stopped in the event of a known or potential compromise to the health and safety of a STL North Canton associate. The situation must be reported immediately to a laboratory supervisor and the EH&S Coordinator.

6. EQUIPMENT AND SUPPLIES

6.1 Gas Chromatograph/Mass Spectrometer System: An analytical system complete with a temperature-programmable gas chromatograph suitable for split/splitless injection and all required accessories, including syringes, analytical columns, and gases. The capillary column should be directly coupled to the source.

6.2 Column: 20m x 0.18mm ID, 0.36µm film thickness silicon-coated fused-silica capillary column (J & W Scientific DB-5.625 or equivalent). Alternate columns are acceptable if they provide acceptable performance.

6.3 Mass Spectrometer: Capable of scanning from 35 to 500 AMU every one second or less, using 70 volts (nominal) electron energy in the electron impact ionization mode. The mass spectrometer must be capable of producing a mass spectrum for decafluorotriphenylphosphine (DFTPP) which meets all of the criteria in Table 6 when the GC/MS tuning standard is injected through the GC.

6.4 GC/MS Interface: Any GC-to-MS interface that gives acceptable calibration points and achieves acceptable tuning performance criteria may be used.

6.5 Data System: A computer system must be interfaced to the mass spectrometer. The system must allow the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that can search any GC/MS data file for ions of a specific mass and that can plot such ion abundances versus time or scan number. This type of plot is defined as the Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundances in any EICP between specified time or scan-number limits. The most recent version of the EPA/NIH Mass Spectral Library is recommended.

6.6 Syringe: 5 µL Hamilton Laboratory grade syringes or equivalent.

6.7 Carrier gas: Ultra high purity helium.

7. REAGENTS AND STANDARDS

7.1 A minimum five point calibration curve is prepared. If a quadratic regression is used, six points must be analyzed for the calibration curve. The low point should be at or below the reporting limit. Refer to Tables 12 and 13 for typical calibration levels for all analytes. Other calibration levels may be used, depending on instrument capability, but the low standard must support the reporting limit and the high standard defines the range of the calibration.

7.2 An Internal Standard solution is prepared by diluting a purchased standard. Compounds in the I.S. Mix are: acenaphthene-d10, chrysene-d12, 1,4-dichlorobenzene-d4, naphthalene-d8, perylene-d12, and phenanthrene-d10.

7.3 Surrogate Standard Spiking Solution: Prepare as indicated in the preparative methods. See appropriate preparation SOP. Surrogate compounds and levels are listed in Table 11.

7.4 GC/MS Tuning Standard: A methylene chloride solution containing decafluorotriphenylphosphine (DFTPP) is prepared. Pentachlorophenol, benzidine, and DDT, should also be included in the Tuning Standard. All components are at 25 ug/mL.

7.5 The standards listed in 7.1 to 7.4 should be refrigerated at $\leq 6^{\circ}C$ when not in use. Refrigeration at -10°C to -20°C may be used if it can be demonstrated that analytes do not fall out of solution at this temperature. The standards must be replaced at least once a year.

8. SAMPLE PRESERVATION AND STORAGE

8.1 Sample extracts are stored at $4 \pm 2^{\circ}C$. Samples and extracts should be stored in suitable glass containers with Teflon lined caps. (Extracts will be stored for 30 days after invoicing.)

8.3 Water samples are extracted within seven days of sampling and the extracts are analyzed within forty days of extraction. Solids, sludges, and organic liquids are extracted within fourteen days of sampling and the extracts are analyzed within forty days of extraction.

9. QUALITY CONTROL

9.1 Initial Demonstration of Capability

9.1.1 For the standard analyte list, the initial demonstration and method detection limit (MDL) studies described in Section 13 must be acceptable before analysis of samples may begin.

9.1.2 For non-standard analytes an MDL study should be performed and calibration curve generated before analyzing any samples, unless lesser requirements are previously agreed to with the client. In any event, the minimum initial demonstration required is analysis of an extracted standard at the reporting limit and a single point calibration.

9.2 Control Limits

In-house historical control limits must be determined for surrogates, matrix spikes, and laboratory control samples (LCS). These limits must be determined periodically. The recovery limits are mean recovery +/- 3 standard deviations for surrogates, MS and LCS. Precision limits for matrix spikes / matrix spike duplicates are mean relative percent difference +/- 3 standard deviations. Control limits are established by the laboratory as described in SOP NC-QA-0018. Control limits are easily accessible via the LIMs (QC Browser program).

9.2.2 If samples are diluted, the surrogate and matrix spike recoveries will be reported with a DIL flag. Any analyte outside of the control limits will be flagged with JDIL. For DoD projects all surrogates must be within control limits.

9.2.3 All surrogate, LCS, and MS recoveries (except for dilutions) must be entered into LIMS

(when available) or other database so that accurate historical control limits can be generated.

9.2.4 Refer to the QC program document (QA-003) for further details of control limits.

9.3 Method Blank

9.3.1 A method blank is prepared and analyzed with each batch of samples. The method blank consists of reagent water for aqueous samples, and sodium sulfate for soil samples (Refer to SOP No. CORP-OP-0001NC for details). Surrogates are added and the method blank is carried through the entire analytical procedure. The method blank must not contain any analyte of interest at or above the reporting limit (except common lab contaminants, see below). Any blank contamination above the reporting limit must be less than 1/10 of the measured concentration of any sample in the associated preparation batch.

9.3.1.1 If the analyte is a common laboratory contaminant (phthalate esters), the data may be reported with qualifiers if the concentration of the analyte is less than five times the RL. Such action must be taken in consultation with the client.

9.3.1.2 Reanalysis of any samples with reportable concentrations of analytes found in the method blank is required unless other actions are agreed with the client.

9.3.1.3 If there is no target analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. Such action should be taken in consultation with the client. NOTE: For Ohio VAP work, there can be no target analyte greater than the RL.

9.3.2 The method blank must have acceptable surrogate recoveries. If surrogate recoveries are not acceptable, the data must be evaluated to determine if the method blank has served the purpose of demonstrating that the analysis is free of contamination. If surrogate recoveries are low and there are reportable analytes in the associated samples, re-extraction of the blank and affected samples will normally be required. Consultation with the client should take place.

9.3.3 If reanalysis of the batch is not possible due to limited sample volume or other constraints, the method blank is reported, all associated samples are flagged with a "B", and appropriate comments may be made in a narrative to provide further documentation.

9.3.4 Refer to the STL North Canton QC Program document (QA-003) for further details of the corrective actions.

9.4 Laboratory Control Sample (LCS)

9.4.1 A laboratory control sample (LCS) is prepared and analyzed with every batch of samples. All control analytes must be within established control limits. The LCS is spiked with the compounds listed in Tables 9 and 10 unless specified by a client or agency.

9.4.2 If any control analyte in the LCS is outside the laboratory established historical control limits, corrective action must occur. Corrective action may include re-extraction and reanalysis of the batch.

9.4.2.1 If the batch is not re-extracted and reanalyzed, the reasons for accepting the batch must be clearly presented in the project records and the report. (An example of acceptable reasons for not reanalyzing might be that the matrix spike and matrix spike duplicate are acceptable, and sample surrogate recoveries are good, demonstrating that the problem was confined to the LCS).

9.4.2.2 If re-extraction and reanalysis of the batch is not possible due to limited sample volume or other constraints, the LCS is reported, all associated samples are flagged, and appropriate comments are made in a narrative to provide further documentation.

9.4.3 Ongoing monitoring of the LCS over time provides evidence that the laboratory is performing the method within accepted QC guidelines for accuracy and precision.

9.4.4 Additionally, when an all-analyte check sample is used, all non-controlling compounds must attain a recovery of 5% or greater if the compound is on the client's list.

9.5 Matrix Spike/Matrix Spike Duplicate (MS/MSD)

9.5.1 A matrix spike/matrix spike duplicate (MS/MSD) is prepared and analyzed with every batch of samples. The MS/MSD is spiked with the same subset of analytes as the LCS (See Tables 9 and 10). Compare the percent recovery and relative percent difference (RPD) to that in the laboratory specific historically generated limits.

9.5.1.1 If the recovery for any component is outside QC limits for both the Matrix spike / spike duplicate and the LCS, the laboratory is out of control and corrective action must be taken. Corrective action will normally include repreparation and reanalysis of the batch.

9.5.1.2 If a MS/MSD is not possible due to limited sample, then a LCS duplicate should be analyzed. RPD of the LCS and LCSD are compared to the matrix spike limits.

9.5.1.3 The matrix spike / duplicate must be analyzed at the same dilution as the unspiked sample, even if the matrix spike compounds will be diluted out.

9.6 Surrogates

9.6.1 Every sample, blank, and QC sample is spiked with surrogate standards. Surrogate spike recoveries must be evaluated by determining whether the concentration (measured as percent recovery) falls within the required recovery limits. The compounds routinely included in the surrogate spiking solution, along with recommended standard concentrations, are listed in Table 11.

9.6.2 If any surrogates are outside limits the following corrective actions must take place (except for dilutions):

9.6.2.1 Check all calculations for error.

9.6.2.2 Ensure that instrument performance is acceptable.

9.6.2.3 Recalculate the data and/or reanalyze the extract if either of the above checks reveal a problem.

9.6.2.3.1 It is only necessary to reprepare / reanalyze a sample once to demonstrate that poor surrogate recovery is due to matrix effect, unless the analyst believes that the repeated out of control results are not due to matrix effect. **Note:** If all associated QC meets criteria (blank, LCS/LCSD), up to one surrogate per fraction may be outside of acceptance criteria , as long as the recovery is greater than 10%. **Note:** For Ohio VAP and DoD samples, all surrogates must be within acceptance criteria.

9.6.3 If the sample with surrogate recoveries outside the recovery limits was a sample used for an MS/MSD and the surrogate recoveries in the MS/MSD are also outside of the control limits, then the sample, the MS, and the MSD do not require reanalysis as this phenomenon would indicate a possible matrix problem.

9.6.4 If the sample is reanalyzed and the surrogate recoveries in the reanalysis are acceptable, then the problem was within the analyst's control and only the reanalyzed data should be reported. (Unless the reanalysis was outside holding times, in which case reporting both sets of results may be appropriate.)

9.6.5 If the reanalysis does confirm the original results, the original analysis is reported and the data flagged as estimated due to matrix effect.

9.7 Nonconformance and Corrective Action

9.7.1 Any deviations from QC procedures must be documented as a nonconformance, with applicable cause and corrective action approved by the facility QA Manager.

10. CALIBRATION AND STANDARDIZATION

10.1 Summary

10.1.1 The instrument is tuned for DFTPP, calibrated initially with a minimum five-point calibration curve, and verified each 12-hour shift with one or more continuing calibration standard(s). Recommended instrument conditions are listed in Table 5.

10.2 All standards and extracts are allowed to warm to room temperature before injecting.

10.3 Instrument Tuning

10.3.1 At the beginning of every twelve hour shift when analyses are to be performed, the GC/MS system must be checked to see if acceptable performance criteria (Table 6) is achieved for DFTPP (decafluorotriphenylphosphine).

10.3.2 Inject the GC/MS tuning standard (Section 7.4) into the GC/MS system. Obtain a background-corrected mass spectra of DFTPP and confirm that all the key m/z criteria in Table 6 are achieved. If all the criteria are not achieved, the analyst must retune the mass spectrometer and repeat the test until all criteria are achieved. The performance criteria must be achieved before any samples, blanks, or standards are analyzed.

10.3.3 The GC/MS tuning standard should also be used to evaluate the inertness of the chromatographic system. Each day Benzidine is to be determined, the tailing factor must be less than 3.0. The tailing factor for pentachlorophenol must be less than 5. If DDT is an analyte of interest, it must be included in the tuning standard, and its breakdown must be < 20%. Refer to Section 12 for the appropriate calculations.

10.4 Initial Calibration

10.4.1 Internal Standard Calibration Procedure: Internal standards are listed in Table 7. Use the base peak m/z as the primary m/z for quantitation of the standards. If interferences are noted, use one of the next two most intense masses for quantitation.

10.4.2 Compounds should be assigned to the IS with the closest retention time.

10.4.3 Prepare calibration standards at a minimum of five concentration levels for each parameter of interest. Six standards must be used for a quadratic least squares calibration. Quadratic fit may NOT be used for samples analyzed under South Carolina Certification. It may also be useful to analyze six calibration levels and use the lower five for most analytes and the upper five for analytes that have poor response. Add the internal standard mixture to result in 2 ng on column. (For example, 5 uL of 80ppm IS mix is added to 100 uL of extract. This results in 4 ng, but only 0.5ul is injected, resulting in a final on column amount of 2 ng.)The concentration ranges of all analytes are listed in Tables 12 and 13.

10.4.4 Analyze each calibration standard and tabulate the area of the primary characteristic m/z against concentration for each compound and internal standard. Calculate response factors (RF), average response factors, and the percent RSD of the response factors for each compound using the equations in Section 12 and verify that the CCC and SPCC criteria in Sections 10.4.5 and 10.4.6 are met. **No sample analysis may be performed unless these criteria are met.**

10.4.5 System Performance Check Compounds (SPCCs): The minimum average RF for semivolatile SPCCs is 0.050. If the minimum response factors are not met, the system must be evaluated and corrective action must be taken before sample analysis begins. Some possible problems are standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, and active sites in the column or chromatographic system. This check must be met before analysis begins.

SPCC Compounds:

N-nitroso-di-n-propylamine
Hexachlorocyclopentadiene
2,4-Dinitrophenol
4-Nitrophenol

10.4.6 Calibration Check Compounds (CCCs): The %RSD of the response factors for each CCC in the initial calibration must be less than 30% for the initial calibration to be considered valid. This criterion must be met before sample analysis begins. Problems similar to those listed under SPCCs could affect this criterion.

10.4.6.1 If none of the CCCs are required analytes, project specific calibration specifications must be agreed with the client.

10.4.6.2 CCC Compounds:

Phenol
Acenaphthene
1,4-Dichlorobenzene
N-nitrosodiphenylamine
2-Nitrophenol
Pentachlorophenol
2,4-Dichlorophenol
Fluoranthene
Hexachlorobutadiene
Di-n-octylphthalate
4-Chloro-3-methylphenol
Benzo(a)pyrene
2,4,6-Trichlorophenol

10.4.7 If the software in use is capable of routinely reporting curve coefficients for data validation purposes, and the necessary calibration reports can be generated, then the analyst should evaluate analytes with %RSD > 15% for calibration on a curve. If it appears that substantially better accuracy would be obtained using quantitation from a curve then the appropriate curve should be used for quantitation.

10.4.7.1 If an analyte in the initial calibration is > 15%, then calibration on a curve must be used. Linear or quadratic curve fits may be used. The analyst should consider instrument maintenance to improve the linearity of response. Use of $1/Concentration^2$ weighting is recommended to improve the accuracy of quantitation at the low end of the curve. If Relative Standard Error (RSE) is used to evaluate the curve it must be better than 15%. If the % RSD is >15%, the analyst may drop the low or high points in the ICAL, as long as a minimum of 5 points are maintained and the quantitation range is adjusted accordingly. If the % RSD is still >15%, a quadratic or linear curve may be used. The coefficient of determination (r^2) must be ≥ 0.990. If the coefficient of determination is < 0.990, then any hits for these compounds must be flagged as estimated. If a curve is not linear for any compound that is found in a samples, the result must be flagged as estimated. Linear is defined as <15% RSD or a coefficient of determination of 0.990.

10.4.7.2 Note: Several components do not respond well by this method (poor linearity). These compounds are indene, acrylamide, 4-Nitroquinoline-1-oxide, famphur, benzenethiol, kepone, and 2,4-toluenediamine. If these compounds are requested by a client and hits are found, alternate standards or methods will be needed for more accurate quantitation. Sensitivity as demonstrated by the low standard is sufficient to substantiate a non-detect.

10.4.8 If time remains in the 12 hour period initiated by the DFTPP injection before the initial calibration, samples may be analyzed. Otherwise, proceed to continuing calibration.

10.4.9 **Quantitation is performed using the calibration curve or average response factor from the initial curve, not the continuing calibration.**

10.5 Initial Calibration Verification (ICV)

10.5.1 Calibration accuracy is verified by analyzing a second source standard (ICV) immediately after the initial calibration. The recovery CCC compounds must be $\leq$ 20%. The recovery for non-CCC compounds must be $\leq$ 50% with an allowance of up to 6 compounds >50%.

10.6 Continuing Calibration

10.6.1 At the start of each 12-hour period, the GC/MS tuning standard must be analyzed. The injection of DFTPP must result in a mass spectrum for DFTPP which meets the criteria given in Table 6.

10.6.2 Following a successful DFTPP analysis the continuing calibration standard(s) are analyzed. The standards must contain all semivolatile analytes, including all required surrogates. A mid level calibration standard is used for the continuing calibration.

10.6.3 The following criteria must be met for the continuing calibration to be acceptable:

- The SPCC compounds must have a response factor of $\geq$ 0.05.
- The percent difference or drift of the CCC compounds from the initial calibration must be $\leq$ 20%. (see Section 12 for calculations) In addition, the percent difference or drift of all analytes must be $\leq$ 50%, with allowance for up to (4) compounds to be greater than 50%.
- The internal standard response must be within 50-200% of the response in the mid level of the initial calibration.
- The internal standard retention times must be within 30 seconds of the retention times in the mid-level of the initial calibration.
- NOTE: There is no internal standard criteria for samples. Criteria is only for continuing and initial calibrations.
- NOTE: Ohio VAP rules require that any sample with internal standard outliers be reanalyzed. The criteria for acceptance is between 50% and 200% of same internal standard in continuing calibration.

10.6.3.1. If none of the CCCs are required analytes, project specific calibration specifications must be agreed with the client.

10.6.4. Once the above criteria have been met, sample analysis may begin. Initial calibration average RFs (or the calibration curve) will be used for sample quantitation, not the continuing calibration RFs. Analysis may proceed until 12 hours from the injection of the DFTPP have passed. (A sample *injected* less than 12 hours after the DFTPP is acceptable.)

11. PROCEDURE

11.1 Sample Preparation

11.1.1 Samples are prepared following SOP CORP-OP-0001NC.

11.2 Sample Analysis Procedure

11.2.1 Calibrate the instrument as described in Section 10. Depending on the target compounds required by the client, it may be necessary to use more than one calibration standard.

11.2.2 All samples must be analyzed using the same instrument conditions as the preceding continuing calibration standard.

11.2.3 Add internal standard to the extract to result in 2 ng injected on column. Mix thoroughly before injection into the instrument.

11.2.4 Inject the sample extract into the GC/MS system using the same injection technique as used for the standards.

11.2.5 The data system will determine the concentration of each analyte in the extract using calculations equivalent to those in Section 12. Quantitation is based on the initial calibration, not the continuing calibration.

11.2.6 Identified compounds are reviewed for proper integration. Manual integrations are performed if necessary and are documented by the analyst or automatically by the data system. Chromatograms before and after manual integration are required by many programs.

11.2.7 Target compounds identified by the data system are evaluated using the criteria listed in Section 12.1.

11.2.8 Library searches of peaks present in the chromatogram that are not target compounds (Tentatively Identified Compounds, TIC) may be performed if required by the client. They are evaluated using the criteria in Section

11.3 Dilutions

11.3.1 If the response for any compound exceeds the working range of the GC/MS system, a dilution of the extract is prepared and analyzed. An appropriate dilution should be in the upper half of the calibration range. Samples may be screened to determine the appropriate dilution for the initial run. If the initial diluted run has no hits or hits below 20% of the calibration range and the matrix allows for analysis at a lesser dilution, the sample must be reanalyzed at a dilution targeted to bring the largest hit above 50% of the calibration range.

11.3.1 Guidance for Dilutions Due to Matrix

11.3.1.1 If the sample is initially run at a dilution and the baseline rise is less than the height of the internal standards, or if individual non-target peaks are less than two times the height of the internal standards, the sample should be reanalyzed

at a more concentrated dilution. This requirement is approximate and subject to analyst judgement. For example, samples containing organic acids may need to be analyzed at a higher dilution to avoid destroying the column.

11.3.2 Reporting Dilutions

11.3.2.1 The most concentrated dilution with target compounds within the calibration range will be reported. Other dilutions will only be reported at client request.

11.4 Perform all qualitative and quantitative measurements. When the extracts are not being used for analyses, refrigerate them at 4 ± 2°C, protected from light in screw cap vials equipped with unpierced Teflon lined septa.

11.5 Retention time criteria for samples

11.5.1 If the retention time for any internal standard changes by more than 0.5 minutes from the last continuing calibration standard, the chromatographic system must be inspected for malfunctions and corrected. Reanalysis of samples analyzed while the system was malfunctioning is required.

11.5.2 If the retention time of any internal standard in any sample varies by more than 0.1 minute from the preceding continuing calibration standard, the data must be carefully evaluated to ensure that no analytes have shifted outside their retention time windows.

11.6 Procedural Variations

11.6.1 One-time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and approved by a Technical Specialist and QA Manager. The Nonconformance Memo shall be filed in the project file. Any unauthorized deviations from this procedure must also be documented as a non-conformance, with a cause and corrective action described.

11.7 Troubleshooting Guide

11.7.1 Daily Instrument Maintenance

11.7.1.1 In addition to the checks listed in the instrument maintenance schedule in the STL North Canton Laboratory Quality Manual (LQM), current version, the following daily maintenance should be performed.

11.7.1.1.1 Clip Column as necessary.

11.7.1.1.2 Install new or cleaned injection port liner as necessary.

11.7.1.1.3 Install new septum as necessary.

11.7.1.1.4 Perform autotune.

11.7.2 Major Maintenance

11.7.2.1 A new initial calibration is necessary following major maintenance. Major maintenance includes changing the column, cleaning the source, and replacing the multiplier. Refer to the manufacturer's manual for specific guidance.

12 DATA ANALYSIS AND CALCULATIONS

12.1 Qualitative identification

12.1.1 An analyte is identified by retention time and by comparison of the sample mass spectrum with the mass spectrum of a standard of the suspected compound (standard reference spectrum). Mass spectra for standard reference may be obtained on the user's GC/MS by analysis of the calibration standards or from the NBS library. Two criteria must be satisfied to verify identification: (1) elution of sample component at the same GC retention time as the standard component; and (2) correspondence of the sample component and the standard component characteristic ions. (Note: Care must be taken to ensure that spectral distortion due to co-elution is evaluated.)

12.1.1.1 The sample component retention time must compare to within ± 0.2 min. of the retention time of the standard component. For reference, the standard must be run within the same twelve hours as the sample.

12.1.1.2 All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100%) should be present in the sample spectrum.

12.1.1.3 The characteristic ions of a compound must maximize in the same scan or within one scan of each other.

12.1.1.4 The relative intensities of ions should agree to within ±30% between the standard and sample spectra. (Example: For an ion with an abundance of 50% in the standard spectra, the corresponding sample abundance must be between 20% and 80%.)

12.1.2 If a compound cannot be verified by all the above criteria, but in the technical judgment of the analyst the identification is correct, the analyst shall report that identification and proceed with quantitation.

12.2 Mass chromatogram searches.

12.2.1 Certain compounds are unstable in the calibration standard and cannot be calibrated in the normal way. In particular, the compound hexachlorophene (CAS 70-30-4) falls into this category, and is required for Appendix IX analysis. For this analyte a mass chromatogram search is made.

12.2.1.1 Hexachlorophene

12.2.1.1.1 Display the mass chromatograms for mass 196 and mass 198 for the region of the chromatogram from at least 2 minutes before chrysene-d12 to at least 4 minutes after chrysene-d12. If peaks for both ions coincide then the analyst evaluates the spectrum for the presence of hexachlorophene. No quantitation is possible.

12.3 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 type of analyses being conducted. Computer generated library search routines should 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 shall the mass spectral interpretation specialist assign a tentative identification. Guidelines for making tentative identification are:

12.3.1 Relative intensities of major ions in the reference spectrum (ions >10% of the most abundant ion) should be present in the sample spectrum.

12.3.2 The relative intensities of the major ions should agree within ±20%. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance should be between 30%and 70%.)

12.3.3 Molecular ions present in the reference spectrum should be present in the sample spectrum.

12.3.4 Ions present in the sample spectrum, but not in the reference spectrum, should be reviewed for possible background contamination or presence of coeluting compounds.

12.3.5 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 coeluting peaks. Data system library reduction programs can sometimes create these discrepancies.

12.3.6 Automatic background subtraction can severely distort spectra from samples with unresolved hydrocarbons.

12.3.7 Note: For water samples, the TIC searches begin with compounds eluting after the first surrogate (2-Fluorophenol). For solid samples, the TIC searches begin with compounds eluting after the Aldol Condensation Product. Any compounds eluting before these analytes are considered volatile analytes are reported in the volatile analysis. A possible exception to this general rule would be if an early eluting compound was the reason for a sample dilution.

12.3.8 If a client requests 10 TICs, the laboratory supplies a minimum of 10. For a request of 20 TICS, the laboratory would supply a minimum of 20, assuming that number of compounds were available.

12.4 Anyone evaluating data is trained to know how to handle isomers with identical mass spectra and close elution times. These include:

Dichlorobenzenes
Methylphenols
Trichlorophenols
Phenanthrene, anthracene
Fluoranthene, pyrene
Benzo(b) and (k)fluoranthene
Chrysene, benzo(a)anthracene

Extra precautions concerning these compounds are to more closely scrutinize retention time vs. the calibration standard and also to check that all isomers have distinct retention times.

A second category of problem compounds would be the poor responders or compounds that chromatograph poorly. Included in this category would be:

Benzoic acid
Chloroanilines
Nitroanilines
2,4-Dinitrophenol
4-Nitrophenol
Pentachlorophenol
3,3'-Dichlorobenzidine
Benzyl alcohol
4,6-Dinitro-2-methylphenol

Manually checking the integrations would be appropriate for these compounds.

12.5 Calculations

12.5.1 Percent Relative Standard Deviation for Initial Calibration

$$\%RSD = \frac{SD}{\overline{RF}} \times 100$$

$\overline{RF}$ = Mean of RFs from intial caibration for a compound

SD = Standard deviation of RFs from initial calibration for a compound,

$$= \sqrt{\sum_{i=1}^{N} \frac{\left(RFi - \overline{RF}\right)^2}{N-1}}$$

RFi = RF for each of the calibration levels

N = Number of RF values

12.5.2 Continuing calibration percent drift

$$\%Drift = \frac{C_{actual} - C_{found}}{C_{actual}} \times 100\%$$

C_{actual} = Known concentration in standard

C_{found} = Measured concentration using selected quantitation method

12.5.3 Concentration in the extract

The concentration of each identified analyte and surrogate in the extract is calculated from the linear or quadratic curve fitted to the initial calibration points, or from the average RF of the initial calibration.

12.5.3.1 Average response factor

If the average of all the %RSDs of the response factors in the initial calibration is $\leq$ 15%, the average response factor from the initial calibration may be used for quantitation.

$$C_{ex} = \frac{R_x C_{is}}{R_{is} \overline{RF}}$$

12.5.3.2 Linear fit

$$C_{ex} = A + B\frac{(R_x C_{is})}{R_{is}}$$

Where: C_{ex}= Concentration in extract, µg/mL

R_x= Response for analyte

C_{is}= Concentration of internal standard

A= Intercept

B= Slope

12.5.3.3 Quadratic fit

$$C_{ex} = A + B\left(\frac{R_x C_{is}}{R_{is}}\right) + C\left(\frac{R_x C_{is}}{R_{is}}^2\right)$$

Where: C = Curvature

12.5.4 The concentration in the sample is then calculated.

12.5.4.1 Aqueous Calculation

$$\text{Concentration, } \mu g / L = \frac{C_{ex} V_t}{V_o}$$

Where: V_t= Volume of total extract, µL, taking into account dilutions (i.e., a 1-to-10 dilution of a 1 mL extract will mean V_t = 10,000 µL. If half of the base/neutral extract and half of the acid extract are

combined, V_t = 2,000.)

V_o = Volume of water extracted (mL)

12.5.5 Sediment/Soil, Sludge (on a dry-weight basis) and Waste (normally on a wet-weight basis:

$$\text{Concentration, } \mu g / kg = \frac{C_{ex} V_t}{W_s D}$$

Where: W_s = Weight of sample extracted or diluted in grams

D = (100 - % moisture in sample)/100, for a dry weight basis or one for a wet weight basis

12.6 MS/MSD percent recovery calculation.

$$\text{Matrix Spike Recovery} = \frac{S_{SR} - S_R}{S_A} \times 100\%$$

Where: S_{SR} = Spike sample result

S_R=Sample result

S_A = Spike added

12.7 Relative % Difference calculation for the MS/MSD

$$RPD = \frac{MS_R - MSD_R}{1/2(MS_R + MSD_R)} \times 100$$

Where: RPD = Relative percent difference

MS_R = Matrix spike result

MSD_R = Matrix spike duplicate result

12.8 Relative response factor calculation.

$$RF = \frac{A_x C_{is}}{A_{is} C_x}$$

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_x=Concentration of the compound being measured (µg/L)

C_{is} =Concentration of the specific internal standard (µg/L)

12.9 Calculation of TICs: The calculation of TICs (tentatively identified compounds) is identical to the above calculations with the following exceptions:

A_x =Area of the total ion chromatogram for the compound being measured

A_{is}=Area of the total ion chromatogram for the nearest internal standard without interference

RF=1

12.10 Percent DDT breakdown

$$\% \text{ DDT breakdown} = \frac{\text{DDEarea} + \text{DDDarea}}{\text{DDTarea} + \text{DDEarea} + \text{DDarea}}$$

The total ion current areas are used for this calculation

13. METHOD PERFORMANCE

13.1 Method Detection Limit

13.1.1 Each laboratory must generate a valid method detection limit for each analyte of interest. The MDL must be below the reporting limit for each analyte. The procedure for determination of the method detection limit is given in 40 CFR Part 136, Appendix B, and further defined in policy S-Q-003 and SOP NC-QA-0021.

13.2 Initial Demonstration

13.2.1 Each laboratory must make an initial demonstration of capability for each individual method. Demonstration of capability for both soil and water matrices is required. This requires analysis of QC check samples containing all of the standard analytes for the method. For some tests it may be necessary to use more than one QC check mix to cover all analytes of interest.

13.2.1.1 Four aliquots of the QC check sample are analyzed using the same procedures used to analyze samples, including sample preparation.

13.2.1.2 Calculate the average recovery and standard deviation of the recovery for each analyte of interest.

13.2.1.3 If any analyte does not meet the acceptance criteria the test must be repeated.

Only those analytes that did not meet criteria in the first test need to be evaluated. Repeated failure for any analyte indicates the need for the laboratory to evaluate the analytical procedure and take corrective action.

13.3 Non-standard analytes

13.3.1 For non-standard analytes, an MDL study must be performed and calibration curve generated before analyzing any samples, unless lesser requirements are previously agreed to with the client. In any event, the minimum initial demonstration required is analysis of an extracted standard at the reporting limit and a single point calibration.

13.4 Training Qualification

13.4.1 The Group/Team Leader has the responsibility to ensure that this procedure is performed by an analyst who has been properly trained in its use and has the required experience.

13.4.2 Method validation information (where applicable) in the form of laboratory demonstrations of capabilities is maintained for this method in the laboratory QA files.

14. POLLUTION PREVENTION

14.1 This section is not applicable to this procedure.

15. WASTE MANAGEMENT

15.1 All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in Section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

15.2 Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices of STL. They must have training on the hazardous waste disposal practices upon initial assignment to these tasks, followed by an annual refresher training.

15.3 Waste Streams Produced by the Method

15.3.1 **Vials containing sample extracts:** These vials are placed in the vial waste located in the GC/MS laboratory.

16. REFERENCES

16.1 References

16.1.1 SW846, Test Methods for Evaluating Solid Waste, Third Edition, Update III October 1994, Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS): Capillary Column Technique, Method 8270C.

16.1.2 J. W. Eichelberger, L. E. Harris, and W. L. Budde, "Reference Compound to Calibrate Ion Abundance Measurement in Gas Chromatography/Mass Spectrometry," Analytical Chemistry, 47, 995 (1975)

16.1.3 Corporate Quality Management Plan (QMP), current version.

16.1.4 STL Laboratory Quality Manual (LQM), current version.

16.2 Associated SOPs and Policies, latest version

16.2.1 QA Policy, QA-003

16.2.2 Glassware Washing, NC-QA-0014

16.2.3 Statistical Evaluation of Data and Development of Control Charts, NC-QA-0018

16.2.4 Method Detection Limits and Instrument Detection Limits, NC-QA-0021

16.2.5 Supplemental Practices for DoD Project Work, SOP, NC-QA-0016

16.2.6 Standard and Reagents, SOP NC-QA-0017.

17. MISCELLANEOUS

17.1 Modifications from Reference Method

17.1.1 A retention time window of 0.2 minutes is used for all components, since some data systems do not have the capability of using the relative retention time units specified in the reference method.

17.1.2 The quantitation and qualifier ions from compounds have been changed from those recommennded in SW-846 in order to improve the reliability of qualitative identification.

17.2 Tables

Table 1 - STL North Canton Primary Standard and Standard Reporting Limits

Analytes	CAS Number	Water µg/L	Soil µg/kg	Low Level Water, µg/L	Low Level Soil, µg/kg	TCLP mg/L
1,1-Biphenyl	92-52-4	10	330	1	50	
1,2,4-Trichlorobenzene	120-82-1	10	330	1	50	
1,2-Dichlorobenzene	95-50-1	10	330	1	50	
1,3-Dichlorobenzene	541-73-1	10	330	1	50	
1,4-Dichlorobenzene	106-46-7	10	330	1	50	0.004
1-Methyl Naphthalene	90-12-0	10	330	0.2	6.67	
2,2'-oxybis(1-chloropropane)[1]	108-60-1	10	330	2	100	
2,4,5-Trichlorophenol	95-95-4	10	330	1	150	0.02
2,4,6-Trichlorophenol	88-06-2	10	330	1	150	0.02
2,4-Dichlorophenol	120-83-2	10	330	2	150	
2,4-Dimethylphenol	105-67-9	10	330	2	150	
2,4-Dinitrophenol	51-28-5	50	1600	5	330	
2,4-Dinitrotoluene	121-14-2	10	330	5	200	0.02
2,6-Dinitrotoluene	606-20-2	10	330	5	200	
2-Chloronaphthalene	91-58-7	10	330	1	50	
2-Chlorophenol	95-57-8	10	330	1	50	
2-Methylnaphthalene	91-57-6	10	330	0.2	6.67	
2-Methylphenol	95-48-7	10	330	1	200	
2-Nitroaniline	88-74-4	50	1600	2	200	
2-Nitrophenol	88-75-5	10	330	2	50	
3,3'-Dichlorobenzidine	91-94-1	50	1600	5	100	
3-Nitroaniline	99-09-2	50	1600	2	200	
4,6-Dinitro-2-methylphenol	534-52-1	50	1600	5	150	
4-Bromophenyl phenyl ether	101-55-3	10	330	2	50	
4-Chloro-3-methylphenol	59-50-7	10	330	2	150	
4-Chloroaniline	106-47-8	10	330	2	150	
4-Chlorophenyl phenyl ether	7005-72-3	10	330	2	50	
4-Methylphenol	106-44-5	10	330	1	200	
4-Nitroaniline	100-01-6	50	1600	2	200	
4-Nitrophenol	100-02-7	50	1600	5	330	
Acenaphthene	83-32-9	10	330	0.2	6.67	
Acenaphthylene	208-96-8	10	330	0.2	6.67	
Aniline	62-53-3	10	330	1	330	
Anthracene	120-12-7	10	330	0.2	6.67	
Atrazine	1912-24-9	10	330	1	200	
Azobenzene	103-33-3	10	330	10	330	
Benzaldehyde	100-52-7	10	330	1	100	
Benzenethiol	108-98-5	10	330	10	330	
Benzidine	92-87-5	100	3300	5	330	
Benzo(a)anthracene	56-55-3	10	330	0.2	6.67	
Benzo(a)pyrene	50-32-8	10	330	0.2	6.67	
Benzo(b)fluoranthene	205-99-2	10	330	0.2	6.67	
Benzo(g,h,i)perylene	191-24-2	10	330	0.2	6.67	
Benzo(k)fluoranthene	207-08-9	10	330	0.2	6.67	
Benzoic acid	65-85-0	50	1600	10	660	

Table 1 (Cont'd)

Analytes	CAS Number	Water µg/L	Soil µg/kg	Low Level Water, µg/L	Low Level Soil, µg/kg	TCLP mg/L
Benzyl alcohol	100-51-6	10	330	5	330	
Bis(2-chloroethoxy)methane	111-91-1	10	330	1	100	
Bis(2-chloroethyl)ether	111-44-4	10	330	1	100	
Bis(2-ethylhexyl)phthalate	117-81-7	10	330	1	50	
Butyl benzyl phthalate	85-68-7	10	330	1	50	
Caprolactam	105-60-2	10	330	5	330	
Carbazole	86-74-8	10	330	1	50	
Chrysene	218-01-9	10	330	0.2	6.67	
Dibenz(a,h)anthracene	53-70-3	10	330	0.2	6.67	
Dibenzofuran	132-64-9	10	330	1	50	
Diethylphthalate	84-66-2	10	330	1	50	
Dimethyl phthalate	131-11-3	10	330	1	50	
Di-n-butyl phthalate	84-74-2	10	330	1	50	
Di-n-octylphthalate	117-84-0	10	330	1	50	
Fluoranthene	206-44-0	10	330	0.2	6.67	
Fluorene	86-73-7	10	330	0.2	6.67	
Hexachlorobenzene	118-74-1	10	330	0.2	6.67	0.02
Hexachlorobutadiene	87-68-3	10	330	1	50	0.02
Hexachlorocyclopentadiene	77-47-4	50	1600	10	330	0.02
Hexachloroethane	67-72-1	10	330	1	50	
Indene	95-13-6	10	330	5	330	
Indeno(1,2,3-cd)pyrene	193-39-5	10	330	0.2	6.67	
Isophorone	78-59-1	10	330	1	50	
Naphthalene	91-20-3	10	330	0.2	6.67	
Nitrobenzene	98-95-3	10	330	1	100	0.004
N-nitrosodimethylamine	62-75-9	10	330	1	100	
N-Nitroso-di-n-propylamine	621-64-7	10	330	1	50	
N-Nitrosodiphenylamine	86-30-6	10	330	1	50	
Pentachlorophenol	87-86-5	50	1600	5	150	0.04
Phenanthrene	85-01-8	10	330	0.2	6.67	
Phenol	108-95-2	10	330	1	50	
Pyrene	129-00-0	10	330	0.2	6.67	
Pyridine	110-86-1	20	660	1	100	0.02
Quinoline	91-22-5	10	330	5	330	
m-Cresol & p Cresol						0.04
o-Cresol						0.004

[1] 2,2'oxybis(1-chloropropane) was formerly known as bis(2-chloroisopropyl)ether.

Table 2 - STL North Canton Appendix IX[1] Standard Reporting Limits

Analytes	CAS Number	Water µg/L	Soil µg/kg	Low Level Water, µg/L	Low Level Soil, µg/kg
1,2,4,5-Tetrachlorobenzene	95-94-3	10	330	1	100
1,3,5-Trinitrobenzene	99-35-4	50	1600	5	1600
1,3-Dinitrobenzene	99-65-0	10	330	2	330
1,4-Dinitrobenzene	100-25-4	10	330	2	100
1,4-Naphthoquinone	130-15-4	50	1600	50	330
1-Naphthylamine	134-32-7	10	330	2	330
2,3,4,6-Tetrachlorophenol	58-90-2	50	1600	10	100
2,6-Dichlorophenol	87-65-0	10	330	5	150
2-Acetylaminofluorene	53-96-3	100	3300	10	330
2-Naphthylamine	91-59-8	10	330	2	200
2-Picoline	109-06-8	20	660	5	330
2-secbutyl-4,6-dinitrophenol (Dinoseb2)	88-85-7	20	660	2	330
3,3'-Dimethylbenzidine	119-93-7	50	1600	5	330
3-Methylcholanthrene	56-49-5	20	660	5	200
3-Methylphenol	108-39-4	10	330	1	200
4-Aminobiphenyl	92-67-1	50	1600	5	330
4-Nitroquinoline-1-oxide	56-57-5	100	3300	5	330
4-Nitro-o-toluidine	99-55-8	20	660	2	330
7,12-Dimethylbenz(a)anthracene	57-97-6	20	660	2	330
a,a-Dimethyl-phenethylamine	122-09-8	50	1600	5	660
Acetophenone	98-86-2	10	330	1	100
Aramite	140-57-8	20	660	5	330
Diallate[2]	2303-16-4	20	660	10	330
Dibenz(a,j)acridine	224-42-0	20	660	5	330
Dimethoate	60-51-5	20	660	2	330
Disulfoton	298-04-4	50	1600	2	330
Ethyl methanesulfonate	62-50-0	10	330	2	330
Famphur	52-85-7	100	3300	10	3300
Hexachloropropene	1888-71-7	100	3300	5	0.02
Isosafrole	120-58-1	20	660	5	330
Methapyrilene	91-80-5	50	1600	2	330
Methyl methanesulfonate	66-27-3	10	330	2	330
N-Nitrosodiethylamine	55-18-5	10	330	2	100
n-Nitrosodi-n-butylamine	924-16-3	10	330	2	100
N-Nitrosomethylethylamine	10595-95-6	10	330	2	100
N-Nitrosomorpholine	59-89-2	10	330	2	330
N-Nitrosopiperidine	100-75-4	10	330	2	330
N-Nitrosopyrrolidine	930-55-2	10	330	2	50
o,o,o-Triethyl-Phosphorothioate	126-68-1	50	1600	2	330
o-Toluidine	95-53-4	20	660	2	330
p-(Dimethylamino)azobenzene	60-11-7	20	660	2	330
p-Chlorobenzilate	510-15-6	10	330	2	330
Pentachlorobenzene	608-93-5	10	330	2	100

Table 2 (Cont'd)

Analytes	CAS Number	Water µg/L	Soil µg/kg	Low Level Water, µg/L	Low Level Soil, µg/kg
Pentachloroethane	76-01-7	50	1600	20	330
Pentachloronitrobenzene	82-68-8	50	1600	2	330
Phenacetin	62-44-2	20	660	2	330
Phorate	298-02-2	50	1600	2	330
p-Phenylenediamine	106-50-3	100	3300	40	660
Pronamide	23950-58-5	20	660	2	330
Safrole	94-59-7	20	660	2	330
Sulfotepp	3689-24-5	50	1600	5	330
Thionazin	297-97-2	50	1600	2	330
1,2,4,5-Tetrachlorobenzene	95-94-3	10	330	1	100
1,3,5-Trinitrobenzene	99-35-4	50	1600	5	1600
1,3-Dinitrobenzene	99-65-0	10	330	2	330
1,4-Dinitrobenzene	100-25-4	10	330	2	100

[1] The Appendix IX standard contains additional analytes required for the Appendix IX list. The STL North Canton primary standard must also be analyzed to include all of the Appendix IX list

Table 2A – STL North Canton Michigan Program[1]

Semivolatile	CAS Number	Michigan Reporting Limits	
		Aqueous µg/L	Low Soil/Sediment µg/kg
Acenaphthene	83-32-9	5	330
Acenaphthylene	208-96-8	5	330
Acetophenone	98-86-2	5	330
Anthracene	120-12-7	5	330
Atrzine	1912-24-9	5	330
Benzaldehyde	100-52-7	10	330
Benzo(a)anthracene	56-55-3	1	330
Benzo(a)pyrene	50-32-8	2	330
Benzo(b)fluoranthene	205-99-2	2	330
Benzo(g,h,i)perylene	191-24-2	5	330
Benzo(k)fluoranthene	207-08-9	5	330
1,1'-Biphenyl	92-52-4	10	330
4-Bromophenylphenyl ehter	101-55-3	5	330
Butylbenzylphthalate	85-68-7	5	330
di-n-Butylphthalate	84-74-2	5	330
Caprolactam	105-60-2	10	330
Carbazole	86-74-8	10	330
4-Chloroaniline	106-47-8	20	1700
bis(2-Chloroethoxy)methane	111-91-1	5	330
bis(2-Chloroethyl)ether	111-44-4	4	330
bis(2-Chloroisopropyl)ether	108-60-1	5	330
4-Chloro-3-Methylphenol	59-50-7	5	330
2-Chloronaphthalene	91-58-7	5	330
2-Chlorophenol	95-57-8	5	330
4-Chlorophenyl phenyl ether	7005-72-3	5	330
Chrysene	218-01-9	5	330
Dibenz(a,h)anthracene	53-70-3	2	330
Dibenzofuran	132-64-9	5	330
3,3'-Dichlorobenzidine	91-94-1	4	2000
2,4-Dichlorophenol	120-83-2	10	330
Diethylphthalate	84-66-2	5	330
2-4-Dimethylphenol	105-67-9	5	330
Dimethylphthalate	131-11-3	5	330
4,6-Dinitro-2-methylphenol	534-52-1	20	1700
2,4-Dinitrophenol	51-28-5	20	1700
2,4-Dinitrotoluene	121-14-2	5	330
2,6-Dinitrotoluene	606-20-2	5	330
bis(2-Ethylhexyl)phthalate	117-81-7	5	330
Fluoranthene	206-44-0	5	330
Fluorene	86-73-7	5	330
Hexachlorobenzene	118-74-1	5	330
Hexachlorobutadiene	87-68-3	5	330
Hexachlorocyclopentadiene	77-47-4	5	330
Hexachloroethane	67-72-1	5	330

Table 2A (Cont'd)

Semivolatile	CAS Number	Michigan Reporting Limits	
		Aqueous µg/L	Low Soil/Sediment µg/kg
Indeno(1,2,3-cd)pyrene	193-39-5	2	330
Isophorone	78-59-1	5	330
2-Methylnapthalene	91-57-6	5	330
2-Methylphenol	95-48-7	5	330
4-Methylphenol	106-44-5	5	330
Naphthalene	91-20-3	5	330
2-Nitroaniline	88-74-4	20	1700
3-Nitroaniline	99-09-2	20	1700
4-Nitroaniline	100-01-6	20	1700
Nitrobenzene	95-95-3	4	330
2-Nitrophenol	88-75-5	5	330
4-Nitrophenol	100-02-7	20	1700
N-Nitroso-di-n-propylamine	621-64-7	5	330
N-Nitrosodiphenylamine (diphenylamine)	62-75-9	5	330
di-n-Octylphthalate	117-84-0	5	330
Pentachlorophenol	87-86-5	20	800
Phenanthrene	85-01-8	5	330
Phenol	108-95-2	5	330
Pyrene	129-00-0	5	330
2,4,5-Trichlorophenol	95-95-4	5	330
2,4,6-Trichlorophenol	88-06-2	4	330

[1] Reporting Limits are only for samples performed under the Michigan program.

Table 3 - Reportable Analytes for STL North Canton Standard Tests, Primary Standard

Analyte	CAS Number	TCLP	TCL	Appendix IX
Pyridine	110-86-1	X		X
N-nitrosodimethylamine	62-75-9			X
Aniline	62-53-3			X
Phenol	108-95-2		X	X
Bis(2-chloroethyl)ether	111-44-4		X	X
2-Chlorophenol	95-57-8		X	X
1,3-Dichlorobenzene	541-73-1		X	X
1,4-Dichlorobenzene	106-46-7	X	X	X
Benzyl alcohol	100-51-6			X
1,2-Dichlorobenzene	95-50-1		X	X
2-Methylphenol	95-48-7	X	X	X
2,2'-oxybis(1-chloropropane)	180-60-1		X	X
4-Methylphenol	106-44-5	X	X	X
N-Nitroso-di-n-propylamine	621-64-7		X	X
Hexachloroethane	67-72-1	X	X	X
Nitrobenzene	98-95-3	X	X	X
Isophorone	78-59-1		X	X
2-Nitrophenol	88-75-5		X	X
2,4-Dimethylphenol	105-67-9		X	X
Benzoic acid	65-85-0			
Bis(2-chloroethoxy)methane	111-91-1		X	X
2,4-Dichlorophenol	120-83-2		X	X
1,2,4-Trichlorobenzene	120-82-1		X	X
Naphthalene	91-20-3		X	X
4-Chloroaniline	106-47-8		X	X
Hexachlorobutadiene	87-68-3	X	X	X
4-Chloro-3-methylphenol	59-50-7		X	X
2-Methylnaphthalene	91-57-6		X	X
Hexachlorocyclopentadiene	77-47-4		X	X
2,4,6-Trichlorophenol	88-06-2	X	X	X
2,4,5-Trichlorophenol	95-95-4	X	X	X
2-Chloronaphthalene	91-58-7		X	X
2-Nitroaniline	88-74-4		X	X
Dimethyl phthalate	131-11-3		X	X
Acenaphthylene	208-96-8		X	X
3-Nitroaniline	99-09-2		X	X
Acenaphthene	83-32-9		X	X
2,4-Dinitrophenol	51-28-5		X	X
4-Nitrophenol	100-02-7		X	X
Dibenzofuran	132-64-9		X	X
2,4-Dinitrotoluene	121-14-2	X	X	X

1 Azobenzene is formed by decomposition of 1,2-diphenyhydrazine. If 1,2-diphenylhydrazine is requested, it will be analyzed as azobenzene.

Table 3 (Cont'd)

Analyte	CAS Number	TCLP	TCL	Appendix IX
2,6-Dinitrotoluene	606-20-2		X	X
Diethylphthalate	84-66-2		X	X
4-Chlorophenyl phenyl ether	7005-72-3		X	X
Fluorene	86-73-7		X	X
4-Nitroaniline	100-01-6		X	X
4,6-Dinitro-2-methylphenol	534-52-1		X	X
N-Nitrosodiphenylamine	86-30-6		X	X
Azobenzene[1]	103-33-3			
4-Bromophenyl phenyl ether	101-55-3		X	X
Hexachlorobenzene	118-74-1	X	X	X
Pentachlorophenol	87-86-5	X	X	X
Phenanthrene	85-01-8		X	X
Anthracene	120-12-7		X	X
Carbazole	86-74-8		X	
	84-74-2		X	X
Fluoranthene	206-44-0		X	X
Benzidine	92-87-5			
Pyrene	129-00-0		X	X
Butyl benzyl phthalate	85-68-7		X	X
3,3'-Dichlorobenzidine	91-94-1		X	X
Benzo(a)anthracene	56-55-3		X	X
Bis(2-ethylhexyl)phthalate	117-81-7		X	X
Chrysene	218-01-9		X	X
Di-n-octylphthalate	117-84-0		X	X
Benzo(b)fluoranthene	205-99-2		X	X
Benzo(k)fluoranthene	207-08-9		X	X
Benzo(a)pyrene	50-32-8		X	X
Indeno(1,2,3-cd)pyrene	193-39-5		X	X
Dibenz(a,h)anthracene	53-70-3		X	X
Benzo(g,h,i)perylene	191-24-2		X	X
Benzaldehyde	100-52-7		X	
Caprolactam	105-60-2		X	
1,1-Biphenyl	92-52-4		X	
Atrazine	1912-24-9		X	

[1] Azobenzene is formed by decomposition of 1,2-diphenyhydrazine. If 1,2-diphenylhydrazine is requested, it will be analyzed as azobenzene.

Table 4 - Reportable Analytes for STL North Canton Standard Tests, Appendix IX Standard

Semivolatiles	CAS Number	TCLP	TCL	Appendix IX
2-Picoline	109-06-8			X
N-Nitrosomethylethylamine	10595-95-6			X
Methyl methanesulfonate	66-27-3			X
N-Nitrosodiethylamine	55-18-5			X
Ethyl methanesulfonate	62-50-0			X
Pentachloroethane	76-01-7			X
Acetophenone	98-86-2		X	X
N-Nitrosopyrrolidine	930-55-2			X
N-Nitrosomorpholine	59-89-2			X
o-Toluidine	95-53-4			X
3-Methylphenol	108-39-4			X
N-Nitrosopiperidine	100-75-4			X
o,o,o-Triethyl-Phosphorothioate	126-68-1			X
a,a-Dimethyl-phenethylamine	122-09-8			X
2,6-Dichlorophenol	87-65-0			X
Hexachloropropene	1888-71-7			X
p-Phenylenediamine	106-50-3			X
n-Nitrosodi-n-butylamine	924-16-3			X
Safrole	94-59-7			X
1,2,4,5-Tetrachlorobenzene	95-94-3			X
Isosafrole	120-58-1			X
1,4-Dinitrobenzene	100-25-4			X
1,4-Naphthoquinone	130-15-4			X
1,3-Dinitrobenzene	99-65-0			X
Pentachlorobenzene	608-93-5			X
1-Naphthylamine	134-32-7			X
2-Naphthylamine	91-59-8			X
2,3,4,6-Tetrachlorophenol	58-90-2			X
5-Nitro-o-toluidine	99-55-8			X
Thionazin	297-97-2			X
1,3,5-Trinitrobenzene	99-35-4			X
Sulfotepp	3689-24-5			X
Phorate	298-02-2			X
Phenacetin	62-44-2			X
Diallate	2303-16-4			X
Dimethoate	60-51-5			X
4-Aminobiphenyl	92-67-1			X
Pentachloronitrobenzene	82-68-8			X
Pronamide	23950-58-5			X
Disulfoton	298-04-4			X
2-secbutyl-4,6-dinitrophenol (Dinoseb)	88-85-7			X

Table 4 (Cont'd)

Semivolatiles	CAS Number	TCLP	TCL	Appendix IX
4-Nitroquinoline-1-oxide	56-57-5			X
Famphur	52-85-7			X
Methapyrilene	91-80-5			X
Aramite	140-57-8			X
p-(Dimethylamino)azobenzene	60-11-7			X
p-Chlorobenzilate	510-15-6			X
3,3'-Dimethylbenzidine	119-93-7			X
2-Acetylaminofluorene	53-96-3			X
Dibenz(a,j)acridine[1]	224-42-0			
7,12-Dimethylbenz(a)anthracene	57-97-6			X
3-Methylcholanthrene	56-49-5			X
Hexachlorophene[2]	70-30-4			X
Diphenylamine[3]	122-39-4			X

[1] Skinner List Compound

[2] Hexachlorophene is a required analyte for Appendix IX. This compound is not stable, and therefore not included in the calibration standard. The characteristic ions for hexachlorophene are searched for in the chromatogram. (See Section 12.2.1)

[3] Diphenylamine is a required compound for Appendix IX. N-nitrosodiphenylamine decomposes in the injection port to form diphenylamine. Therefore, these two compounds cannot be distinguished. Diphenylamine is not included in the calibration standard.

Table 5 - Suggested Instrumental Conditions

Mass Range	35-500 amu
Scan Time	≤1 second/scan
Initial Column Temperature/Hold Time	45°C for 1 minutes
Column Temperature Program	45- 100°C at 25°C/min for 0 min 100 - 280°C at 30°C/min for 0 min 280 - 100°C at 25°C/min for 2 min
Final Column Temperature/Hold Time	320°C (until at least one minute after benzo(g,h,i)perylene has eluted)
Injector Temperature	250 - 300°C
Transfer Line Temperature	250 - 300°C
Source Temperature	According to manufacturer's Specifications
Injector	Grob-type, split / splitless
Sample Volume	0.5 µl
Carrier Gas	Helium at 30 cm/sec

Table 6 - DFTPP Key Ions and Ion Abundance Criteria

Mass	Ion Abundance Criteria
51	30 – 60% of mass 198
68	<2% of mass 69
70	<2% of mass 69
127	40 – 60% of mass 198
197	<1% of mass 198
198	Base peak, 100% relative abundance
199	5 – 9% of mass 198
275	10 – 30% of mass 198
365	>1% of mass 198
441	Present, but less than mass 443
442	>40% of mass 198
443	17 – 23% of mass 442

Table 7 - Analytes in Approximate Retention Time Order and Characteristic Ions, Primary Standard

Analyte	Primary	Secondary	Tertiary
N-nitrosodimethylamine	74	42	
Pyridine	79	52	
2-Fluorophenol (Surrogate Standard)	112	64	63
Phenol-d5 (Surrogate Standard)	99	42	71
Benzaldehyde	77	105	106
Aniline	93	66	
Phenol	94	65	66
Bis(2-chloroethyl)ether	93	63	95
2-Chlorophenol	128	64	130
1,3-Dichlorobenzene	146	148	113
1,4-Dichlorobenzene-d4 (Internal Standard)	152	150	115
1,4-Dichlorobenzene	146	148	113
Benzyl Alcohol	108	79	77
1,2-Dichlorobenzene	146	148	113
2-Methylphenol	108	107	79
2,2'-oxybis(1-chloropropane)[1]	45	77	79
4-Methylphenol	108	107	79
N-Nitroso-di-n-propylamine	70	42	101,130
Hexachloroethane	117	201	199
Nitrobenzene-d5 (Surrogate Standard)	82	128	54
Nitrobenzene	77	123	65
Isophorone	82	95	138
2-Nitrophenol	139	65	109
2,4-Dimethylphenol	107	121	122
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-d8 (Internal Standard)	136	68	54
Naphthalene	128	129	127
4-Chloroaniline	127	129	65
Hexachlorobutadiene	225	223	227
Caprolactam	113	55	56
4-Chloro-3-methylphenol	107	144	142
2-Methylnaphthalene	142	141	115
Hexachlorocyclopentadiene	237	235	272
2,4,6-Trichlorophenol	196	198	200
2,4,5-Trichlorophenol	196	198	200
1,1'-Biphenyl	154	153	76

Table 7 (Cont'd)

Analyte	Primary	Secondary	Tertiary
2-Fluorobiphenyl (Surrogate Standard)	172	171	170
2-Chloronaphthalene	162	164	127
2-Nitroaniline	65	92	138
Dimethylphthalate	163	194	164
Acenaphthylene	152	151	153
2,6-Dinitrotoluene	165	63	89
Acenaphthene-d10 (Internal Standard)	164	162	160
3-Nitroaniline	138	108	92
Acenaphthene	153	152	154
2,4-Dinitrophenol	184	63	154
Dibenzofuran	168	139	84
4-Nitrophenol	109	139	65
2,4-Dinitrotoluene	165	63	89
Diethylphthalate	149	177	150
Fluorene	166	165	167
4-Chlorophenylphenylether	204	206	141
4-Nitroaniline	138	92	108
4,6-Dinitro-2-methylphenol	198	182	77
N-Nitrosodiphenylamine	169	168	167
2,4,6-Tribromophenol (Surrogate Standard)	330	332	141
Azobenzene	77	182	105
4-Bromophenylphenylether	248	250	141
Hexachlorobenzene	284	142	249
Atrazine	200	173	215
Pentachlorophenol	266	264	268
Phenanthrene-d10 (Internal Standard)	188	94	80
Phenanthrene	178	179	176
Anthracene	178	179	176
Carbazole	167	166	139
Di-n-butylphthalate	149	150	104
Fluoranthene	202	101	100
Benzidine	184	92	185
Pyrene	202	101	100
Terphenyl-d14 (Surrogate Standard)	244	122	212
Butylbenzylphthalate	149	91	206
Benzo(a)Anthracene	228	229	226
Chrysene-d12 (Internal Standard)	240	120	236
3,3'-Dichlorobenzidine	252	254	126
Chrysene	228	226	229
Bis(2-ethylhexyl)phthalate	149	167	279
Di-n-octylphthalate	149	167	43
Benzo(b)fluoranthene	252	253	125

Table 7 (Cont'd)

Analyte	Primary	Secondary	Tertiary
Benzo(k)fluoranthene	252	253	125
Benzo(a)pyrene	252	253	125
Perylene-d12 (Internal Standard)	264	260	265
Indeno(1,2,3-cd)pyrene	276	138	277
Dibenz(a,h)anthracene	278	139	279
Benzo(g,h,i)perylene	276	138	277

Table 8 - Additional Appendix IX Analytes in Approximate Retention Time Order and Characteristic Ions

Analyte	Primary	Secondary	Tertiary
2-Picoline	93	66	92
N-Nitrosomethylethylamine	88	42	43
Methyl methanesulfonate	80	79	65
N-Nitrosodiethylamine	102	44	57
Ethyl methanesulfonate	79	109	97
Pentachloroethane	117	119	167
Acetophenone	105	77	120
N-Nitrosopyrrolidine	100	41	42
N-Nitrosomorpholine	116	56	86
o-Toluidine	106	107	
3-Methylphenol	108	107	77
N-Nitrosopiperidine	114	42	55
o,o,o-Triethyl-Phosphorothioate	198	121	93
a,a-Dimethyl-phenethylamine	58	91	
2,6-Dichlorophenol	162	164	63
Hexachloropropene	213	215	211
p-Phenylenediamine	108	80	
n-Nitrosodi-n-butylamine	84	57	41
Safrole	162	104	77
1,2,4,5-Tetrachlorobenzene	216	214	218
Isosafrole 1	162	104	131
Isosafrole 2	162	104	131
1,4-Dinitrobenzene	168	75	122
1,4-Naphthoquinone	158	104	102
1,3-Dinitrobenzene	168	75	76
Pentachlorobenzene	250	248	252
1-Naphthylamine	143	115	
2-Naphthylamine	143	115	
2,3,4,6-Tetrachlorophenol	232	230	131
5-Nitro-o-toluidine	152	77	106
Thionazin	97	96	143
1,3,5-Trinitrobenzene	213	75	120
Sulfotepp	97	322	202
Phorate	75	97	121
Phenacetin	108	179	109
Diallate	86	234	
Dimethoate	87	93	125
4-Aminobiphenyl	169		
Pentachloronitrobenzene	237	142	214
Pronamide	173	175	255
Disulfoton	88	97	89
2-secbutyl-4,6-dinitrophenol (Dinoseb)	211	163	147

Table 8 (Cont'd)

Analyte	Primary	Secondary	Tertiary
Methyl parathion	109	125	263
4-Nitroquinoline-1-oxide	190	128	160
Famphur	218	125	93
Methapyrilene	97	58	
Aramite 1	185	319	
Aramite 2	185	319	
p-(Dimethylamino)azobenzene	120	225	77
p-Chlorobenzilate	251	139	253
3,3'-Dimethylbenzidine	212	106	
2-Acetylaminofluorene	181	180	223
Dibenz(a,j)acridine	279	280	
7,12-Dimethylbenz(a)anthracene	256	241	120
3-Methylcholanthrene	268	252	253

Table 9 - 8270C LCS Control Compounds

LCS Compounds	Spiking Level, Conc. Added = 20 ug/L
1,2,4-Trichlorobenzene	20
Acenaphthene	20
2,4-Dinitrotoluene	20
Pyrene	20
N-Nitroso-di-n-propylamine	20
1,4-Dichlorobenzene	20
Pentachlorophenol	20
Phenol	20
2-Chlorophenol	20
4-Chloro-3-methylphenol	20
4-Nitrophenol	20

Table 9A 8270C All Analyte Spike Mix	
Acenaphthene	100
Acenaphthylene	100
Anthracene	100
Benzo(a)anthracene	100
Benzo(b)fluoranthene	100
Benzo(k)fluoranthene	100
Benzo(a)pyrene	100
Benzo(ghi)perylene	100
Benzyl butyl phthalate	100
Bis(2-chloroethyl)ether	100
Bis(2-chloroethoxy)methane	100
Bis(2-ethylhexyl)phthalate	100
Bis(2-chloroisopropyl)ether	100
4-Bromophenyl phenyl ether	100
2-Chloronaphthalene	100
4-Chlorophenyl phenyl ether	100
Chrysene	100
Dibenzo(a,h)anthracene	100
Di-n-butylphthalate	100
1,3-Dichlorobenzene	100
1,2-Dichlorobenzene	100

Table 9A (Cont'd)

Table 9A 8270C All Analyte Spike Mix	
1,4-Dichlorobenzene	100
3,3'-Dichlorobenzidine	100
Diethyl phthalate	100
Dimethyl phthalate	100
2,4-Dinitrotoluene	100
2,6-Dinitrotoluene	100
Di-n-octylphthalate	100
Fluoranthene	100
Fluorene	100
Hexachlorobenzene	100
Hexachlorobutadiene	100
Hexachloroethane	100
Indeno(1,2,3-cd)pyrene	100
Isophorone	100
Naphthalene	100
Nitrobenzene	100
N-Nitrosodi-n-propylamine	100
Phenanthrene	100
Pyrene	100
1,2,4-Trichlorobenzene	100
4-Chloro-3-methylphenol	100
2-Chlorophenol	100

Table 9A (Cont'd)

Table 9A 8270C All Analyte Spike Mix	
2,4-Dichlorophenol	100
2,4-Dimethylphenol	100
2,4-Dinitrophenol	100
2-Methyl-4,6-dinitrophenol	100
2-Nitrophenol	100
4-Nitrophenol	100
Pentachlorophenol	100
Phenol	100
2,4,6-Trichlorophenol	100
	100
Acetophenone	100
Atrazine	100
Caprolactam	100
Benzaldehyde	100
1,1'-Biphenyl	100
Benzoic Acid	100
1,4-Dioxane	100
Benzyl Alcohol	100
Carbazole	100
4-Chloroaniline	100
Dibenzofuran	100
Hexachlorocyclopentadiene	100
2-Methylnaphthalene	100
Quinoline	100
1-Methylnaphthalene	100

Table 9A 8270C All Analyte Spike Mix	
2-Methylphenol	100
4-Methylphenol	100
4-Nitroaniline	100
2-Nitroaniline	100
3-Nitroaniline	100
Pyridine	100
2,3,5,6-Tetrachlorophenol	100
2,4,5-Trichlorophenol	100
N-Nitrosodimethylamine	100
N-Nitrosodiphenylamine	100

Table 10 - TCLP LCS Compounds

LCS Compounds	Spiking Level, mg/L in extract
1,4-Dichlorobenzene	0.08
2,4-Dinitrotoluene	0.08
Hexachlorobenzene	0.08
Hexachlorobutadiene	0.08
Hexachloroethane	0.08
2-Methylphenol	0.08
3-Methylphenol	0.08
4-Methylphenol	0.08
Nitrobenzene	0.08
Pentachlorophenol	0.08
Pyridine	0.08
2,4,5-Trichlorophenol	0.08
2,4,6-Trichlorophenol	0.08

Recovery limits for the LCS and for matrix spikes are generated historical data, and are maintained by the QA Dept.

Table 11 - 8270C Surrogate Compounds

Surrogate Compounds	Spiking Level, Conc. Added = 20 ug/L / 30 ug/L
Nitrobenzene-d5	20
2-Fluorobiphenyl	20
Terphenyl-d14	20
1,2-Dichlorobenzene-d4[1]	20
Phenol-d5	30
2-Fluorophenol	30
2,4,6-Tribromophenol	30
2-Chlorophenol-d4[1]	30

Recovery limits for surrogates are generated from historical data and are maintained by the QA department.

Table 12 - Calibration Ranges, µg/mL

Analyte	Calibration Range
Pyridine	0.25-12.5 ug/mL
N-nitrosodimethylamine	0.25-12.5 ug/mL
Aniline	0.25-12.5 ug/mL
Phenol	0.25-12.5 ug/mL
Bis(2-chloroethyl)ether	0.25-12.5 ug/mL
2-Chlorophenol	0.25-12.5 ug/mL
1,3-Dichlorobenzene	0.25-12.5 ug/mL
1,4-Dichlorobenzene	0.25-12.5 ug/mL
Benzyl alcohol	0.25-12.5 ug/mL
1,2-Dichlorobenzene	0.25-12.5 ug/mL
2-Methylphenol	0.25-12.5 ug/mL
2,2'-oxybis(1-chloropropane)[1]	0.25-12.5 ug/mL
4-Methylphenol	0.25-12.5 ug/mL
N-Nitroso-di-n-propylamine	0.25-12.5 ug/mL
Hexachloroethane	0.25-12.5 ug/mL
Nitrobenzene	0.25-12.5 ug/mL
Isophorone	0.25-12.5 ug/mL
2-Nitrophenol	0.25-12.5 ug/mL
2,4-Dimethylphenol	0.25-12.5 ug/mL
Benzoic acid	0.25-12.5 ug/mL
Bis(2-chloroethoxy)methane	0.25-12.5 ug/mL
2,4-Dichlorophenol	0.25-12.5 ug/mL
1,2,4-Trichlorobenzene	0.25-12.5 ug/mL
Naphthalene	0.05-10 ug/mL
4-Chloroaniline	0.25-12.5 ug/mL
Hexachlorobutadiene	0.25-12.5 ug/mL
4-Chloro-3-methylphenol	0.25-12.5 ug/mL
2-Methylnaphthalene	0.05-10 ug/mL
Hexachlorocyclopentadiene	0.25-12.5 ug/mL
2,4,6-Trichlorophenol	0.25-12.5 ug/mL
2,4,5-Trichlorophenol	0.25-12.5 ug/mL
2-Chloronaphthalene	0.25-12.5 ug/mL
2-Nitroaniline	0.25-12.5 ug/mL
Dimethyl phthalate	0.25-12.5 ug/mL
Acenaphthylene	0.05-10 ug/mL
3-Nitroaniline	0.25-12.5 ug/mL
Acenaphthene	0.05-10 ug/mL
2,4-Dinitrophenol	0.25-12.5 ug/mL
4-Nitrophenol	0.25-12.5 ug/mL
Dibenzofuran	0.25-12.5 ug/mL
2,4-Dinitrotoluene	0.25-12.5 ug/mL
2,6-Dinitrotoluene	0.25-12.5 ug/mL

Table 12 (Cont'd)

Analyte	Calibration Range
Diethylphthalate	0.25-12.5 ug/mL
4-Chlorophenyl phenyl ether	0.25-12.5 ug/mL
Fluorene	0.05-10 ug/mL
4-Nitroaniline	0.25-12.5 ug/mL
4,6-Dinitro-2-methylphenol	0.25-12.5 ug/mL
N-Nitrosodiphenylamine	0.25-12.5 ug/mL
Azobenzene[2]	0.25-12.5 ug/mL
4-Bromophenyl phenyl ether	0.25-12.5 ug/mL
Hexachlorobenzene	0.25-12.5 ug/mL
Pentachlorophenol	0.25-12.5 ug/mL
Phenanthrene	0.05-10 ug/mL
Anthracene	0.05-10 ug/mL
Carbazole	0.05-10 ug/mL
Di-n-butyl phthalate	0.25-12.5 ug/mL
Fluoranthene	0.05-10 ug/mL
Benzidine	0.25-12.5 ug/mL
Pyrene	0.05-10 ug/mL
Butyl benzyl phthalate	0.25-12.5 ug/mL
3,3'-Dichlorobenzidine	0.25-12.5 ug/mL
Benzo(a)anthracene	0.05-10 ug/mL
Bis(2-ethylhexyl)phthalate	0.25-12.5 ug/mL
Chrysene	0.05-10 ug/mL
Di-n-octylphthalate	0.25-12.5 ug/mL
Benzo(b)fluoranthene	0.05-10 ug/mL
Benzo(k)fluoranthene	0.05-10 ug/mL
Benzo(a)pyrene	0.05-10 ug/mL
Indeno(1,2,3-cd)pyrene	0.05-10 ug/mL
Dibenz(a,h)anthracene	0.05-10 ug/mL
Benzo(g,h,i)perylene	0.05-10 ug/mL
Benzaldehyde	0.25-12.5 ug/mL
Caprolactam	0.25-12.5 ug/mL
1,1'-Biphenyl	0.25-12.5 ug/mL
Atrazine	0.25-12.5 ug/mL

[1] 2,2'oxybis(1-chloropropane) was formerly known as bis(2-chloroisopropyl)ether

[2] Azobenzene is formed by decomposition of 1,2-diphenyhydrazine. If 1,2-diphenylhydrazine is requested, it will be analyzed as azobenzene.

Note: Nine calibrations standards are prepared varying in concentration from 0.05 ug/mL to 12.5 ug/mL. A minimum of 5 calibration concentrations will be used for initial calibration . The concentration range of each analyte is listed in the table.

Table 13 - Calibration Ranges, Appendix IX, µg/mL

Semivolatiles	Calibration Range
2-Picoline	0.25-12.5 ug/mL
N-Nitrosomethylethylamine	0.25-12.5 ug/mL
Methyl methanesulfonate	0.25-12.5 ug/mL
N-Nitrosodiethylamine	0.25-12.5 ug/mL
Ethyl methanesulfonate	0.25-12.5 ug/mL
Pentachloroethane	0.25-12.5 ug/mL
Acetophenone	0.25-12.5 ug/mL
N-Nitrosopyrrolidine	0.25-12.5 ug/mL
N-Nitrosomorpholine	0.25-12.5 ug/mL
o-Toluidine	0.25-12.5 ug/mL
3-Methylphenol	0.25-12.5 ug/mL
N-Nitrosopiperidine	0.25-12.5 ug/mL
o,o,o-Triethyl-Phosphorothioate	0.25-12.5 ug/mL
a,a-Dimethyl-phenethylamine	0.25-12.5 ug/mL
2,6-Dichlorophenol	0.25-12.5 ug/mL
Hexachloropropene	0.25-12.5 ug/mL
p-Phenylenediamine	0.25-12.5 ug/mL
n-Nitrosodi-n-butylamine	0.25-12.5 ug/mL
Safrole	0.25-12.5 ug/mL
1,2,4,5-Tetrachlorobenzene	0.25-12.5 ug/mL
Isosafrole 1 + 2	0.25-12.5 ug/mL
1,4-Dinitrobenzene	0.25-12.5 ug/mL
1,4-Naphthoquinone	0.25-12.5 ug/mL
1,3-Dinitrobenzene	0.25-12.5 ug/mL
Pentachlorobenzene	0.25-12.5 ug/mL
1-Naphthylamine	0.25-12.5 ug/mL
2-Naphthylamine	0.25-12.5 ug/mL
2,3,4,6-Tetrachlorophenol	0.25-12.5 ug/mL
5-Nitro-o-toluidine	0.25-12.5 ug/mL
Thionazin	0.25-12.5 ug/mL
1,3,5-Trinitrobenzene	0.25-12.5 ug/mL
Sulfotepp	0.25-12.5 ug/mL
Phorate	0.25-12.5 ug/mL
Phenacetin	0.25-12.5 ug/mL
Diallate 1 + 2	0.25-12.5 ug/mL
Dimethoate	0.25-12.5 ug/mL
4-Aminobiphenyl	0.25-12.5 ug/mL
Pentachloronitrobenzene	0.25-12.5 ug/mL
Pronamide	0.25-12.5 ug/mL
Disulfoton	0.25-12.5 ug/mL
2-secbutyl-4,6-dinitrophenol (Dinoseb)	0.25-12.5 ug/mL
Methyl parathion	0.25-12.5 ug/mL
4-Nitroquinoline-1-oxide	0.25-12.5 ug/mL

Table 13 (Cont'd)

Semivolatiles	Calibration Range
Parathion	0.25-12.5 ug/mL
Isodrin	0.25-12.5 ug/mL
Kepone	0.25-12.5 ug/mL
Famphur	0.25-12.5 ug/mL
Methapyrilene	0.25-12.5 ug/mL
Aramite 1 and 2	0.25-12.5 ug/mL
p-(Dimethylamino)azobenzene	0.25-12.5 ug/mL
p-Chlorobenzilate	0.25-12.5 ug/mL
3,3'-Dimethylbenzidine	0.25-12.5 ug/mL
2-Acetylaminofluorene	0.25-12.5 ug/mL
Dibenz (a,j)acridine	0.25-12.5 ug/mL
7,12-Dimethylbenz(a)anthracene	0.25-12.5 ug/mL
3-Methylcholanthrene	0.25-12.5 ug/mL

Note: Nine calibrations standards are prepared varying in concentration from 0.05 ug/mL to 12.5 ug/mL. A minimum of 5 calibration concentrations will be used for initial calibration . The concentration range of each analyte is listed in the table.

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TestAmerica North Canton

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[Method: SW846 and MCAWW 200 Series Methods]

Approvals (Signature/Date):

Roger K. Toth 12-14-07
Technology Specialist Date

12-14-07
Health & Safety Coordinator Date

Dorothy J. Leeson 12/13/07
Quality Assurance Manager Date

12/14/07
Laboratory Director Date

Mark L Bruce 12/14/07
Technical Director Date

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Page 1 of 29

STL STANDARD OPERATING PROCEDURE

TITLE: ACID DIGESTION OF AQUEOUS SAMPLES BY SW846 AND MCAWW 200 SERIES METHODS

(Supersedes: Revision 1.5, Dated 12/07/04)

Reviewed by:	Roger K. Yoch	3-6-07
	Technology Specialist	Date
Reviewed by:	Dorothy J. Leeson	3/7/07
	Quality Assurance Manager	Date
Reviewed by:	William J. Beard	2-27-07
	Environmental Health and Safety	Date
Reviewed by:	[signature]	3/7/07
	Laboratory Director	Date
Reviewed by:	Mark Burns	3/13/07
	Technical Director	Date

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1. SCOPE AND APPLICATION

1.1. This procedure describes the preparation of aqueous samples for the analysis of certain metals by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP), and Inductively Coupled Plasma-Mass Spectrometry (ICP/MS) using the MCAWW 200 series methods (NPDES) and SW846 Methods 3005A, 3010A, and 3020A.

1.2. The applicability of each of these preparation protocols to specific analytes is detailed in Tables I and II (Appendix A). Additional elements may be analyzed following digestion by these protocols provided that the method performance criteria specified in Section 13.0 of this SOP are met.

1.3. This SOP provides procedures applicable to the preparation of dissolved, suspended, total recoverable and total elements in ground water, aqueous samples, certain aqueous sludges, and leachates/extracts.

1.4. SW-846 Method 3005A is used to prepare surface and groundwater samples for total recoverable and dissolved metals determination by ICP.

1.5. MCAWW Method 200.7 is used to prepare surface water, domestic and industrial waste samples for total recoverable and dissolved metals determination by ICP.

1.6. SW-846 Method 3010A is used to prepare aqueous samples, mobility-procedure extracts, and wastes that contain suspended solids for total metals analysis by ICP.

1.7. MCAWW Method 200.7 is used to prepare surface water and wastes that contain suspended solids for total metals analysis by ICP.

1.8. All matrices require digestion prior to analysis with the exception of analyses for dissolved metals in filtered and acidified aqueous samples. Although digestion is not specifically required by the method, some clients and regulators do require digestion of dissolved samples and this must be clarified before project initiation.

1.9. SW846 Method 3020A is used to prepare surface and groundwater samples for total recoverable and dissolved metals determination by ICP/MS.

1.10. MCAWW Method 200.8 is used to prepare surface and groundwater samples for total recoverable and dissolved metals determination by ICP/MS.

2. SUMMARY OF METHOD

2.1. Method 3005A / Method 200.7 - Preparation for Total Recoverable or Dissolved Metals Analysis by ICP Spectroscopy

2.1.1. A representative aliquot of sample is heated with nitric and hydrochloric acids and substantially reduced in volume. The digestate is filtered (if necessary) and diluted to volume.

2.2. Method 3010A / Method 200.7 - Preparation for Total Metals Analysis by ICP Spectroscopy

2.2.1. A representative aliquot of sample is refluxed with nitric acid. After the digestate has been reduced to a low volume, it is refluxed with hydrochloric acid, filtered (if necessary) and brought up to volume.

2.3. Method 3020A/Method 200.8 – Preparation for total recoverable or dissolved metals analysis by ICP/MS.

2.3.1. A representative aliquot of sample is heated with nitric acid and until the digestate has been reduced to a low volume. The sample is cooled, filtered (if necessary), and brought up to volume.

3. DEFINITIONS

Additional definitions of terms used in this SOP may be found in the glossary of the LQM.

3.1. Dissolved Metals: Those elements which pass through a 0.45 um membrane. (Sample is acidified after filtration).

3.2. Suspended Metals: Those elements which are retained by a 0.45 um membrane.

3.3. Total Metals: The concentration determined on an unfiltered sample following digestion.

3.4. Total Recoverable Metals: The concentration determined on an unfiltered sample following treatment with hot, dilute mineral acid.

4. INTERFERENCES

4.1. There are numerous routes by which samples may become contaminated. Potential sources of trace metals contamination include: metallic or metal-containing labware (e.g., talc gloves which contain high levels of zinc), containers, impure reagents, dirty glassware, improper sample transfers, dirty work areas, atmospheric inputs such as dirt and dust, etc. Be aware of potential sources of contamination and take appropriate measures to minimize or avoid them.

4.2. The entire work area, including the bench top and fume hood, should be thoroughly cleaned on a routine schedule in order to minimize the potential for environmental contamination. Refer to Appendix B for additional contamination control guidelines.

4.3. Boron and silica from the glassware will migrate into the sample solution during and following sample processing. For critical low level determinations of boron and silica, only quartz and/or plastic labware should be used.

4.4. Physical interference effects may contribute to inaccuracies in the determinations of trace elements. Oils, solvents and other matrices may not be digested using these methods if they are not soluble with acids. If physical interferences are present, they should be documented.

4.5. Visual interferences or anomalies (such as foaming, emulsions, precipitates, etc.) must be documented.

4.6. Allowing samples to boil or go dry during digestion may result in the loss of volatile metals. If this occurs the sample must be reprepared. Antimony is easily lost by volatilization from hydrochloric acid media.

4.7. Precipitation of silver chloride (AgCl) may occur when chloride ions and high concentrations of silver (i.e., greater than 1 mg/L) are present in the sample.

4.8. Specific analytical interferences are discussed in each of the determinative methods.

5. SAFETY

5.1. Employees must abide by the policies and procedures in the Corporate Safety and this document.

5.2. Samples that contain high concentrations of carbonates or organic material or samples that are at elevated pH can react violently when acids are added.

5.3. The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Hydrochloric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Nitric Acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

5.4. Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Cut-resistant gloves must be worn doing any other task that presents a strong possibility of getting cut. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.5. The acidification of samples containing reactive materials may result in the release of toxic gases, such as cyanides or sulfides. Acidification of samples should be done in a fume hood. The analyst should also be aware of the potential for a vigorous reaction.

5.6. Exposure to chemicals must be maintained **as low as reasonably achievable.** Therefore, unless they are known to be non-hazardous, all samples should be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. All samples with stickers that read "Caution/Use Hood!" **must** be opened in the hood. Contact the EH&S Coordinator if this is not possible. Solvent and waste containers will be kept closed unless transfers are being made.

5.7. All work must be stopped in the event of a known or potential compromise to the health and safety of a STL associate. The situation must be reported **immediately** to the EH&S Coordinator and the Laboratory Supervisor.

5.8. Always carry bulk concentrated acid bottles in appropriate impact proof containers.

5.9. Acid/peroxide spills must be neutralized immediately, flushed with water and cleaned up using appropriate spill kits.

5.10. Discard chipped or broken beakers to prevent injury. Chipped glassware may be fire polished as an alternative to disposal.

6. EQUIPMENT AND SUPPLIES

6.1. Hot plate, digestion block or other adjustable heating source capable of maintaining a temperature of 90-95°C.

6.2. Calibrated thermometer that covers a temperature range of 0-200°C.

6.3. Griffin beakers of assorted sizes or equivalent.

6.4. Watch glasses, ribbed or equivalent.

6.5. Whatman No. 41 filter paper or equivalent.

6.6. Funnels or equivalent filtration apparatus.

6.7. Centrifugation equipment (if desired method of removing particulates is centrifugation).

6.8. Graduated cylinder or equivalent capable of measuring 50 mL within 3% accuracy.

6.9. Analytical balance capable of accurately weighing to the nearest 0.01 grams.

6.10. Repipetors or suitable reagent dispensers.

6.11. Calibrated automatic pipettes with corresponding pipette tips or Class A glass volumetric pipettes.

6.12. Class A volumetric flasks.

6.13. pH indicator strips (pH range 0 - 6).

6.14. Plastic digestate storage bottles.

7. REAGENTS AND STANDARDS

7.1. Reagent water must be produced by a Millipore DI system or equivalent. Reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks as defined in the determinative SOPs.

7.2. Laboratory Control Sample (LCS) and matrix spike (MS) solutions are purchased as custom solutions. All standards must be stored in FEP fluorocarbon or previously unused polyethylene or polypropylene bottles. Stock standard solutions must be replaced prior to the expiration date provided by the manufacturer. If no expiration date is provided, the stock solutions may be used for up to one year and must be replaced sooner if verification from an independent source indicates a problem.

7.3. Working ICP LCS/MS spike solution: Prepare the ICP LCS/MS working spike solution from custom stock standards to the final concentration listed in Table III. The working spike must be prepared in a matrix of 5% HNO_3. This acid (5 mL of concentrated HNO_3 per 100 mL) must be added to the volumetric flask before the addition of the stock standard aliquot. The working ICP LCS solution must be made fresh every three months.

7.4. The ICP/MS LCS/MS spike solution is provided directly by the vendor. No further standard preparation is necessary.

7.5. The TCLP MS working spike solution is provided directly by the vendor, no further standard preparation is necessary. Refer to Table V for final digestate spike concentrations.

7.6. The LCS and MS samples must contain all the elements designated for analysis in each batch of samples. If a non-routine element is required that is not contained in the custom solution, the individual facility must purchase a solution from the designated vendor that will cover the additional analyte(s) of interest and provide for a final spike concentration that is appropriate to the determinative method.

7.7. Aqueous laboratory control samples (LCSW) and matrix spike samples are prepared as described in Sections 9.5 and 9.6. Refer to Tables III and IV (Appendix A) for details regarding the stock, working standard and final digestate spike concentrations for ICP and ICP/MS LCS and matrix spike preparations.

7.8. Nitric acid (HNO_3), concentrated, trace metal grade or better.

7.9. Nitric acid, 1:1 - dilute concentrated HNO_3 with an equal volume of reagent water.

Note: When preparing diluted acids always add acid to water. If the water is added to the acid a violent reaction may occur.

7.10. Hydrochloric acid (HCl), concentrated, trace metal grade or better.

7.11. Hydrochloric acid, 1:1 - dilute concentrated HCl with an equal volume of reagent water.

Note: When preparing diluted acids always add acid to water. If the water is added to the acid a violent reaction may occur.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Sample holding time for metals included under the scope of this SOP is 180 days from the date of collection to the date of analysis.

8.2. Aqueous samples are preserved with nitric acid to a pH of <2 and may be stored in either plastic or glass. If boron or silica are to be determined, plastic containers are preferred. Refrigeration is not required. Preservation must be verified prior to analysis.

8.3. For dissolved metals analysis, the samples should be filtered through a 0.45 um filter prior to preservation. Filtration must be done in the field. In the event that samples are not field filtered, filtration occurs in the laboratory prior to preparation.

Note: If a sample being analyzed for dissolved metals is found to contain sediment the analyst should contact their supervisor or group leader. The client should be notified of the problem to decide how to treat the sample.

9. QUALITY CONTROL

Table VI (Appendix A) provides a summary of quality control requirements including type, frequency, acceptance criteria and corrective action.

9.1. Initial Demonstration of Capability

Prior to analysis of any analyte using any method contained within this SOP the following requirements must be met:

9.1.1. Method Detection Limit (MDL) - An MDL must be determined for each analyte/matrix prior to the analysis of any samples. The MDL is determined using seven replicates of reagent water, spiked with all the analytes of interest, that have been carried through the entire analytical procedure. MDL's must be redetermined on an annual basis in accordance with 40 CFR Part 136 Appendix B requirements as detailed in STL QA Policy S-Q-003 and SOP NC-QA-0021. The spike level must be between the calculated MDL and 10X the MDL to be valid. The result of the MDL determination must be below the STL reporting limit.

9.1.2. Initial Demonstration Study - This requires the analysis of four QC check samples. The QC check sample is a well-characterized laboratory generated sample used to monitor method performance, which should contain all the analytes of interest. The results of the initial demonstration study must be acceptable before analysis of samples may begin. The results of the initial demonstration study may be used to extend a method for the analysis of other elements provided all acceptance criteria are met.

9.1.2.1. Four aliquots of the check sample (LCS) are prepared and analyzed using the procedures detailed in this SOP and the determinative SOPs.

9.1.2.2. Calculations and acceptance criteria for QC check samples are given in the determinative SOP (CORP-MT-0001).

9.2. Preparation Batch - A group of up to 20 samples that are of the same matrix and are processed together using the same procedures and reagents. The preparation batch must contain a method blank, a LCS and a matrix spike/matrix spike duplicate. In some cases, at client request, it may be appropriate to process a matrix spike and sample duplicate in place of the MS/MSD. If clients specify specific samples for MS/MSD, the batch may contain multiple MS/MSD pairs. In cases where there is insufficient sample volume to perform an MS/MSD, an LCS/LCS duplicate is required.

9.3. Sample Count - Laboratory generated QC samples (method blanks, LCS, MS/MSD) are not included in the sample count for determining the size of a preparation batch. MS/MSD are not included in the sample count unless there are multiple sets of MS/MSD per batch. In other words, the first MS/MSD are not counted; all additional MS and MSDs are counted as samples.

9.4. Method Blank (MB) - One method blank must be processed with each preparation batch. The method blank consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. Criteria for the acceptance of blanks are contained within the individual analytical method SOP's. If the method blank does not meet the criteria contained within the analytical method SOPs; the blank and all associated samples in the batch must be redigested.

9.4.1. Aqueous method blanks are prepared by taking 50 mL of reagent water through the appropriate procedure as described in Section 11.

9.4.2. TCLP method blanks are prepared by taking 50 mL of leachate fluid through the appropriate procedure as described in Section 11.

9.5. Laboratory Control Sample (LCS) - One aqueous LCS must be processed with each preparation batch. The LCS must contain all analytes of interest and must be carried through the entire analytical procedure. The LCS is used to monitor the accuracy of the analytical process. On going monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines. Criteria for the acceptance of LCS results are contained within the individual analytical method SOP's. Corrective action when LCS results fail to meet control limits will be repreparation and reanalysis of the batch. Refer to Section 7.3 and 7.4 for instructions on preparation of the aqueous LCS spike solution.

9.5.1. The aqueous LCS is prepared by spiking a 50 mL aliquot of reagent water with 1.0 mL for ICP and 0.5 mL for ICP/MS of the working LCS/MS spike solution (Sections 7.3 or 7.4). The LCS is then processed through the appropriate procedure as described in Section 11.

9.6. Matrix Spike/Matrix Spike Duplicate (MS/MSD) - One MS/MSD pair must be processed for each preparation batch. A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added. A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked identically as the MS) prepared and analyzed along with the sample and matrix spike. Some client specific data quality objectives (DQO's) may require the use of sample duplicates in place of or in addition to MS/MSD's. The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Samples identified as field blanks cannot be used for MS/MSD analysis. If any analyte recovery or RPD falls outside the acceptance range, the recovery of that analyte must be in control for the LCS. If the recovery of the LCS is outside limits, corrective action must be taken. Corrective action will include repreparation and reanalysis of the batch. Corrective action when MS results fail to meet control limits does not include repreparation of samples unless the results indicate that a spiking error may have occurred.

9.6.1. The aqueous matrix spike sample is prepared by spiking a 50 mL aliquot of a sample with 1.0 mL for ICP and 0.5 mL for ICP/MS of the working LCS/MS spike solution (Sections 7.3 or 7.4). The matrix spike sample is then processed as described in Section 11.

9.6.2. The TCLP matrix spike sample is prepared by spiking a 50 mL aliquot of a leachate with 0.5 mL of the working TCLP spike solution (Section 7.5). The matrix spike sample is then processed as described in Section 11.

NOTE: The TCLP matrix spike must be added prior to preservation of the leachate.

9.6.3. If insufficient sample is available to process a MS/MSD, then a second LCS must be processed. The LCS pair is then evaluated according to the MS/MSD criteria.

10. CALIBRATION AND STANDARDIZATION

10.1 The hotplate/hotblock temperature must be verified daily for each hotplate used, and must be recorded on a hotplate/hotblock temperature log.

11. PROCEDURE

11.1. One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file.

11.2. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

11.3. All digestion procedures must be carried out in a properly functioning hood.

11.4. All samples are to be checked out of Sample Control with an electronic chain of custody.

11.5. Proper sample identification is extremely important in any preparation procedure. Labeling of beakers and bottles must be done in a manner to ensure connection with the proper sample.

11.6. Samples are typically logged in as either waters or soils. Wastes such as organic liquids or sludges and tissues (animal/vegetable) are usually logged in with solid test codes. When initiating prep, examine the sample to see if the sample matches the matrix designation. If the sample is logged in as aqueous but it appears more like a waste (biphasic, sludge like, organic liquid, lots of sediment etc.) contact the lab supervisor or project manager for further instructions. In some cases it may be more appropriate to process these samples as solids.

11.7. If possible prepare all the samples of a project at the same time to minimize the QC required and streamline the flow of the project through the lab and reporting group.

11.8. Guidelines are provided in the appendices on procedures to minimize contamination of samples and standards.

11.9. The following procedure must be followed for all aqueous sample preparations.

11.9.1. Mix sample by shaking the container.

11.9.2. Measure and transfer 50 mL of the sample into a beaker.

11.9.3. Measure two extra aliquots of sample selected for the MS/MSD analysis. Spike each aliquot with the appropriate spiking solutions (Sections 7.3-7.5 and 9.6).

11.9.4. Measure and transfer 50 mL of reagent water into a beaker for the method blank.

11.9.5. Measure and transfer 50 mL of reagent water into a beaker for the LCS and add the appropriate spiking solutions (Sections 7.3-7.5 and 9.6).

11.10. **Method 3005A / Method 200.7 - Preparation for Total Recoverable or Dissolved Metals Analysis by ICP**

11.10.1. To the sample container, add 1 mL of concentrated HNO_3 and 2.5 mL of concentrated HCl.

11.10.2. Cover with ribbed watch glass.

11.10.3. Heat at 90-95°C until volume is reduced to between 15 and 20 mL.

NOTE: DO NOT ALLOW SAMPLE TO BOIL OR GO DRY. Doing so will result in the loss of analyte and the sample must be reprepared.

11.10.4. Cool the beaker in a fume hood.

11.10.5. Filter sample, if insoluble materials are present, through Whatman 41 filter paper.

Note: If any samples in a preparation batch are filtered, the method blank and LCS associated with that batch must also be filtered.

Note: In place of filtering, the samples, after dilution and mixing, may be centrifuged or allowed to settle by gravity overnight to remove insoluble material.

11.10.6. Rinse container and filter paper with reagent water to ensure complete sample transfer.

11.10.7. Adjust the final volume/mass to 50 mL or 50 g with reagent water. The sample is now ready for analysis

11.11. **Method 3010A / Method 200.7 - Preparation for Total Metals Analysis by ICP Spectroscopy**

11.11.1. To the sample container, add 3.0mL of concentrated HNO_3.

11.11.2. Cover with ribbed watch glass.

11.11.3. Place container on hotblock 90-95°C, and evaporate for 4-5 hours or to low volume of 15-20 mL, while ensuring that no portion of the bottom of the beaker is allowed to go dry.

NOTE: DO NOT ALLOW SAMPLE TO BOIL OR GO DRY. Doing so will result in the loss of analyte and the sample must be re-prepared.

11.11.4. Add 5 mL of 1:1 HCl.

11.11.5. Cover and reflux for an additional 15 minutes to dissolve precipitate or residue. Cool in a fume hood.

11.11.6. Filter sample, if insoluble materials are present, through Whatman 41 filter paper.

Note: If any samples in the QC batch are filtered the method blank and LCS associated with that batch must also be filtered.

Note: In place of filtering, the samples, after dilution and mixing, may be centrifuged or allowed to settle by gravity overnight to remove insoluble material.

11.11.7. Rinse container and filter paper with reagent water to ensure complete sample transfer.

11.11.8. Adjust final volume to 50 mL with reagent water. The sample is now ready for analysis.

11.12. **Method 3020A / Method 200.8 - Preparation for Total or Total Recoverable Metals by ICP/MS**

11.12.1. To the sample container, add 1.5 mL of concentrated HNO_3.

11.12.2. Cover with ribbed watch glass.

11.12.3. Place beaker on hotplate 90-95°C and evaporate to low volume of 15-20 mL while ensuring that no portion of the bottom of the beaker is allowed to go dry.

NOTE: DO NOT ALLOW SAMPLE TO BOIL OR GO DRY. Doing so will result in the loss of analyte and the sample must be re-prepared.

11.12.4. Filter sample, if insoluble materials are present, through Whatman 41 filter paper.

Note: If any samples in the QC batch are filtered the method blank and LCS associated with that batch must also be filtered.

Note: In place of filtering, the samples, after dilution and mixing, may be centrifuged or allowed to settle by gravity overnight to remove insoluble material.

11.12.5. Rinse beaker and filter paper with reagent water to ensure complete sample transfer.

11.12.6. Adjust final volume to 50 mL with reagent water. The sample is now ready for analysis.

11.12.7. ready for analysis.

12. DATA ANALYSIS AND CALCULATIONS

Not Applicable.

13. METHOD PERFORMANCE

13.1. Method performance is determined by the analysis of matrix spike and matrix spike duplicate samples as well as method blanks and laboratory control samples. In general, the matrix spike recovery should fall within +/- 20 % and the matrix spike duplicates should compare within 20% RPD. Method blanks must meet the criteria specified in determinative SOPs. The laboratory control samples should recover within 20% of the true value until in house control limits are established. Acceptance criteria are given in the determinative SOPs.

13.2. The initial demonstration study as detailed in Section 9.1.2 must be acceptable before the analysis of field samples under this SOP may begin. The results of the initial demonstration

study may be used to extend a method for the analysis of other elements provided all acceptance criteria are met.

13.3. Training Qualification:

The group/team leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience.

14. POLLUTION PREVENTION

14.1. This method allows for the proportional reduction of sample and reagent volumes to decrease waste generation.

15. WASTE MANAGEMENT

15.1. All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

15.2. Waste Streams Produced by the Method

15.2.1. The following waste streams are produced when this method is carried out.

15.2.1.1. Acidic waste containing nitric acid generated by the extraction. This waste is disposed of in the designated container labeled "Acid Waste".

15.2.1.2. Contaminated disposable materials utilized for the analysis. This waste is disposed of in a designated container identified as "Solid Waste".

15.3. Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices of STL. They must have training on the hazardous waste disposal practices upon initial assignment to these tasks, followed by an annual refresher training.

16. REFERENCES

16.1. References

16.1.1. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition, Final Update I, Revision 1, July 1992. Methods 3005A and 3020A.

16.1.2. Methods for the Chemical Analysis of Water and Waste (MCAWW), 1983.

16.1.3. CORP-MT-0001, Inductively Coupled Plasma-Atomic Emission Spectroscopy, Spectrometric Method for Trace Element Analysis of Water and Wastes, Method 6010A, 6010B, and Method 200.7.

16.1.4. Corporate Quality Management Plan (QMP), current version.

16.1.5. STL Laboratory Quality Manual (LQM), current version.

16.1.6. STL Corporate Safety Manual, M-E-0001 and STL North Canton Facility Addendum and Contingency Plan, current version.

16.2. Associated SOPs and Policies, latest version

16.2.1. QA-003, STL QC Program.

16.2.2. QA-004, Rounding and Significant Figures.

16.2.3. Glassware Washing, NC-QA-0014

16.2.4. Statistical Evaluation of Data and Development of Control Charts, NC-QA-0018

16.2.5. Method Detection Limits and Instrument Detection Limits, S-Q-003 and NC-QA-0021

16.2.6. Supplemental Practices for DoD Project Work, NC-QA-0016

16.2.7. Standards and Reagents, NC-QA-0017

17. MISCELLANEOUS (TABLES, APPENDICES, ETC. . .)

17.1. Modifications/Interpretations from reference methods.

17.1.1. Modifications applicable to SW-846 reference methods.

17.1.1.1. Chapter 1of SW-846 states that the method blank should not contain any analyte of interest at or above the MDL. This SOP states that the method blank must not contain any analyte of interest at or above the reporting limit. Common lab contaminants are allowed up to two times the reporting limit in the blank.

17.1.1.2. The referenced methods as well as Table 3-1 of SW-846 refer to the use of a 100 mL aliquot for digestion. This SOP requires the use of a 50 mL sample size to reduce waste generation. The use of reduced sample volumes are supported in EPA's document "Response to Public Comments Background Document, Promulgation of the Second Update to SW-846, Third Edition" dated November 3, 1994. This document stated "flexibility to alter digestion volumes is addressed and "allowed" by the table (3-1) and is also inherently allowed by specific digestion methods. Table 3-1 is only to be used as guidance when collecting samples..." EMSL-Ci has also taken the stance that "reduction in sample size and appropriate corresponding reduction in sample volume is not considered a significant change in the methodology." Additionally, in written correspondence from the Office of Solid Waste, Oliver Fordham stated " As a "representative sample" can be assured, scaling causes no loss of precision and accuracy in the analysis."

17.1.2. Modifications Specific to Method 3010A

17.1.2.1. Section 11.12.3 of this SOP requires the sample be reduced to a volume of 15 - 20 mL. Section 7.2 of Method 3010A states the volume should be reduced to 3 mL but also states that no portion of the bottom of the beaker should go dry. The SOP required volume is a closer approximation of the volume required to provide an adequate covering of the beaker so as to prevent the loss of critical analytes through volatilization.

17.1.2.2. The scope of 3010A has been expanded to include silver based on comparison studies with 7760A. Method 3010A consistently demonstrated improved accuracy and precision over Method 7760A in the matrices tested (reagent water, surface water and TCLP leachate) up to a concentration of 1 ppm silver.

17.1.3. Modifications Specific to Method 3020A

17.1.3.1. Section 11.13.3 of this SOP requires the sample be reduced to a volume of 15 - 20 mL. Section 7.2 of Method 3010A states the volume should be reduced to 3 mL but also states that no portion of the bottom of the beaker should go dry. The SOP required volume is a closer approximation of the volume required to provide an adequate covering of the beaker so as to prevent the loss of critical analytes through volatilization.

17.1.4. Modifications Specific to MCAWW Methods

It was determined by technical review that several of the MCAWW methods were equivalent to the SW-846 methods and therefore were combined under the scope of this SOP as described in Section 11.0. The nature of the differences were deemed insignificant in regards to the amount of acid added and the evaporative volume based on the flexibility allowed by the methods (i.e., add additional acid as required) and the subjective wording of the methods (i.e., evaporate to near dryness vs. an exact volume).

17.2. Documentation and Record Management

17.2.1. The preparation benchsheet should, at a minimum, include the following information:

- Preparation date, analyst name, matrix, prep type (ICP or ICP/MS), Method reference.
- Sample ID with initial weight/volume and final weight/volume.
- Standards documentation (source, lot, volume added).
- Analyst
- Reagents

APPENDIX A

TABLES

TABLE I. Approved Preparation Method Analytes - SW846

ELEMENT	Symbol	CAS Number	3005A	3010A	3020A
Aluminum	Al	7429-90-5	X	X	
Antimony	Sb	7440-36-0	X		
Arsenic	As	7440-38-2	X	X	
Barium	Ba	7440-39-3	X	X	
Beryllium	Be	7440-41-7	X	X	X
Cadmium	Cd	7440-43-9	X	X	X
Calcium	Ca	7440-70-2	X	X	
Chromium	Cr	7440-47-3	X	X	X
Cobalt	Co	7440-48-4	X	X	X
Copper	Cu	7440-50-8	X	X	
Iron	Fe	7439-89-6	X	X	
Lead	Pb	7439-92-1	X	X	X
Magnesium	Mg	7439-95-4	X	X	
Manganese	Mn	7439-96-5	X	X	
Molybdenum	Mo	7439-98-7	X	X	X
Nickel	Ni	7440-02-0	X	X	
Potassium	K	7440-09-7	X	X	
Selenium	Se	7782-49-2	X	X	
Silver	Ag	7440-22-4	X	X	
Sodium	Na	7440-23-5	X	X	
Thallium	Tl	7440-28-0	X	X	X
Vanadium	V	7440-62-2	X	X	X
Zinc	Zn	7440-66-6	X	X	

X - Designates that the preparation method is approved for an element.

Note: Additional elements may be analyzed following digestion by these protocols provided the method performance criteria specified in Section 13.0 of the SOP are met.

TABLE II. Approved Preparation Method Analytes – NPDES

ELEMENT	Symbol	CAS Number	200.7 (9.4)	200.7 (9.3)
Aluminum	Al	7429-90-5	X	X
Antimony	Sb	7440-36-0	X	X
Arsenic	As	7440-38-2	X	X
Boron	B	7440-42-8	X	X
Barium	Ba	7440-39-3	X	X
Beryllium	Be	7440-41-7	X	X
Cadmium	Cd	7440-43-9	X	X
Calcium	Ca	7440-70-2	X	X
Chromium	Cr	7440-47-3	X	X
Cobalt	Co	7440-48-4	X	X
Copper	Cu	7440-50-8	X	X
Iron	Fe	7439-89-6	X	X
Lead	Pb	7439-92-1	X	X
Magnesium	Mg	7439-95-4	X	X
Manganese	Mn	7439-96-5	X	X
Molybdenum	Mo	7439-98-7	X	X
Nickel	Ni	7440-02-0	X	X
Potassium	K	7440-09-7	X	X
Selenium	Se	7782-49-2	X	X
Silicon	Si	7631-86-9	X	X
Silver	Ag	7440-22-4	X	X
Sodium	Na	7440-23-5	X	X
Thallium	Tl	7440-28-0	X	X
Vanadium	V	7440-62-2	X	X
Zinc	Zn	7440-66-6	X	X

X - Designates that the preparation method is approved for an element

Note: Additional elements may be analyzed following digestion by these protocols provided the method performance criteria specified in Section 13.0 of the SOP are met.

TABLE III. ICP Matrix Spike and Aqueous Laboratory Control Sample Levels

ELEMENT	Working LCS/MS Standard (mg/L)	Aqueous LCS/ MS Level * (ug/l)
Aluminum	100	2000
Antimony	25	500
Arsenic	100	2000
Barium	100	2000
Beryllium	2.5	50
Cadmium	2.5	50
Calcium	2500	50000
Chromium	10	200
Cobalt	25	500
Copper	12.5	250
Iron	50	1000
Lead	50	500
Magnesium	2500	50000
Manganese	25	500
Molybdenum	50	1000
Nickel	25	500
Potassium	2500	50000
Selenium	100	2000
Silver	2.5	50
Sodium	2500	50000
Thallium	100	2000
Vanadium	25	500
Zinc	25	500
Boron	50	1000
Tin	100	2000
Titanium	50	1000

* Levels shown indicate the spike concentration in the final digestate of the aqueous LCS or matrix spike based on the addition of 1.0 mL working spike (7.3) to 50 mL of sample.

TABLE IV. ICP/MS Aqueous LCS and Matrix Spike Levels

ELEMENT	Working LCS/MS Standard (mg/L)	Aqueous LCS/MS Level* (ug/L)
Aluminum	100	1000
Antimony	10	100
Arsenic	10	100
Barium	10	100
Beryllium	10	100
Cadmium	10	100
Calcium	100	1000
Chromium	10	100
Cobalt	10	100
Copper	10	100
Iron	100	1000
Lead	10	100
Magnesium	100	1000
Manganese	10	100
Molybdenum	10	100
Nickel	10	100
Potassium	100	1000
Selenium	10	100
Silver	10	100
Sodium	100	1000
Strontium	10	100
Thallium	10	100
Vanadium	10	100
Zinc	10	100
Boron	10	100
Tin	10	100
Titanium	10	100
Zirconium	10	100

* Levels shown indicate the spike concentration in the final digestate of the aqueous LCS or matrix spike based on the addition of 0.5 mL working spike (7.4) to 50 mL of sample.

TABLE V. TCLP Reporting Limits, Regulatory Limits and Matrix Spike Levels

ELEMENT	RL (ug/L)	Regulatory Limit (ug/L)	Spike Level (ug/L)*
Arsenic	500	5000	5000
Barium	10000	100000	50000
Cadmium	100	1000	1000
Chromium	500	5000	5000
Lead	500	5000	5000
Selenium	250	1000	1000
Silver	500	5000	1000

* Levels shown indicate the spike concentration in the final digestate of the aqueous LCS or matrix spike based on the addition of 0.5 mL working spike (7.4) to 50 mL of sample.

TABLE VI. Summary of Quality Control Requirements

QC PARAMETER	FREQUENCY	ACCEPTANCE CRITERIA	CORRECTIVE ACTION
Method Blank	One per sample preparation batch of up to 20 samples.	Refer to determinative SOPs: - NC-MT-0002 - CORP-MT-0001	Redigest and reanalyze samples associated with the method blank.
Laboratory Control Sample (LCS)	One per sample preparation batch of up to 20 samples.	Refer to determinative SOPs: - NC-MT-0002 - CORP-MT-0001	Redigest and reanalyze all samples associated with the LCS.
Matrix Spike	One per sample preparation batch of up to 20 samples.	Refer to determinative SOPs: - NC-MT-0002 - CORP-MT-0001	Reprep not required unless preparation error suspected.
Matrix Spike Duplicate	See Matrix Spike	Refer to determinative SOPs: - NC-MT-0002 - CORP-MT-0001	See Corrective Action for Matrix Spike.

APPENDIX B

CONTAMINATION CONTROL GUIDELINES

APPENDIX B. CONTAMINATION CONTROL GUIDELINES

The following procedures are strongly recommended to prevent contamination:

All work areas used to prepare standards and spikes should be cleaned before and after each use.

All glassware should be washed with detergent and tap water and rinsed with 1:1 nitric acid followed by deionized water.

Proper laboratory housekeeping is essential in the reduction of contamination in the metals laboratory. All work areas must be kept scrupulously clean.

Powdered or Latex Gloves must not be used in the metals laboratory since the powder contains silica and zinc, as well as other metallic analytes. Only vinyl or nitrile gloves should be used in the metals laboratory.

Glassware should be periodically checked for cracks and etches and discarded if found. Etched glassware can cause cross contamination of any metallic analytes.

Autosampler trays should be covered to reduce the possibility of contamination. Trace levels of elements being analyzed in the samples can be easily contaminated by dust particles in the laboratory.

The following are helpful hints in the identification of the source of contaminants:

Reagents or standards can contain contaminants or be contaminated with the improper use of a pipette.

Improper cleaning of glassware can cause contamination.

Separate glassware if an unusually high sample is analyzed and soak with sulfuric acid prior to routine cleaning.

TESTAMERICA NORTH CANTON STANDARD OPERATING PROCEDURE

TITLE: ACID DIGESTION OF SOILS, SW846 METHOD 3050B

(SUPERSEDES: REVISION 2.5, DATED 12/02/04)

Reviewed by:	Roger K. Doty	8-31-07
	Technology Specialist	Date
Reviewed by:	Dorothy J. Leeson	9/5/07
	Quality Assurance Manager	Date
Reviewed by:		9/4/07
	Environmental Health and Safety	Date
Reviewed by:		9/4/07
	Laboratory Director	Date
Reviewed by:	Mark Bruce	9/5/07
	Technical Director	Date

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1. SCOPE AND APPLICATION

1.1. This procedure describes the preparation of soil samples for the analysis of certain metals by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP) and Inductively Coupled Plasma-Mass Spectrometry (ICP/MS) as specified in SW846 Method 3050B.

1.2. Samples prepared by the protocols detailed in this SOP may be analyzed by ICP or ICP/MS for the elements listed in Table I (Appendix A). Other elements and matrices may be analyzed following digestion by these protocols provided that the method performance criteria specified in Section 13.0 of this SOP are met.

1.3. This method is not a total digestion, but will dissolve almost all metals that could become "environmentally available". By design, metals bound in silicate structures are not dissolved by this procedure, as they are not usually mobile in the environment. This SOP can be applied to metals in solids, sludges, wastes and sediments.

1.4. This document accurately reflects current laboratory standard operating procedures (SOP) as of the date above. All facility SOPs are maintained and updated as necessary.

2. SUMMARY OF METHOD

2.1. A representative 1 gram (wet weight) portion of sample is digested in nitric acid and hydrogen peroxide. The digestate is refluxed with hydrochloric acid for ICP and ICP/MS (Ag, Sb, Sn) analysis. The digestates are then filtered and diluted to 100 mL.

3. DEFINITIONS

3.1. Refer to the glossary in the Laboratory Quality Manual (LQM), latest version.

3.2. Total Metals: The concentration determined on an unfiltered sample following digestion. Note that this method is designed to determine the total *environmentally available* metals.

4. INTERFERENCES

4.1. There are numerous routes by which samples may become contaminated. Potential sources of trace metals contamination include: metallic or metal-containing labware (e.g., talc gloves which contain high levels of zinc), containers, impure reagents, dirty glassware, improper sample transfers, dirty work areas, atmospheric inputs such as dirt and dust, etc. Be aware of potential sources of contamination and take appropriate measures to minimize or avoid them.

4.2. The entire work area, including the bench top and fume hood, should be thoroughly cleaned on a routine schedule in order to minimize the potential for environmental contamination.

4.3. Boron and silica from the glassware will grow into the sample solution during and following sample processing. For critical low level determinations of boron and silica, only quartz and/or plastic labware should be used.

4.4. Physical interference effects may contribute to inaccuracies in the determinations of trace elements. Oils, solvents and other matrices may not be digested using these methods if they are not soluble with acids. If physical interferences are present, they should be documented.

4.5. Visual interferences or anomalies (such as foaming, emulsions, precipitates, etc.) must be documented.

4.6. Allowing samples to boil or go dry during digestion may result in the loss of volatile metals. If this occurs, the sample must be reprepared. Antimony is easily lost by volatilization from hydrochloric media.

4.7. Specific analytical interferences are discussed in each of the determinative methods.

5. SAFETY

5.1. Employees must abide by the policies and procedures in the Corporate Safety Manual and this document.

5.2. Samples that contain high concentrations of carbonates or organic material or samples that are at elevated pH can react violently when acids are added.

5.3. The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Hydrochloric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.

Hydrogen Peroxide	Oxidizer Corrosive	1 ppm-TWA	Vapors are corrosive and irritating to the respiratory tract. Vapors are very corrosive and irritating to the eyes and skin.
Nitric Acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

5.4. Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Cut resistant gloves must be worn doing any other task that presents a strong possibility of getting cut. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.5. The acidification of samples containing reactive materials may result in the release of toxic gases, such as cyanides or sulfides. Acidification of samples should be done in a fume hood. The analyst should also be aware of the potential for a vigorous reaction.

5.6. Exposure to chemicals must be maintained **as low as reasonably achievable.** Therefore, unless they are known to be non-hazardous, all samples should be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. All samples with stickers that read "Caution/Use Hood!" **must** be opened in the hood. Contact the EH&S Coordinator if this is not possible. Solvent and waste containers will be kept closed unless transfers are being made.

5.7. The preparation of standards and reagents will be conducted in a fume hood with the sash closed as far as the operation will permit or under other means of mechanical ventilation.

5.8. All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica North Canton associate. The situation must be reported **immediately** to the EH&S Coordinator and the Laboratory Supervisor.

5.9. Always carry bulk concentrated acid bottles in appropriate impact proof containers.

5.10. Acid/peroxide spills must be neutralized immediately, flushed with water and cleaned up using appropriate spill kits.

5.11. Discard chipped or broken beakers to prevent injury. Chipped glassware may be fire polished as an alternative to disposal.

6. EQUIPMENT AND SUPPLIES

6.1. Hot plate, digestion block, steam bath or other heating source capable of maintaining a temperature of 90-99°C

6.2. Calibrated thermometer that covers a temperature range of 0-200°C

6.3. Griffin beakers of assorted sizes or equivalent

6.4. Vapor recovery device (Watch glasses, ribbed or other device)

6.5. Whatman No. 41 filter paper or equivalent

6.6. Funnels or equivalent filtration apparatus

6.7. Centrifugation equipment (if desired method of removing particulates is centrifugation).

6.8. Graduated cylinder or equivalent capable of measuring 100 mL within 3% accuracy.

6.9. Analytical balance capable of accurately weighing to the nearest 0.01 grams.

6.10. Repippetors or suitable reagent dispensers

6.11. Calibrated automatic pipettes with corresponding pipette tips or Class A glass volumetric pipettes, 100uL, 500uL, 1mL-5mL.

6.12. Class A volumetric flasks

6.13. pH indicator strips (pH range 0 - 6)

6.14. Plastic bottles, 120-150mL or equivalent

6.15. Boiling Stones – Ultra Pura PTFE or equivalent

7. REAGENTS AND STANDARDS

7.1. Reagent water must be produced by a Millipore DI system or equivalent. Reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks as

defined in the determinative SOPs.

7.2. Laboratory Control Sample (LCS) and matrix spike (MS) solutions are purchased as custom solutions. All standards must be stored in FEP fluorocarbon or previously unused polyethylene or polypropylene bottles. Stock standard solutions must be replaced prior to the expiration date provided by the manufacturer. If no expiration date is provided, the stock solutions may be used for up to one year and must be replaced sooner if verification from an independent source indicates a problem.

7.3. Working ICP LCS/MS spike solution: Prepare the ICP LCS/MS working spike solutions from custom stock standards to the final concentration listed in Table II. The working spike must be prepared in a matrix of 5% HNO_3. This acid (5 mL of concentrated HNO_3 per 100 mL) must be added to the volumetric flask before the addition of the stock standard aliquot. The working ICP LCS solution must be made fresh every three months.

7.4. ICP/MS spike solution. Laboratory Control Sample (LCS) and matrix spike (MS) solutions are custom made with the exception of Ag, Sb, and Sn, so that the final concentrations after spiking equals the concentrations listed in Table III. The ICP working solution (Section 7.3) is used for the Ag, Sb, and Sn spiking solution, which is also listed in Table III.

7.5. The LCS and MS samples must contain all the elements designated for analysis in each batch of samples. If a non-routine element is required that is not contained in the custom solution, the individual facility must purchase a solution from the designated vendor that will cover the additional analyte(s) of interest and provide for a final spike concentration that is appropriate to the determinative method.

7.6. Nitric acid (HNO_3), concentrated, trace metal grade or better.

7.7. Nitric acid, 1:1 - dilute concentrated HNO_3 with an equal volume of reagent water.

Note: When preparing diluted acids always add acid to water. If the water is added to the acid a violent reaction may occur.

7.8. Hydrochloric acid (HCl), concentrated, trace metal grade or better.

7.9. Hydrochloric acid, 1:1 - dilute concentrated HCl with an equal volume of reagent water.

Note: When preparing diluted acids always add acid to water. If the water is added to the acid a violent reaction may occur.

7.10. 30% Hydrogen peroxide (H_2O_2), reagent grade.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Sample holding time for metals included under the scope of this SOP is 180 days from the date

of collection to the date of analysis.

8.2. Soil samples do not require preservation with the exception of mercury, which must be stored at 4 °C ± 2 °C until time of preparation.

9. QUALITY CONTROL

Table IV (Appendix A) provides a summary of quality control requirements including type, frequency, acceptance criteria and corrective action.

9.1. Initial Demonstration of Capability

Prior to analysis of any analyte using Method 3050B the following requirements must be met.

9.1.1. Method Detection Limit (MDL) - An MDL must be determined for each analyte/matrix prior to the analysis of any samples. The MDL is determined using seven replicates of reagent water, spiked with all the analytes of interest, that have been carried through the entire analytical procedure. MDLs must be redetermined on an annual basis in accordance with 40 CFR Part 136 Appendix B requirements or verified as detailed in TestAmerica Corporate S-Q-003 and TestAmerica North Canton SOP NC-QA-0021. The spike level must be between the calculated MDL and 10X the MDL to be valid. The result of the MDL determination must be below the TestAmerica North Canton reporting limit. Criteria for DoD work is noted in SOP NC-QA-0016.

9.1.2. Initial Demonstration Study- this requires the analysis of four QC check samples. The QC check sample is a well characterized laboratory generated sample used to monitor method performance, which should contain all the analytes of interest. The results of the initial demonstration study must be acceptable before analysis of samples may begin. The results of the initial demonstration study may be used to extend a method for the analysis of other elements provided all acceptance criteria are met.

9.1.2.1. Four aliquots of the check sample (LCS) are prepared and analyzed using the procedures detailed in this SOP and the determinative SOPs.

9.1.2.2. Calculations and acceptance criteria for QC check samples are given in the determinative SOPs (CORP-MT-0001)

9.2. Preparation Batch - A group of up to 20 samples that are of the same matrix and are processed together using the same procedures and reagents. The preparation batch must contain a method blank, a LCS and a matrix spike/matrix spike duplicate. In some cases, at client request, it may be appropriate to process a matrix spike and sample duplicate in place of the MS/MSD. If clients specify specific samples for MS/MSD, the batch may contain multiple MS/MSD pairs.

9.3. Sample Count - Laboratory generated QC samples (method blanks, LCS, MS/MSD) are not counted towards the maximum 20 samples in a batch. Field QC samples are included in the batch count.

9.4. Method Blank (MB) - One method blank must be processed with each preparation batch. The method blank consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. Criteria for the acceptance of blanks are contained within the individual analytical method SOP's. If the method blank does not meet the criteria contained within the analytical method SOPs, the blank and all associated samples in the batch must be redigested.

9.4.1. The MB is prepared by weighing a 1 g aliquot of boiling chips. The MB is then processed as described in Section 11.10.

9.5. Laboratory Control Sample (LCS) - One aqueous LCS must be processed with each preparation batch. The LCS must contain all analytes of interest and must be carried through the entire analytical procedure. The LCS is used to monitor the accuracy of the analytical process. On going monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines. Criteria for the acceptance of LCS results are contained within the individual analytical method SOP's. Corrective action when LCS results fail to meet control limits will be repreparation and reanalysis of the batch. Tables II and III provide the details regarding the stock, working standards and final spike concentrations for ICP and ICP/MS. Refer to Section 7.4 for instructions on preparation of the aqueous LCS.

9.5.1. The LCS is prepared by spiking a 1g aliquot of boiling chips with 2 mL of the working LCS/MS spike solution (Section 7.3) for ICP and ICP/MS (Ag, Sb, Sn) analysis and 1 mL of the LCS/MS solution (Section 7.4) for the ICP/MS analysis. The LCS is then processed as described in Section 11.10.

9.6. Matrix Spike/Matrix Spike Duplicate (MS/MSD) - One MS/MSD pair must be processed for each preparation batch. A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added. A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked identically as the MS) prepared and analyzed along with the sample and matrix spike. Some client specific data quality objectives (DQO's) may require the use of sample duplicates in place of or in addition to MS/MSD's. The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Samples identified as field blanks cannot be used for MS/MSD analysis. If any analyte recovery or RPD falls outside the acceptance range, the recovery of that analyte must be in control for the LCS. If the recovery of the LCS is outside limits, corrective action must be taken. Corrective action will include repreparation and reanalysis of the batch. Corrective action when MS results fail to meet control limits does not include repreparation of samples unless the results indicate that a spiking error may have occurred. Tables II through III provide the details regarding the stock, working standards and final matrix spike concentrations for ICP

and ICP/MS. Refer to Sections 7.4 for instructions on preparation of the working matrix spike solutions.

9.6.1. The soil matrix spike sample is prepared by spiking a 1 g aliquot of a sample with 2mL of the working LCS/MS spike solution (Section 7.3) for ICP analysis and 1 mL of the LCS/MS solution (Section 7.4) for ICP/MS analysis. The matrix spike sample is then processed as described in Section 11.10.

10. CALIBRATION AND STANDARDIZATION

10.1. Hotplate or hotblock temperature must be verified daily for each unit used, and must be recorded in a hotplate/hotblock temperature log. The hotplate temperature should be verified by measuring the temperature of a beaker of reagent water placed on each hotplate/hotblock. For block digestors, use a tube containing water.

11. PROCEDURE

11.1. One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo. The Nonconformance Memo shall be filed in the project file.

11.2. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

11.3. The heating procedures are carried out in a properly functioning hood.

11.4. All samples are to be checked out of Sample Control with an electronic chain of custody.

11.5. Proper sample identification is extremely important in any preparation procedure. Labeling of beakers and bottles must be done in a manner to ensure connection with the proper sample. An automatic label printing programs is used to reduce transcription errors (QuantIMS option).

11.6. Samples are typically logged in as either waters or soils. Wastes such as organic liquids or sludges and tissues (animal/vegetable) are usually logged in with solid test codes. When initiating prep, examine the sample to see if the sample matches the matrix designation. If the sample is logged in as aqueous but it appears more like a waste (biphasic, sludge like, organic liquid, lots of sediment etc.) contact the lab supervisor or project administrator for further instructions. In some cases it may be more appropriate to process these samples as solids.

11.7. If possible prepare all the samples of a project at the same time to minimize the QC required and streamline the flow of the project through the lab and reporting group.

11.8. In some cases, both ICP/MS and ICP digestates are required on each sample. It is recommended that both aliquots be weighed out and processed at the same time.

11.9. Guidelines are provided in the appendices on procedures to minimize contamination of samples and standards.

11.10. Preparation of Soils, Sediments and Sludges for Analysis by ICP and ICP/MS.

11.10.1. Mix sample thoroughly by stirring with a clean plastic or wooden spoon or spatula.

11.10.2. For each digestion procedure required (i.e., ICP or ICP/MS), weigh a 1g portion of solid and record the exact weight to the nearest 0.01g. A 2g sample size may also be used if needed to meet the reporting limits.

11.10.3. Measure additional aliquots of the designated samples for the MS and MSD analyses.

11.10.4. Spike each of the MS and MSD aliquots with 2 mL of the working LCS/MS spiking solution (Section 7.3) for ICP analysis and 1 mL of the LCS/MS spiking solution for ICP/MS analysis.

11.10.5. Prepare a beaker, or equivalent container, for the method blank.

11.10.6. Prepare a beaker, or equivalent container, for the LCS. Add 2 mL of the working LCS/MS spiking solution (Section 7.3) for ICP analysis and 1 mL of the LCS/MS spiking solution (Section 7.4) for ICP/MS analysis.

11.10.7. Add 10 mL of 1:1 HNO_3 and mix the sample.

11.10.8. Heat sample to 95° ±4° C and reflux for 10 minutes without boiling, using a vapor recovery device.

Note: DO NOT ALLOW SAMPLE TO BOIL OR GO DRY during any part of the digestion. Doing so will result in the loss of analyte and the sample must be reprepared. Allow sample to cool, if necessary.

11.10.9. Add 5 mL of concentrated HNO_3.

11.10.10. Reflux at 95° ±4° C for 30 minutes. (Add reagent water as needed to ensure that the volume of solution is not reduced to less than 5 mL.)

11.10.11. Allow the samples to cool, if necessary.

11.10.12. Add approximately 2 mL of reagent water and 1 mL of 30 % H_2O_2. Care must be taken to ensure that losses do not occur due to excessively vigorous effervescence.

11.10.13. Heat sample until effervescence subsides.

11.10.14. Allow the sample to cool, if necessary.

11.10.15. Continue adding 30% H_2O_2 in 1 mL aliquots with warming until effervescence is minimal or sample appearance is unchanged.

Note: Do not add more than a total of 10 mL of 30 % H_2O_2.

11.10.16. Continue heating at 95° ±4° C until the volume is reduced to approximately 5-10 mL. Alternatively the sample may be heated for two hours.

11.10.17. If the sample is being prepared for ICP or ICP/MS (Ag, Sb, Sn) analysis, add 10 mL of concentrated HCL and reflux for an additional 10 minutes (15 minutes for DoD projects) without boiling. This step is omitted for ICP/MS elements not requesting Ag, Sb, and/or Sn.

11.10.18. Allow the sample to cool.

11.10.19. Wash down beaker walls and vapor recovery device with reagent water.

11.10.20. Filter sample through Whatman 41 filter paper or equivalent into a graduated cylinder or equivalent or a pre-weighed bottle. Other measuring bottles (for example, Corning Snap Seals™) may be used if their accuracy is documented and is better than ± 2%. Rinse beaker and filter paper with reagent water to ensure complete sample transfer.

Note: In place of filtering, the samples, after dilution and mixing, may be centrifuged or allowed to settle by gravity overnight to remove insoluble material

11.10.21. Dilute sample to 100 mL with reagent water. The sample is now ready for analysis.

12. DATA ANALYSIS AND CALCULATIONS

Not Applicable

13. METHOD PERFORMANCE

13.1. Method performance is determined by the analysis of matrix spike and matrix spike duplicate samples as well as method blanks and laboratory control samples. Acceptance criteria are given in the determinative SOPs.

13.2. The initial demonstration study as detailed in Section 9.1.2 must be acceptable before the

analysis of field samples under this SOP may begin. The results of the initial demonstration study may be used to extend a method for the analysis of other elements provided all acceptance criteria are met.

13.3. Training Qualification:

The group/team leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience.

14. POLLUTION PREVENTION

14.1. This method does not contain any specific modifications that serve to minimize or prevent pollution.

15. WASTE MANAGEMENT

15.1. All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in Section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

15.2. Waste Streams Produced by the Method

15.2.1. The following waste streams are produced when this method is carried out.

15.2.1.1. Acidic waste containing nitric acid generated by the extraction. This waste is disposed of in a designated container labeled "Acid Waste".

15.2.1.2. Contaminated disposable materials utilized for the analysis. This waste is disposed of in a designated container labeled "Solid Waste".

16. REFERENCES

16.1. References

16.1.1. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition, Final Update III, December 1996. Method 3050B.

16.1.2. Corporate Quality Management Plan (QMP), current version.

16.1.3. TestAmerica Laboratory Quality Manual (LQM), current version.

16.1.4. TestAmerica Corporate Safety Manual, M-E-0001 and TestAmerica North Canton Facility Addendum and Contingency Plan, current version.

16.2. Associated SOPs and Policies, latest version

16.2.1. CORP-MT-0001, Inductively Coupled Plasma-Atomic Emission Spectroscopy, Spectrometric Method for Trace Element Analysis of Water and Wastes, Method 6010B and Method 200.7.

16.2.2. NC-MT-0002, Inductively Coupled Plasma-Mass Spectrometry, EPA Methods 6020 and 200.8.

16.2.3. QA-003, TestAmerica North Canton QC Program.

16.2.4. Glassware Washing, NC-QA-0014

16.2.5. Statistical Evaluation of Data and Development of Control Charts, NC-QA-0018

16.2.6. Method Detection Limits and Instrument Detection Limits, S-Q-003 and NC-QA-0021

16.2.7. Supplemental Practices for DOD Project Work, NC-QA-0016

16.2.8. Standards and Reagents, NC-QA-0017

17. MISCELLANEOUS (TABLES, APPENDICES, ETC. . .)

17.1. Modifications/Interpretations from reference method.

17.1.1. Chapter 1 of SW-846 states that the method blank should not contain any analyte of interest at or above the MDL. This SOP states that the method blank must not contain any analyte of interest at or above the reporting limit. Common lab contaminants, as defined in the determinative SOPs, are allowed up to two times the reporting limit in the blank.

17.2. Documentation and Record Management

The preparation benchsheet should, at a minimum, include the following information:

- Preparation date, analyst, matrix, prep type (ICP or ICP/MS)
- Sample ID; initial weight/volume and final weight/volume
- Standards Documentation (source, lot, prep date, volume added)
- Reagents

APPENDIX A

TABLES

TABLE I. Method 3050A Approved Analyte List

ELEMENT	Symbol	CAS Number
Aluminum	Al	7429-90-5
Antimony	Sb	7440-36-0
Arsenic	As	7440-38-2
Barium	Ba	7440-39-3
Beryllium	Be	7440-41-7
Cadmium	Cd	7440-43-9
Calcium	Ca	7440-70-2
Chromium	Cr	7440-47-3
Cobalt	Co	7440-48-4
Copper	Cu	7440-50-8
Iron	Fe	7439-89-6
Lead	Pb	7439-92-1
Magnesium	Mg	7439-95-4
Manganese	Mn	7439-96-5
Molybdenum	Mo	7439-98-7
Nickel	Ni	7440-02-0
Potassium	K	7440-09-7
Selenium	Se	7782-49-2
Silver	Ag	7440-22-4
Sodium	Na	7440-23-5
Thallium	Tl	7440-28-0
Vanadium	V	7440-62-2
Zinc	Zn	7440-66-6

TABLE II. ICP Soil Matrix Spike and LCS Levels

ELEMENT	Working LCS/MS Standard (mg/L)	Soil MS/LCS Level * (mg/kg)
Aluminum	100	200
Antimony	25	50
Arsenic	100	200
Barium	100	200
Beryllium	2.5	5
Cadmium	2.5	5
Calcium	2500	5000
Chromium	10	20
Cobalt	25	50
Copper	12.5	25
Iron	50	100
Lead	25	50
Lithium	50	100
Magnesium	2500	5000
Manganese	25	50
Molybdenum	50	100
Nickel	25	50
Potassium	2500	5000
Selenium	100	200
Silver	2.5	5
Sodium	2500	5000
Strontium	50	100
Thallium	100	200
Vanadium	25	50
Zinc	25	50
Boron	50	100
Tin	100	200
Titanium	50	100

* Final soil spike concentration based on the addition of 2.0 mL working spike (7.3) to 1.0 g of sample/100 mL final volume (assumes 100% solids).

TABLE III. ICP/MS Soil Matrix Spike and LCS Levels

ELEMENT	Working LCS/MS Standard (mg/L)	Soil MS/LCS Level * (mg/kg)
Antimony **	25	50
Arsenic	10	10
Barium	10	10
Beryllium	10	10
Cadmium	10	10
Chromium	10	10
Cobalt	10	10
Copper	10	10
Lead	10	10
Manganese	10	10
Molybdenum	10	10
Nickel	10	10
Selenium	10	10
Silver **	2.5	5
Strontium	10	10
Thallium	10	10
Vanadium	10	10
Zinc	10	10
Boron	10	10
Tin **	1 00	200
Titanium	10	10
Zirconium	10	10

- Final soil spike concentration based on the addition of 1.0 mL working spike (7.4) to 1.0 g of sample/100 mL final volume (assumes 100% solids).

** In order to reduce the amount of sample digestions, Ag, Sb, and Sn will be spiked at the same concentration as the ICP spike levels. A 10x dilution is recommended for the MS/MSD and LCS before analysis.

TABLE IV. Summary of Quality Control Requirements

QC PARAMETER	FREQUENCY	ACCEPTANCE CRITERIA	CORRECTIVE ACTION
Method Blank	One per sample preparation batch of up to 20 samples.	Refer to determinative SOPs: NC-MT-0002 CORP-MT-0001	Redigest and reanalyze samples.
Laboratory Control Sample (LCS)	One per sample preparation batch of up to 20 samples.	Refer to determinative SOPs: NC-MT-0002 CORP-MT-0001	Redigest and reanalyze all samples associated with the LCS.
Matrix Spike	One per sample preparation batch of up to 20 samples.	Refer to determinative SOPs: NC-MT-0002 CORP-MT-0001	Reprep not required unless preparation error suspected.
Matrix Spike Duplicate	See Matrix Spike	Refer to determinative SOPs: NC-MT-0002 CORP-MT-0001	See Corrective Action for Matrix Spike.

APPENDIX B

CONTAMINATION CONTROL GUIDELINES

APPENDIX B. CONTAMINATION CONTROL GUIDELINES

The following procedures are strongly recommended to prevent contamination:

All work areas used to prepare standards and spikes should be cleaned before and after each use.

All glassware should be washed with detergent and tap water and rinsed with 1:1 nitric acid followed by deionized water.

Proper laboratory housekeeping is essential in the reduction of contamination in the metals laboratory. All work areas must be kept scrupulously clean.

Powdered or latex gloves must not be used in the metals laboratory since the powder contains silica and zinc, as well as other metallic analytes. Only vinyl or nitrile gloves should be used in the metals laboratory.

Glassware should be periodically checked for cracks and etches and discarded if found. Etched glassware can cause cross contamination of any metallic analytes.

Autosampler trays should be covered to reduce the possibility of contamination. Trace levels of elements being analyzed in the samples can be easily contaminated by dust particles in the laboratory.

The following are helpful hints in the identification of the source of contaminants:

Reagents or standards can contain contaminants or be contaminated with the improper use of a pipette.

Improper cleaning of glassware can cause contamination.

Separate glassware if an unusually high sample is analyzed and soak with sulfuric acid prior to routine cleaning.

Title: INDUCTIVELY COUPLED PLASMA – ATOMIC EMISSION SPECTROSCOPY, SPECTROMETRIC METHOD FOR TRACE ELEMENT ANALYSES

[SW846 Method 6010B and EPA Method 200.7]

Approvals (Signature/Date):

Roger K. Jobs	1-14-08		1-14-08
Technology Specialist	Date	Health & Safety Coordinator	Date
Dorothy J. Reeson	1/14/08		1/14/08
Quality Assurance Manager	Date	Laboratory Director	Date
Mark Bruce	1/14/08		
Technical Director	Date		

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1. SCOPE AND APPLICATION

1.1. This procedure describes the analysis of trace elements including metals in solution by Inductively Coupled Plasma -Atomic Emission Spectroscopy (ICP-AES) using SW-846 Method 6010B and EPA Method 200.7. Table I of Appendix A lists the elements appropriate for analysis by Methods 6010B and 200.7. Additional elements may be analyzed under Methods 6010B and 200.7 provided that the method performance criteria presented in Section 13.0 are met.

1.2. ICP analysis provides for the determination of metal concentrations over several orders of magnitude. Detection limits, sensitivity and optimum concentration ranges of the metals will vary with the matrices and instrumentation used.

1.3. Method 6010B is applicable to the determination of dissolved, suspended, total recoverable and total elements in ground water, aqueous samples, soils, sludges, wastes, sediments, biological, and TCLP, EP and other leachates/extracts. All matrices require digestion prior to analysis with the exception of analyses for dissolved metals in filtered and acidified aqueous samples. Although digestion is not specifically required by the method, some clients and regulators may require digestion of **dissolved samples** and this must be clarified and documented before project initiation. Silver concentrations must be below 2.0 mg/L in aqueous samples and 100 mg/kg in solid matrix samples. Precipitation may occur in samples where silver concentrations exceed these levels and lead to the generation of erroneous data.

1.4. Method 200.7 is applicable to the determination of dissolved, suspended, total recoverable, and total elements in water, waste water, and solid wastes. All matrices require digestion prior to analysis with the exception of analyses for dissolved metals in filtered and acidified aqueous samples if the criteria in Section 11.1 are met. Silver concentrations must be below 0.1 mg/L in aqueous samples.

2. SUMMARY OF METHOD

2.1. This method describes a technique for the determination of multi elements in solution using sequential or simultaneous optical systems and axial or radial viewing of the plasma. The basis of the method is the measurement of atomic emission by an optical spectroscopic technique. Samples are nebulized and the aerosol that is produced is transported to the plasma torch where excitation occurs. Characteristic atomic-line emission spectra are produced by radio frequency inductively coupled plasma (ICP). The spectra are dispersed by a grating spectrometer and the intensities of the emission lines are monitored by photomultiplier tubes. The photocurrents from the photomultiplier tubes are processed and controlled by a computer system. A background correction technique is required to compensate for variable background contribution to the determination of trace elements. Background must be measured adjacent to analyte lines during analysis. The position selected for the background intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The

position used must be free of spectral interferences and reflect the same change in background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result. The possibility of additional interferences should also be recognized and appropriate actions taken. Alternatively, multivariate calibration methods may be chosen for which point selection for background correction is superfluous since whole spectral regions are processed.

2.2. Refer to CORP-IP-0002NC, Acid Digestion of Soils, SW846 Method 3050B and CORP-IP-0003NC, Acid Digestion of Aqueous Samples by SW846 and MCAWW 200 Series Methods for details on sample preparation methods.

3. DEFINITIONS

3.1. Dissolved Metals: Those elements which pass through a 0.45 um membrane. (Sample is acidified after filtration).

3.2. Suspended Metals: Those elements which are retained by a 0.45 um membrane.

3.3. Total Metals: The concentration determined on an unfiltered sample following vigorous digestion.

3.4. Total Recoverable Metals: The concentration determined on an unfiltered sample following treatment with hot, dilute mineral acid.

4. INTERFERENCES

4.1. Spectral, physical and chemical interference effects may contribute to inaccuracies in the determinations of trace elements by ICP. Spectral interferences are caused by:

- Overlap of a spectral line from another element.
- Unresolved overlap of molecular band spectra.
- Background contribution from continuous or recombination phenomena.
- Stray light from the line emission of high concentration elements.

4.1.1. A background correction technique is required to compensate for variable background contribution to the determination of trace elements. Background correction is not required in cases where a background corrective measurement would actually degrade the analytical result.

4.1.2. Inter-element correction factors (IECs) are necessary to compensate for spectral overlap. Inter-element interferences occur when elements in the sample emit radiation at wavelengths so close to that of the analyte that they

contribute significant intensity to the analyte channel. If such conditions exist, the intensity contributed by the matrix elements will cause an excessively high (or sometimes low) concentration to be reported for the analyte. Inter-element corrections IECs must be applied to the analyte to remove the effects of these unwanted emissions.

4.1.3. Physical interferences are generally considered to be effects associated with sample transport, nebulization and conversion within the plasma. These interferences may result in differences between instrument responses for the sample and the calibration standards. Physical interferences may occur in the transfer of solution to the nebulizer (e.g., viscosity effects), at the point of aerosol formation and transport to the plasma (e.g., surface tension) or during excitation and ionization processes within the plasma itself. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples containing high dissolved solids or high acid concentrations. If physical interferences are present, dilution of the sample, use of a peristaltic pump, mass flow controller, use of an internal standard and/or use of a high solids nebulizer can reduce the effect.

4.1.4. Chemical interferences are characterized by molecular compound formation, ionization effects and solute vaporization effects. Normally these effects are not significant with the ICP technique but if observed can be minimized by buffering the sample, matrix matching or standard addition procedures.

5. SAFETY

5.1. Employees must abide by the policies and procedures in the Corporate Safety Manual and this document.

5.2. Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.3. The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure

Nitric Acid	Corrosive Oxidizer Poison	2 ppm-TWA 4-ppm STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Hydrochloric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
1 – Always add acid to water to prevent violent reactions			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

5.3.1. The plasma emits strong UV light and is harmful to vision. **NOTE: AVOID looking directly at the plasma.**

5.3.2. The RF generator produces strong radio frequency waves, most of which are unshielded. People with pacemakers should not go near the instrument while in operation.

5.4. Exposure to chemicals must be maintained **as low as reasonably achievable**; therefore, unless they are known to be non-hazardous, all samples should be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation, where possible. All samples with stickers that read "Caution/Use Hood!" **must** be opened in the hood. Contact the EH&S Coordinator if this is not possible. Metals digestates can be processed outside of a fume hood. Solvent and waste containers will be kept closed unless transfers are being made.

5.5. All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica North Canton associate. The situation must be reported **immediately** to the EH&S Coordinator and the Laboratory Supervisor.

6. EQUIPMENT AND SUPPLIES

6.1. Inductively Coupled Plasma Atomic Emission Spectrometer equipped with autosampler and background correction.

6.2. Radio Frequency Generator

6.3. Argon gas supply, welding grade or equivalent

6.4. Coolflow or appropriate water cooling device

6.5. Peristaltic Pump

6.6. Calibrated automatic pipettes or Class A glass volumetric pipettes – ranging from 5 µL → 10 ml

6.7. Class A volumetric flasks – range from 50 ml → 2000 ml

6.8. Autosampler tubes – range from 8 ml → 14 ml

7. REAGENTS AND STANDARDS

7.1. Intermediate standards are purchased as custom multi-element mixes or as single-element solutions. All standards must be stored in FEP fluorocarbon or unused polyethylene or polypropylene bottles. Intermediate standard solutions must be replaced prior to the expiration date provided by the manufacturer. If no expiration date is provided, the intermediate solutions may be used for up to one year and must be replaced sooner if verification from an independent source indicates a problem. Expiration dates can be extended provided that the acceptance criteria described in laboratory-specific SOPs are met.

7.2. Working calibration and calibration verification solutions may be used for up to 3 months and must be replaced sooner if verification from an independent source indicates a problem. Standards should be prepared in a matrix of 5% hydrochloric and 5% nitric acids. Refer to Tables III, IV, IVA, V and VI (Appendix A) for details regarding the working standard concentrations for calibration, calibration verification, interference correction and spiking solutions.

7.3. Concentrated nitric acid (HNO_3), trace metal grade or better.

7.4. Concentrated hydrochloric acid (HCl), trace metal grade or better.

7.5. Reagent water must be produced by a Millipore DI system or equivalent. Reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Sample holding times for metals are six months from time of collection to the time of analysis.

8.2. Aqueous samples are preserved with nitric acid to a pH of <2 and may be stored in either plastic or glass. If boron or silica are to be determined, plastic containers are preferred. Refrigeration is not required. Preservation must be verified prior to analysis.

8.3. Soil samples do not require preservation but must be stored at 4°C ± 2° until the time of preparation.

9. QUALITY CONTROL

Table VII (Appendix A) provides a summary of quality control requirements including type, frequency, acceptance criteria and corrective action.

9.1. Initial Demonstration of Capability

9.1.1. Prior to analysis of any analyte using either Method 200.7 or Method 6010B, the following requirements must be met.

9.1.2. Instrument Detection Limit (IDL) - The IDL for each analyte must be determined for each analyte wavelength used for each instrument. The IDL must be determined annually. If the instrument is adjusted in anyway that may affect the IDL, the IDL for that instrument must be redetermined. The IDL shall be determined by multiplying by 3, the standard deviation obtained from the analysis of a blank solution, with seven consecutive measurements. 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 performed between the analysis of separate samples). The result of the IDL determination must be below the TestAmerica North Canton reporting limit.

9.1.3. Method Detection Limit (MDL) - An MDL must be determined for each analyte prior to the analysis of any client samples. Refer to TestAmerica North Canton SOP NC-QA-0021 and S-Q-003 for details on MDL analysis and criteria.

9.1.4. Linear Range Verification (LR) - The linear range must be verified every six months for each analyte wavelength used on each instrument. The linear range is the concentration above which results cannot be reported without dilution of the sample. The standards used to verify the linear range limit must be analyzed during a routine analytical run and must read within 10% of the expected value.

For the **initial** determination of the upper limit of the linear dynamic range (LDR) for each wavelength, determine the signal responses from a minimum of three to five different concentration standards across the estimated range.

One standard should be near the upper limit of the estimated range. The concentration measured at the LDR must be no more than 10% less than the expected level extrapolated from lower standards. If the instrument is adjusted in any way that may affect the LRs, new dynamic ranges must be determined. The LR data must be documented and kept on file.

9.1.5. Background Correction Points - To determine the appropriate location for off-line background correction when establishing methods, the user must scan the area on either side adjacent to the wavelength and record the apparent emission intensity from all other method analytes. This spectral information must be documented and kept on file. The location selected for background correction must be either free of off-line interelement spectral interference or a computer routine must be used for automatic correction on all determinations. Tests to determine spectral interference must be done using analyte concentrations that will adequately describe the interference. Background correction points must be set prior to determining IECs. Refer to the ICP instrument manual for specific procedures to be used in setting background correction points.

9.1.6. Inter-element Corrections (IECs) - ICP interelement correction factors must be determined prior to the analysis of samples and every six months thereafter. If the instrument is adjusted in any way that may affect the IECs, the IECs must be redetermined. When initially determining IECs for an instrument, wavelength scans must be performed to ensure that solutions in use are free from contaminants. If an IEC varies significantly from the previously determined IEC then the possibility of contamination should be investigated. The purity of the IEC check solution can be verified by using a standard from a second source or an alternate method (i.e., ICP-MS). Published wavelength tables (e.g., MIT tables, Inductively Coupled Plasma-Atomic Spectroscopy: Prominent Lines) can also be consulted to evaluate the validity of the IECs. Refer to the instrument manufacturer's recommendations for specific procedures to be used in setting IECs. An IEC must be established to compensate for any interelement interference which results in a false analyte signal greater than ± the RL as defined in Tables I, IA or II. For elements with a reporting limit of 10 ug/L or less, the signal should be ± 2X the RL. To determine IECs, run a single element standard at the established linear range. To calculate an IEC, divide the observed concentration of the analyte by the actual concentration of the "interfering element."

Note: Trace ICP IECs are more sensitive to small changes in the plasma and instrument setup conditions. Adjustments in the IECs will be required on a more frequent basis for the Trace as reflected by the ICSA response. Additional spectral interference is present from easily ionizable elements such as potassium and sodium in axial viewing instruments.

9.1.7. Rinse Time Determination - Rinse times must be determined upon initial set-up of an ICP instrument. To determine the appropriate rinse time for a particular ICP system, the linear range verification standard (see 9.1.4) should be aspirated as a regular sample followed by the analysis of a series of rinse blanks. The length of time required to reduce the analyte signals to < RL will define the rinse time for a particular ICP system. For some analytes it may be impractical to set the rinse time based on the linear range standard result (i.e., analyte not typically detected in environmental samples at that level and an excessive rinse time would be required at the linear range level). Until the required rinse time is established, the method recommends a rinse period of at least 60 seconds between samples and standards. If a memory effect is suspected, the sample must be reanalyzed after a rinse period of sufficient length. Rinse time studies can be conducted at additional concentration levels. These additional studies must be documented and kept on file, if a concentration other than the linear range level is used to set the rinse time. The concentration levels used to establish the rinse time must be taken into consideration when reviewing the data.

9.2. Method Blank (MB) - One method blank must be processed with each preparation batch. The method blank consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. The method blank should not contain any analyte of interest at or above the reporting limit (exception: common laboratory contaminants, see below) or at or above 5% of the measured concentration of that analyte in associated samples, whichever is higher (sample result must be a minimum of 20x higher than the blank contamination level). For Ohio VAP projects, all analytes must be less than the reporting limit.

- If the analyte is a common laboratory contaminant (copper, iron, lead, or zinc) the data may be reported with qualifiers if the concentration of the analyte in the method blank is less than two times the RL. Such action must be addressed in the project narrative.

- Repreparation and reanalysis of all samples associated with an unacccptable method blank is required when reportable concentrations are determined in the samples (see exception noted above).

- If there is no analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. Such action must be addressed in the project narrative.

- If the above criteria are not met and reanalysis is not possible, then the sample data must be qualified. This anomaly must be addressed in the project narrative.

- For dissolved metal samples, which have not been digested, a CCB result is

reported as the method blank. The CCB run immediately prior to the start of the dissolved sample analyses must be used for this purpose. No more than 20 samples can be associated with one CCB.

9.3. Laboratory Control Sample (LCS) - One aqueous LCS must be processed with each preparation batch. The LCS must contain all analytes of interest and must be carried through the entire analytical procedure. Aqueous LCS spike levels are provided in Table III (Appendix A). The LCS is used to monitor the accuracy of the analytical process. On-going monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines.

- If any analyte is outside established control limits the system is out of control and corrective action must occur. Unless in-house control limits are established, a control limit of 80 - 120% recovery must be applied.

- In the event that an MS/MSD analysis is not possible a Laboratory Control Sample Duplicate (LCSD) must be analyzed. The LCSD recovery is evaluated using the same control limits as the LCS. The RPD of the LCS and LCSD must be compared to the matrix spike RPD limits.

- In the instance where the LCS recovery is greater than the upper control limit and the sample results are < RL, the data may be reported with qualifiers. Such action must be addressed in the report narrative.

- Corrective action will be repreparation and reanalysis of the batch unless the client agrees that other corrective action is acceptable.

- For dissolved metals samples which have not been digested, a CCV result is reported as the LCS. The CCV run immediately prior to the start of the dissolved sample analyses must be used for this purpose. No more than 20 samples can be associated with one CCV.

9.4. Matrix Spike/Matrix Spike Duplicate (MS/MSD) - One MS/MSD pair must be processed for each preparation batch. A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added. A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked identically as the MS) prepared and analyzed along with the sample and matrix spike. Some client-specific data quality objectives (DQOs) may require the use of sample duplicates in place of or in addition to MS/MSDs. The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Due to the potential variability of the matrix of each sample, these results may have immediate bearing only on the specific sample spiked. Samples identified as field blanks cannot be used for MS/MSD analysis. Spiking levels are provided in Tables III and VI (Appendix A).

- If any analyte recovery or RPD falls outside the acceptance range, the recovery of

that analyte must be in control for the LCS. For both methods 200.7 and 6010B, control limits of 75-125% recovery and 20% RPD or historical acceptance criteria must be applied to the MS/MSD. If the LCS recovery is within limits, then the laboratory operation is in control and the results may be accepted. If the recovery of the LCS is outside limits corrective action must be taken. Corrective action will include repreparation and reanalysis of the batch. MS/MSD results which fall outside the control limits must be addressed in the narrative.

- If the native analyte concentration in the MS/MSD exceeds 4x the spike level for that analyte, the recovery data is reported as NC, MSB (i.e., not calculated). Two other narrative notes for metals analyses: Matrix spike/spike duplicate spike recovery/recoveries was/were outside the acceptance limits of some analytes. The acceptable LCS analysis data indicated that the analytical system was operating within control and this condition is most likely due to matrix interference. See the Matrix Spike Report for the affected analytes which will be flagged with N. Matrix spike/spike duplicate relative percent difference (RPD) exceeded the acceptance limits for some analytes. The imprecision may be attributed to sample heterogeneity. See the Matrix Spike Report for the affected analytes, which will be flagged with *.

- If an MS/MSD is not possible due to limited sample volume then a laboratory control sample duplicate (LCSD) should be analyzed. The RPD of the LCS and LCSD must be compared to the matrix spike RPD limits.

- For dissolved metals samples which have not been digested, a MS/MSD must be performed per batch of up to 20 samples by spiking two aliquots of the sample at the levels specified in Table III (Appendix A).

9.5. Dilution test – A dilution test is performed to determine whether significant physical or chemical interferences exist due to the sample matrix. One sample per preparation batch must be processed as a dilution test. The test is performed by running a sample at a 5x (1:4) dilution. Samples identified as field blanks cannot be used for dilution tests. The results of the diluted sample, after correction for dilution, should agree within 10% of the original sample determination when the original sample concentration is greater than 50x the IDL. If the results are not within 10%, the possibility of chemical or physical interference exists and the data is flagged.

9.6. Initial Calibration Verification (ICV/ICB) - Calibration accuracy is verified by analyzing a second source standard (ICV). For analyses conducted under Method 200.7, the ICV result must fall within 5% of the true value for that solution with relative standard deviation <3% from replicate (minimum of two) exposures. For Method 6010B, the ICV must fall within 10% of the true value for that solution with relative standard deviation <5% from replicate (minimum of two) exposures. An ICB is analyzed immediately following the ICV to monitor low level accuracy and system cleanliness. The ICB result must fall within +/- the RL from zero. If either the ICV or ICB fail to meet criteria, the analysis should be terminated, the problem corrected, the instrument recalibrated and the calibration reverified. (See Section 11.8 or 11.11

for required run sequence).

9.7. Continuing Calibration Verification (CCV/CCB) - Calibration accuracy is monitored throughout the analytical run through the analysis of a known standard after every 10 samples and at the end of the sample run. The CCV is be a mid-range standard made from a dilution of the calibration standard. The CCV for both methods must fall within 10% of the true value for that solution with relative standard deviation <5% from replicate (minimum of two) exposures. A CCB is analyzed immediately following each CCV. (See Section 11.8 or 11.11 for required run sequence.) The CCB result must fall within +/- RL from zero. Sample results may only be reported when bracketed by valid CCV/CCB pairs. If a mid-run CCV or CCB fails, all affected samples will be re-analyzed with valid CCV/CCB pairs. (Refer to Section 11.13 for an illustration of the appropriate rerun sequence). Exceptions: If CCB > RL, samples < RL can be reported with an NCM. If CCV is outside of criteria on the high side, samples < RL can be reported with an NCM.

9.8. Interference Check Analysis (ICSA/ICSAB) - The validity of the interelement correction factors is demonstrated through the successful analysis of interference check solutions. The ICSA contains only interfering elements, the ICSAB contains analytes and interferents. Refer to Table V (Appendix A) for the details of ICSA and ICSAB composition. Custom multielement ICS solutions must be used. All analytes should be spiked into the ICSAB solution, therefore, if a non-routine analyte is required then it should be manually spiked into the ICSAB using a certified ultra high purity single element solution or custom lab-specific mix. If the ICP will display overcorrection as a negative number then the non-routine elements can be controlled from the ICSA as described in section 9.8.3. Elements known to be interferents on a required analyte must be included in the ICP run when that analyte is determined. Aluminum, iron, calcium and magnesium must always be included in all ICP runs.

9.8.1. The ICSA and ICSAB solutions must be run at the beginning of the run. (See Section 11.10 or 11.13 for required run sequence.)

9.8.2. The ICSAB results for the interferents must fall within 80 - 120% of the true value. If any ICSAB interferent result fails criteria, the analysis should be terminated, the problem corrected, the instrument recalibrated and the samples rerun.

9.8.3. ICSA results for the non-interfering elements with reporting limits ≤ 10 ug/L must fall within the TestAmerica North Canton guidelines of ± 2x RL from zero. ICSA results for the non-interfering elements with RLs> 10 µg/L must fall within the TestAmerica North Canton guidelines of ± 1x RL from zero. If the ICSA results for the non-interfering elements do not fall within +/- 2x RL (RL ≤10) or ± 1xRL (RL>10) from zero the field sample data must be evaluated as follows:

- If the non-interfering element concentration in the ICSA is the result of

contamination versus a spectral interference, and this reason is documented, the field sample data can be accepted.

- If the affected element was not required then the sample data can be accepted.
- If the interfering elements are not present in the field sample at a concentration which would result in a false positive or negative result greater than +/- 2x RL from zero then the field sample data can be accepted.
- If the interfering element is present in the field sample at a level which would result in a false analyte signal greater than ± 2x RL from zero, the data can be accepted only if the concentration of the affected analyte in the field sample is more than 10x the analyte signal in the ICSA.
- If the data does not meet the above conditions then the IECs must be re-evaluated and corrected if necessary and the affected samples reanalyzed or the sample results manually corrected through application of the new IEC to the raw results. If the results are recalculated manually the calculations must be clearly documented on the raw data.

9.9. CRI - To verify linearity near the RL for ICP analysis, a CRI standard is run at the beginning of each sample analysis run. Additionally, some projects may require CRI analysis at the end of the run. (See Section 11.10 or 11.13 for required run sequence.) Evaluate associated samples based upon advisory limits of +/- 50% of true value.

Note: The custom CRI mix contains most analytes at a level near the standard lab reporting limit.

9.10. Method of Standard Addition (MSA) -This technique involves adding known amounts of standard to one or more aliquots of the processed sample solution. This technique compensates for a sample interferent that may enhance or depress the analyte signal, thus producing a different slope from that of the calibration standards. It will not correct for additive interferences which cause a baseline shift. Refer to Section 11.17 for additional information on when MSA is required as well as Appendix C for specific MSA requirements.

10. CALIBRATION AND STANDARDIZATION

10.1. Set up the instrument with the operating parameters recommended by the manufacturer. Allow the instrument to become thermally stable before beginning calibration (approximately 30 minutes of warm-up is required). Refer to the instructions in Appendix G.

10.2. Profile and calibrate the instrument according to the instrument manufacturer's

recommended procedures. Flush the system with the calibration blank between each standard or as the manufacturer recommends. The calibration curve must consist of a minimum of a blank and a standard. Refer to Appendix G for detailed set up and operation protocols. Refer to Instruction Manuals in laboratory.

10.3. Calibration must be performed daily and each time the instrument is set up. Instrument runs may be continued over periods exceeding 24 hours as long as all calibration verification (CCV) and interference check QC criteria are met. The instrument standardization date and time must be included in the raw data.

10.4. Refer to Section 9.0 for calibration verification procedures, acceptance criteria and corresponding corrective actions.

11. PROCEDURE

11.1. For 200.7 analyses, dissolved (preserved) samples must be digested unless it can be documented that the sample meets all of the following criteria:

A. Visibly transparent with a turbidity measurement of 1 NTU or less.

B. Is of one liquid phase and free of particulate or suspended matter following acidification.

C. Is NOT being analyzed for silver.

11.2. A minimum of <u>two exposures</u> for each standard, field sample and QC sample is required. The average of the exposures is reported. For Trace ICP analyses, the results of the sum channel must be used for reporting.

11.3. Prior to calibration and between each sample/standard the system is rinsed with the calibration blank solution. The minimum rinse time between analytical samples is 60 seconds unless following the protocol outlined in 9.1.5 it can be demonstrated that a shorter rinse time may be used.

11.4. The use of automated QC checks through the instrument software is highly recommended for all calibration verification samples (ICV,CCV), blanks (ICB,CCB,PB), interference checks (ICSA,ICSAB) and field samples (linear range) to improve the data review process.

11.5. To facilitate the early identification of QC failures and samples requiring rerun it is strongly recommended that sample data be reviewed periodically throughout the run.

11.6. To facilitate the data review and reporting processes it is strongly recommended that all necessary dilutions be performed before closing out the instrument run.

11.7. The use of an internal standard is **<u>required</u>** on the Trace ICP unless the calibration and QC standards are matrix matched to each digestion procedure used as follows:

Preparation Method	% HNO_3	% HCl
SW846 3050	10	10
SW846 3005	2	5
SW846 3010	6	5

The following procedural guidelines must be followed when using an internal standard:

11.7.1. Typically used internal standards are: yttrium. (Note: Any element can be used that is not typically found in environmental samples at a high rate of occurrence.)

11.7.2. The internal standard (IS) must be added to every sample and standard at the same concentration. It is recommended that the IS be added to each analytical sample automatically through use of a third pump channel and mixing coil. Internal standards must be added to blanks, samples and standards in a like manner, so that dilution effects resulting from the addition may be disregarded.

11.7.3. The concentration of the internal standard must be sufficiently high to obtain good precision in the measurement of the IS analyte used for data correction and to minimize the possibility of correction errors if the IS analyte is naturally present in the sample.

11.7.4. The internal standard raw intensity counts must be printed on the raw data.

11.7.5. The analyst must monitor the response of the internal standard throughout the sample analysis run. This information is used to detect potential problems and identify possible background contributions from the sample (i.e., natural occurrence of IS analyte). The instrument automatically adjusts sample results based on comparison of the internal standard intensity in the sample to the internal standard intensity at calibration.

11.7.5.1. If the internal standard counts fall within ±30% of the counts observed in the ICB then the data is acceptable.

11.7.5.2. If the internal standard counts in the field samples are more than ±30% higher than the expected level, the field samples must then be diluted and reanalyzed.

11.8. The following analytical sequence must be used for Methods 6010B and 200.7:

Instrument Calibration
ICV
ICB
CRI
ICSA
ICSAB
CCV
CCB
10 samples
CCV
CCB
10 samples
CCV
CCB
Repeat sequence of up to 10 samples between CCV/CCB pairs as required to complete run
CRI (The CRI counts as a sample analysis.)
CCV
CCB

Refer to Quality Control Section 9.0 and Table VII (Appendix A) for Methods 6010B and 200.7 quality control criteria.

11.9. Full method required QC must be available for each wavelength used in determining reported analyte results.

11.10. The following run sequence provides an illustration of a mid-run CCV or CCB failure and the appropriate corrective action run sequence as described in Section 9.7.

Original Run: Instrument Calibration
ICV
ICB
CRI
ICSA
ICSAB
CCV
CCB
10 samples
CCV
CCB
10 samples
CCV
CCB
10 samples **
CCV *
CCB *

* Failure occurs at CCV/CCB
**Samples requiring rerun for affected analytes

10 samples **
CCV
CCB
10 samples
CCV
CCB

11.11 The instrument may be reprofiled between CCV/CCB pairs to correct for environment induced drift.

11.12 Guidelines are provided in the appendices on procedures to minimize contamination of samples and standards, preventive maintenance and troubleshooting.

11.13 All measurements must fall within the defined linear range where spectral interference correction factors are valid. Dilute and reanalyze all samples for required analytes that exceed the linear range or use an alternate wavelength for which QC data are established. If an inter-element correction exists for an analyte, which exceeds the linear range, the IEC may be inaccurately applied. Therefore, even if an overrange analyte may not be required to be reported for a sample, if that analyte is a interferent for any requested analyte in that sample, the sample must be diluted. Acid strength must be maintained in the dilution of samples.

11.14 For TCLP samples, full four-point MSA will be required if all of the following conditions are met:

1) Recovery of the analyte in the matrix spike is not at least 50%,

2) The concentration of the analyte does not exceed the regulatory level, and,

3) The concentration of the analyte is within 20% of the regulatory level.

The reporting and regulatory limits for TCLP analyses as well as matrix spike levels are detailed in Table VI (Appendix A). Appendix C provides guidance on performing MSA analyses.

11.15 Any variation in procedure shall be completely documented using instrument run logs, maintenance logs, report narratives, a Nonconformance Memo, or an anomaly report and is approved by a Supervisor/Group Leader and QA Manager.

11.16 Nonconformance documentation shall be filed in the project file.

11.17 Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

11.18 Analytical Documentation

11.18.1 Record all analytical information in the analytical logbook/logsheet which may be in an electronic format, including the analytical data from standards, blanks, LCSs, MS/MSDs, and any corrective actions or modifications to the method.

11.18.2 All standards are logged into a department standard logbook. All standards are assigned an unique number for identification. Logbooks are reviewed by the supervisor or designee.

11.18.3 Documentation such as all associated instrument printouts (final runs, screens, reruns, QC samples, etc.) and daily calibration data corresponding to all final runs is available for each data file.

11.18.4 Sample results and associated QC are entered into the LIMs after final technical review.

12 DATA ANALYSIS AND CALCULATIONS

12.1. ICV percent recoveries are calculated according to the equation:

$$\%R = 100\left(\frac{Found(ICV)}{True(ICV)}\right)$$

12.2. CCV percent recoveries are calculated according to the equation:

$$\%R = 100\left(\frac{Found(CCV)}{True(CCV)}\right)$$

12.3. Matrix Spike Recoveries are calculated according to the following equation:

$$\%R = 100\left(\frac{SSR - SR}{SA}\right)$$

Where:
SSR = Spike Sample Result
SR = Sample Result
SA = Spike Added

12.4. The relative percent difference (RPD) of matrix spike/matrix spike duplicates are calculated according to the following equations:

$$RPD = 100\left[\frac{|MSD - MS|}{\left(\frac{MSD + MS}{2}\right)}\right]$$

Where:
MS = determined spiked sample concentration
MSD = determined matrix spike duplicate concentration

12.5. The final concentration for a digested aqueous sample is calculated as follows:

$$mg / L = \frac{C \times V1 \times D}{V2}$$

Where:
C = Concentration (mg/L) from instrument readout (mean of two exposures)
D = Instrument dilution factor
V1 = Final volume in liters after sample preparation
V2 = Initial volume of sample digested in liters

12.6. The final concentration determined in digested solid samples when reported on a dry weight basis is calculated as follows:

$$mg / Kg, dry\ weight = \frac{C \times V \times D}{W \times S}$$

Where:
C = Concentration (mg/L) from instrument readout (mean of two exposures)
D = Instrument dilution factor
V = Final volume in liters after sample preparation
W = Weight in Kg of wet sample digested
S = Percent solids/100

Note: A Percent Solids determination must be performed on a separate aliquot when dry weight concentrations are to be reported. If the results are to be reported on wet weight basis the "S" factor should be omitted from the above equation.

12.7. The LCS percent recovery is calculated according to the following equation:

$$\%R = 100\left(\frac{Found(LCS)}{True(LCS)}\right)$$

12.8. The dilution test percent difference for each component is calculated as follows:

$$\%\,Difference = \frac{|I - S|}{I} \times 100$$

Where:
I = Sample result (Instrument reading)
S = Dilution test result (Instrument reading × 5)

12.9. Appropriate factors must be applied to sample values if dilutions are performed.

12.10. Trivalent Chromium

12.10.1. Trivalent chromium (CR^{+3}) is the result obtained by subtracting the hexavalent chromium (CR^{+6}) results for a sample from the total chromium result from that sample. The total chromium result is determined using the procedures in this SOP. The hexavalent chromium result is determined using the procedures in TestAmerica North Canton SOP NC-WC-0024.

12.10.2. Reporting Limits

12.10.2.1. The TestAmerica North Canton water reporting limit for trivalent chromium is 0.02 mg/l.

12.10.2.2. The TestAmerica North Canton solid reporting limit for trivalent chromium is 2.0 mg/kg, wet weight.

12.10.3. Calculations: Cr^{+3} = Cr, total – Cr^{+6}

13. METHOD PERFORMANCE

13.1. Each laboratory must have initial demonstration of performance data on file for each analyte of interest as described in Section 9.0.

13.2. Refer to Tables I, IA & II in Appendix A for the list of Method 6010B and 200.7 analytes as well as additional analytes that may be analyzed using this SOP.

13.3. Method performance is determined by the analysis of MS and MSD samples as well as method blanks and laboratory control samples. The MS or MSD recovery should fall within +/- 25 % and the MS/MSD should compare within 20% RPD or within the laboratory's historical acceptance limits. These criteria apply to analyte concentrations greater than or equal to 10xIDL. Method blanks must meet the criteria specified in Section 9.2. The laboratory control samples should recover within 20% of the true value or within the laboratory's historical acceptance limits.

13.4. Training Qualification:

13.4.1 The Group/Team Leader or the Supervisor has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience.

14. POLLUTION PREVENTION

14.2. This method does not contain any specific modifications that serve to minimize or prevent pollution.

15. WASTE MANAGEMENT

15.1. This method does not contain any specific modifications that serve to minimize or prevent pollution.

15.2. All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

15.3. Waste Streams Produced by this Method

15.3.1 The following waste streams are produced when this method is carried out:

15.3.2 Acid waste consisting of sample and rinse solution - Any sample waste generated must be collected and disposed of in the acid waste drum located in the metals lab.

15.3.3 Standards should be purchased and prepared in volumes consistent with laboratory use to minimize the volume of expired standards to be disposed.

16. REFERENCES

16.1. References

16.1.1. 40 CFR Part 136, Appendix B, 7-5-95, Determination of Method Detection Limits.

16.1.2. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition, Final Update III, Revision 2, December 1996. Method 6010B.

16.1.3. Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma-Atomic Emission Spectrometry, Revision 4.4, May 1994. Method 200.7.

16.1.4. Inductively Coupled Plasma – Atomic Emission Spectrometric Method for Trace Element Analysis of water and wastes Method 200.7, 40 CFR – Chapter I – Part 136 – Appendix C. Electronic version dated September 30, 2002.

16.1.5. Corporate Quality Management Plan (QMP), current version

16.1.6. TestAmerica Laboratory Quality Manual (LQM), current version.

16.2. Associated SOPs and Policies, latest version

16.2.1. TestAmerica North Canton QC Program, QA-003

16.2.2. Glassware Washing, NC-QA-0014

16.2.3. Statistical Evaluation of Data and Development of Control Charts, NC-QA-0018

16.2.4. Method Detection Limits and Instrument Detection Limits, NC-QA-0021

16.2.5. Supplemental Practices for DoD Project Work, NC-QA-0016

16.2.6. Hexavalent Chromium (Colorimetric), NC-WC-0024

16.2.7. Acid Digestion of Soils, SW846 Method 3050B, CORP-IP-0002NC

16.2.8. Acid Digestion of Aqueous Samples by SW846 and MCAWW 200 Series Methods, CORP-IP-0003NC

16.2.10 Standards and Reagents, NC-QA-0017

17. MISCELLANEOUS (TABLES, APPENDICES, ETC.)

17.1. Modifications/Interpretations from reference method

17.1.1. Modifications/interpretations from both Methods 6010B and 200.7.

17.1.1.1. TestAmerca North Canton Laboratories use mixed calibration standard solutions purchased from approved vendors instead of using individual mixes prepared in house as recommended by the subject methods.

17.1.1.2. Methods 200.7 and 6010B state that if the correction routine is operating properly, the determined apparent analyte(s) concentration from analysis of each interference solution should fall within a

specific concentration range around the calibration blank. In determining IECs, because of lack of definition clarification for "concentration range around the calibration blank," TestAmerica North Canton has adopted the procedure in EPA CLP ILMO4.0.

17.1.1.3. Section 8.5 of Method 6010B and Section 9.5 of Method 200.7 recommend that whenever a new or unusual matrix is encountered, a series of tests be performed prior to reporting concentration data for that analyte. The dilution test helps determine if a chemical or physical interference exists. Because TestAmerica North Canton laboratories receive no prior information from clients regarding when to expect a new or unusual matrix, TestAmerica North Canton may select to perform a dilution test on one sample in each prep batch. According to the method, the post digestion spike (PDS) determines any potential matrix interferences. At TestAmerica North Canton, matrix interference is determined by evaluating data for the LCS and MS/MSD. TestAmerica North Canton REQUIRES documented, clear guidance when a new or unusual matrix will be received for a project and a request to perform the dilution test or PDS on a client-identified sample.

17.1.2. Modifications from Method 200.7.

17.1.2.1. Method 200.7 defines the IDL as the concentration equivalent to a signal, due to the analyte, which is equal to three times the standard deviation of a series of ten replicate measurements of the calibration blank signal at the same wavelength. TestAmerica North Canton labs utilize the IDL definition as defined in Section 9.1 of this SOP.

17.1.2.2. The calibration blank is prepared in an acid matrix of 5% HNO_3/5% HCl instead of the specified 2% HNO_3/10% HCl matrix as the former matrix provides for improved performance relative to the wide variety of digestate acid matrices which result from the various EPA preparation protocols applied.

17.1.2.3. Method section 9.3.4 specifies that "Analysis of the IPC (ICSA/AB) solution immediately following calibration must verify that the instrument is within ± 5% of calibration with a relative standard deviation <3% from replicate integrations ≥ 4." TestAmerica North Canton uses a minimum of two exposures.

17.1.2.4. The 40 CFR version of Method 200.7 requires the instrument check standard to agree within ± 5% of expected values. Also, the 40 CFR version requires the interference check sample to be analyzed at the beginning, end, and at periodic intervals throughout the sample run. At TestAmerica North Canton, the instrument check standard equals

the CCV, which must agree within ± 10% of expected values, and the ICSA standards are analyzed only at the beginning of a sample run. TestAmerica's procedures are in line with the Rev. 4.4, May 1994 version of Method 200.7.

17.1.2.5. Section 7.12 of 200.7 indicates that the QCS (ICV) should be prepared at a concentration near 1 ppm. The ICV specified in this SOP accommodates the 1 ppm criteria for the majority of analytes. For the remaining analytes, this SOP specifies ICV concentrations which are appropriate to the range of calibration. The intent of the ICV, verification of calibration standard accuracy, is independent of the ICV concentration used.

17.1.2.6. The ICS criteria applied by this SOP differ from those stated in the method. Method 200.7 section 10.4 states that results should fall within the established control limits of 3 times the standard deviation of the calibration blank for that analyte. The control limits listed in this SOP are those applicable to the EPA designed solution.

17.1.2.7. Method 200.7 section 9.3.4 states the CCB should be less than the IDL, but > the lower 3-sigma control limit of the calibration blank. The intent of this requirement is to ensure that the calibration is not drifting at the low end. TestAmerica North Canton has adopted an absolute control limit of +/- RL from zero for calibration blank criteria. SOP section 9.7 provides the detailed corrective action criteria that must be followed.

17.1.3. Modifications from Method 6010B.

17.1.3.1. Chapter 1 of SW-846 states that the method blank should not contain any analyte of interest at or above the MDL. This SOP states that the method blank must not contain any analyte of interest at or above the reporting limit. Common lab contaminants are allowed up to two

times the reporting limit in the blank following consultation with the client.

17.1.3.2. Method 6010B section 8.6.1.3 states that the results of the calibration blank are to agree within 3x the IDL. If not, repeat the analysis two or more times and average the results. If the average is not within three standard deviations of the background mean, terminate the analysis, correct the problem, recalibrate, and reanalyze the previous 10 samples. The intent of this requirement is to ensure that the calibration is not drifting at the low end. TestAmerica North Canton has adopted an absolute control limit of +/- RL from zero for calibration blank criteria. See SOP Section 9.7

for a detailed description of the required corrective action procedures.

APPENDIX A

TABLES

TABLE I. Method 200.7 and 6010B Target Analyte List

Element	Symbol	CAS #	6010B Analyte	200.7 Analyte	Reporting Limit (ug/L) Water	Reporting Limit (mg/kg) Soil
Aluminum	Al	7429-90-5	X	X	200	20
Antimony	Sb	7440-36-0	X	X	60	6
Arsenic	As	7440-38-2	X	X	300	30
Barium	Ba	7440-39-3	X	X	200	20
Beryllium	Be	7440-41-7	X	X	5.0	0.5
Boron	B	7440-42-8	X	X	200	20
Cadmium	Cd	7440-43-9	X	X	5.0	0.5
Calcium	Ca	7440-70-2	X	X	5000	500
Chromium	Cr	7440-47-3	X	X	10	1
Cobalt	Co	7440-48-4	X	X	50	5
Copper	Cu	7440-50-8	X	X	25	2.5
Iron	Fe	7439-89-6	X	X	100	10
Lead	Pb	7439-92-1	X	X	100	10
Magnesium	Mg	7439-95-4	X	X	5000	500
Manganese	Mn	7439-96-5	X	X	15	1.5
Molybdenum	Mo	7439-98-7	X	X	40	4
Nickel	Ni	7440-02-0	X	X	40	4
Potassium	K	7440-09-7	X	X	5000	500
Selenium	Se	7782-49-2	X	X	250	25
Silver	Ag	7440-22-4	X	X	10	1
Sodium	Na	7440-23-5	X	X	5000	500
Thallium	Tl	7440-28-0	X	X	2000	200
Vanadium	V	7440-62-2	X	X	50	5
Zinc	Zn	7440-66-6	X	X	20	2

TABLE IA. Method 200.7 and 6010B Trace ICP Target Analyte List

Element	Symbol	CAS #	Reporting Limit (ug/L) Water	Reporting Limit (mg/kg) Soil
Arsenic	As	7440-38-2	10	1.0
Lead	Pb	7439-92-1	3.0	0.3
Selenium	Se	7782-49-2	5.0	0.5
Thallium	Tl	7440-28-0	10	1.0
Antimony	Sb	7440-36-0	10	1.0
Cadmium	Cd	7440-43-9	2.0	0.2
Silver	Ag	7440-22-4	5.0	0.5
Chromium	Cr	7440-47-3	5.0	0.5

TABLE II. Non-Routine Analyte List

Element	Symbol	CAS #	Reporting Limit (ug/L) Water	Reporting Limit (mg/kg) Soil
Tin	Sn	7440-31-5	100	10
Titanium	Ti	7440-32-6	50	5

TABLE III. Matrix Spike and Aqueous Laboratory Control Sample Levels

ELEMENT	LCS Level (ug/L)	Matrix Spike Level (ug/L)
Aluminum	2000	2000
Antimony	500	500
Arsenic	2000	2000
Barium	2000	2000
Beryllium	50	50
Cadmium	50	50
Calcium	50000	50000
Chromium	200	200
Cobalt	500	500
Copper	250	250
Iron	1000	1000
Lead	500	500
Magnesium	50000	50000
Manganese	500	500
Molybdenum	1000	1000
Nickel	500	500
Potassium	50000	50000
Selenium	2000	2000
Silver	50	50
Sodium	50000	50000
Thallium	2000	2000
Vanadium	500	500
Zinc	500	500
Boron	1000	1000
Tin	2000	2000
Titanium	1000	1000

TABLE IV. Trace ICP Calibration and Calibration Verification Standards

Element	Calibration Level	RL (ug/L)	ICV (ug/L)	CCV (ug/L)
Aluminum	50000	200	12500	25000
Antimony	1000	10	250	500
Arsenic	1000	10	250	500
Barium	4000	10	1000	2000
Beryllium	4000	5	1000	2000
Cadmium	1000	2	250	500
Calcium	100000	5000	25000	50000
Chromium	4000	5	1000	2000
Cobalt	4000	50	1000	2000
Copper	4000	25	1000	2000
Iron	50000	100	12500	25000
Lead	1000	3	250	500
Magnesium	100000	5000	25000	50000
Manganese	4000	15	1000	2000
Molybdenum	4000	40	1000	2000
Nickel	4000	40	1000	2000
Potassium	100000	5000	25000	50000
Selenium	1000	5	250	500
Silver	2000	5	500	1000
Sodium	100000	5000	25000	50000
Thallium	2000	10	500	1000
Vanadium	4000	50	1000	2000
Zinc	4000	20	1000	2000
Boron	10000	200	1000	5000
Tin	10000	100	1000	5000
Titanium	10000	50	1000	5000

TABLE V. Interference Check Sample Concentrations*

Element	ICSA (ug/L)	ICSAB (ug/L)
Aluminum	500000	500000
Antimony	-	1000
Arsenic	-	1000
Barium	-	500
Beryllium	-	500
Cadmium	-	1000
Calcium	500000	500000
Chromium	-	500
Cobalt	-	500
Copper	-	500
Iron	200000	200000
Lead	-	1000
Magnesium	500000	500000
Manganese	-	500
Molybdenum	-	1000
Nickel	-	1000
Potassium	-	10000
Selenium	-	1000
Silver	-	1000
Sodium	-	10000
Thallium	-	10000**
Vanadium	-	500
Zinc	-	1000
Tin	-	1000
Boron		1000
Titanium		1000

* Non-routine elements not listed above should be spiked into the ICSAB at 1000 ug/L.

** Thallium level for Trace ICP should be at 1000 ug/L.

TABLE VI. TCLP Reporting Limits, Regulatory Limits and Matrix Spike Levels

ELEMENT	Reporting Level (ug/L)	Regulatory Limit (ug/L)	Spike Level (ug/L)
Arsenic	500	5000	5000
Barium	10000	100000	50000
Cadmium	100	1000	1000
Chromium	500	5000	5000
Lead	500	5000	5000
Selenium	250	1000	1000
Silver	500	5000	1000

TABLE VII. Summary of Quality Control Requirements

QC Parameter	Frequency *	Acceptance Criteria	Corrective Action
Two-point Initial Calibration	Beginning of every analytical run, every 24 hours, whenever instrument is modified, or CCV criterion is not met		Terminate analysis. Correct the problem. Prepare new standards. Recalibrate following system performance.
ICV	Beginning of every analytical run.	Method 200.7: 95 - 105 % recovery RSD dupl. exp < 3% Method 6010B: 90 - 110 % recovery RSD dupl. exp < 5%	Terminate analysis. Correct the problem. Recalibrate.
ICB	Beginning of every analytical run, immediately following the ICV.	The result must be within +/- RL from zero.	Terminate analysis. Correct the problem. Recalibrate.
CCV	Every 10 samples and at the end of the run.	Method 200.7 & 6010B: 90 - 110 % recovery RSD dupl. exp < 5%	Terminate analysis. Correct the problem. Recalibrate and rerun all samples not bracketed by acceptable CCV. Samples < RL can be accepted if the CCV is outside on high side with NCM.
CCB	Immediately following each CCV.	The result must be within +/- RL from zero	Terminate analysis. Correct the problem. Recalibrate and rerun all samples not bracketed by acceptable CCB. Samples < RL can be accepted if the CCB is outside on high side with NCM.
CRI	Beginning of every run	50-150% recovery (advisory)	Evaluate associated samples.
ICSA	Beginning of every run	See Section 9.8.3	See Section 9.8.3
ICSAB	Immediately following each ICSA.	Results must be within 80 - 120% recovery.	See Section 9.8.2.

* See Sections 11.10 and 11.13 for exact run sequence to be followed.

TABLE VII. Summary of Quality Control Requirements (Cont'd)

QC Parameter	Frequency *	Acceptance Criteria	Corrective Action
Dilution Test	One per prep batch	For samples > 50x IDL, dilutions must agree within 10%	Narrate the possibility of physical or chemical interference per client request.
Method Blank	One per sample preparation batch of up to 20 samples	The result must be less than or equal to the RL. Common lab contaminants may be accepted up to 2x the RL (See 9.2). Sample results greater than 20x the blank concentration are acceptable. Samples for which the contaminant is < RL may not require re-digestion or reanalysis (see Section 9.2).	Re-digest and reanalyze samples. Note exceptions under criteria section. See Section 9.2 for additional requirements.
Laboratory Control Sample (LCS)	One per sample preparation batch of up to 20 samples	Aqueous LCS must be within 80 - 120% recovery or in-house control limits. Samples for which the contaminant is < RL and the LCS results are > 120% may not require re-digestion or reanalysis (see Section 9.3)	Terminate analysis. Correct the problem. Re-digest and reanalyze all samples associated with the LCS.
Matrix Spike	One per sample preparation batch of up to 20 samples	75 - 125 % recovery or in-house control limits. For TCLP See Section 11.17.	In the absence of client specific requirements, flag the data. No flag required if sample level is > 4x the spike added. For TCLP, see Section 11.17.
Matrix Spike Duplicate	See Matrix Spike	75 - 125 % recovery; RPD ≤ 20% .	See Corrective Action for Matrix Spike.

APPENDIX B

CROSS REFERENCE OF TERMS USED IN METHODS 6010B, 200.7, AND TESTAMERICA NORTH CANTON

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CROSS REFERENCE OF TERMS COMMONLY USED IN METHODS EPA 200.7, SW6010B, AND TESTAMERICA NORTH CANTON SOP

EPA 200.7	SW6010B	TestAmerica North Canton SOP
Calibration blank (CB)	Calibration blank	Initial and continuing calibration blanks (ICB/CCB)
Dilution test	Dilution test	Dilution Test
Instrument detection limit (IDL)	Instrument detection limit (IDL)	Instrument detection limit (IDL)
Instrument performance check (IPC)	Continuing calibration verification (CCV)	Continuing calibration verification (CCV)
Internal standard	Internal standard	Internal standard (IS)
Laboratory duplicates	N/A	N/A
Laboratory fortified blank (LFB)	N/A	Laboratory control sample (LCS)
Laboratory fortified sample matrix (LFM)	Matrix spike and matrix spike duplicate (MS/MSD)	Matrix spike and matrix spike duplicate (MS/MSD)
Laboratory reagent blank (LRB)	Method blank	Method or Prep blank (MB)
Linear dynamic range (LDR)	Linear dynamic range (LDR)	Linear dynamic range (LDR)
Method detection limit (MDL)	Method detection limit (MDL)	Method detection limit (MDL)
Quality control sample (QCS)	Check standard or Initial calibration verification (ICV)	Initial calibration verification (ICV)
Spectral interference check solution (SIC)	Interference check solution (ICS)	Interference check solution (ICSA/ICSAB)

APPENDIX C

MSA GUIDANCE

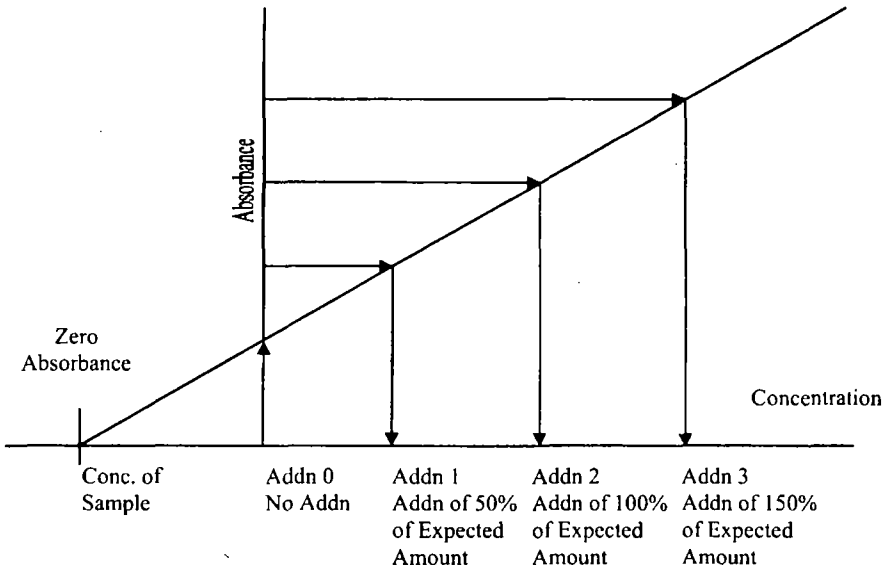
Facility Distribution No. _____	Distributed To:_____

APPENDIX C - MSA Guidance

Method of Standard Addition

Four equal volume aliquots of sample are measured and known amounts of standards are added to three aliquots. The fourth aliquot is the unknown and no standard is added to it. The concentration of standard added to the first aliquot should be 50% of the expected concentration. The concentration of standard added to the second aliquot should be 100% of the expected concentration and the concentration of standard added to the third aliquot should be 150% of the expected concentration. The volume of the unspiked and spiked standard should be the same.

In order to determine the concentration of analyte in the sample, the analytical value of each solution is determined and a plot or linear regression performed. On the vertical axis the analytical value is plotted versus the concentrations of the standards on the horizontal axis. An example plot is shown in Figure 1. When the resulting line is extrapolated back to zero absorbance, the point of interception of the horizontal axis is the concentration of the unknown.



For the method of standard additions to be correctly applied, the following limitations must be taken into consideration:

- The plot of the sample and standards must be linear over the concentration range of concern. For best results, the slope of the curve should be similar to that of a plot of the aqueous standard curve.
- The effect of the interference should not vary as the ratio of the standard added to the sample matrix changes.

APPENDIX D

TROUBLESHOOTING GUIDE

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APPENDIX D - TROUBLESHOOTING GUIDE

Problem	Possible Cause/ Solution
High Blanks	Increase rinse time Clean or replace tip Clean or replace torch Clean or replace sample tubing Clean or replace nebulizer Clean or replace mixing chamber Lower Torch
Instrument Drift	RF not cooling properly Vacuum level is too low Replace torch (Crack) Clean or replace nebulizer (blockage) Check room temperature (changing) Replace pump tubing Room humidity too high Clean torch tip (salt buildup) Check for argon leaks Adjust sample carrier gas Reprofile Horizontal Mirror Replace PA tube
Erratic Readings, Flickering Torch or High RSD	Check for argon leaks Adjust sample carrier gas Replace tubing (clogged) Check drainage(back pressure changing) Increase uptake time (too short) Increase flush time (too short) Clean nebulizer, torch or spray chamber Increase sample volume introduced Check that autosampler tubes are full Sample or dilution of sample not mixed Increase integration time (too short) Realign torch Reduce amount of tubing connectors
Standards reading twice normal absorbance or concentration	Incorrect standard used Incorrect dilution performed

APPENDIX E

CONTAMINATION CONTROL GUIDELINES

Facility Distribution No. _____	**Distributed To:_____**

APPENDIX E - CONTAMINATION CONTROL GUIDELINES

The following procedures are strongly recommended to prevent contamination:

All work areas used to prepare standards and spikes should be cleaned before and after each use.

All glassware should be washed with detergent and tap water and rinsed with 1:1 nitric acid followed by deionized water.

Proper laboratory housekeeping is essential in the reduction of contamination in the metals laboratory. All work areas must be kept scrupulously clean.

Powdered or Latex Gloves must not be used in the metals laboratory since the powder contains silica and zinc as well as other metallic analytes. Only vinyl or nitrile gloves should be used in the metals laboratory.

Glassware should be periodically checked for cracks and etches and discarded if found. Etched glassware can cause cross contamination of any metallic analytes.

Autosampler trays should be covered to reduce the possibility of contamination. Trace levels of elements being analyzed in the samples can be easily contaminated by dust particles in the laboratory.

The following are helpful hints in the identification of the source of contaminants:

Yellow pipet tips and volumetric caps can sometimes contain cadmium.

Some sample cups have been found to contain lead.

The markings on glass beakers have been found to contain lead. If acid baths are in use for glassware cleaning, they should be periodically checked for contaminants since contaminant concentrations will increase over time.

New glassware especially beakers can be a source of silica and boron.

Reagents or standards can contain contaminants or be contaminated with the improper use of a pipette.

Improper cleaning of glassware can cause contamination.

Latex gloves contain over 500 ppb of zinc.

APPENDIX F

PREVENTIVE MAINTENANCE

APPENDIX F - PREVENTIVE MAINTENANCE

A maintenance log is used to record when maintenance is performed on instruments. When an instrument problem occurs indicate the date, time and instrument number, then identify the problem and corrective action in the maintenance log.

The following procedures are required to ensure that that the instrument is fully operational:

Daily
Change sample pump tubing and pump windings
Check rinse solution and fill if needed
Check waste containers and empty if needed
Check sample capillary tubing is clean and in good condition
Check droplet size to verify nebulizer is not clogged.
Check sample flow for cross flow nebulizer
Check pressure for vacuum systems

As Needed
Clean plasma torch assembly to remove accumulated deposits
Clean nebulizer and drain chamber; keep free-flowing to maintain optimum performance
Replace peristaltic pump tubing, sample capillary tubing and autosampler sipper probe
Apply silicon spray on autosampler tracks
Check water level in cool flow

Bi-yearly
Change oil for vacuum systems
Replace coolant water filter (may require more or less frequently depending on quality of cooling water)

APPENDIX G

ICP OPERATING INSTRUCTIONS

ICP Analysis (TJA 61E)

Example

1. **SETUP**

   a. Plasma Control Panel (enter)

   b. (F1)-Startup

   c. (F9)-Continue

   d. (F2)-Levels

      1. Change auxiliary gas to low – use space bar to toggle

      2. Change nebulizer gas flow to 0.5 L/min.

      3. Change pump rate to 130

      4. Esc

      5. Allow instrument to warm up approximately 30 minutes.

2. **DEVELOPMENT**

   a. Methods (enter)

   b. Enter method name

   c. (F3)-Method Info.

   d. Change file name

   e. (F9)-Done

   f. (F9)-Done/Keep

3. **OPERATION**

   a. Analysis (enter)

   b. (F5)-Profile

      1. (F3)-Automatic

2. (F1)-Run

3. If peak position is greater than +/- .05 units from the center peak position, you must adjust the profile. If it is within +/- .05 units, press (F9)-done.

4. To adjust select (F1)-CalcSS and enter current vernier position. (enter)

5. Adjust to new vernier position(F9)-done

6. Rerun profile until peak position is +/- .05 units.

7. (F9)-Done

c. Autosampler (F9)

1. Enter method name (enter)

2. Enter autosampler table name (enter)

3. (F1)-Run

TestAmerica North Canton
STANDARD OPERATING PROCEDURE

TITLE: **INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETRY, EPA METHODS 6020 AND 200.8**

(SUPERSEDES: 4.2 Dated 01/08/04)

Reviewed by:	Roger K. Toth	8-30-07
	Technology Specialist	Date
Approved by:	Dorothy J. Leeson	9/5/07
	Quality Assurance Manager	Date
Approved by:		9/4/07
	Environmental Health and Safety Coordinator	Date
Approved by:		9/4/07
	Laboratory Director	Date

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1. SCOPE AND APPLICATION

1.1. This procedure describes multi-elemental analysis by inductively coupled plasma-mass spectrometry (ICP-MS) based on SW-846 protocol as described in EPA Method 6020 and 200.8. The source method lists fifteen elements approved for analysis by ICP/MS (Al, Sb, As, Ba, Be, Cd, Cr, Co, Cu, Pb, Mn, Ni, Ag, Tl, and Zn). Additional elements may be included provided that the method performance criteria presented in Section 9 is met. However, project approval may be required from the controlling agencies for compliance testing beyond the fifteen elements included in the promulgated method.

1.2. This procedure also describes the requirements for performing analysis of ground waters, surface waters and drinking water.

1.3. The procedure is applicable to the analysis of waters, soils, and wastes. No digestion is required prior to analysis for dissolved elements in water samples, but the samples must be filtered and preserved prior to analysis. Preliminary acid digestion is required for groundwater, aqueous samples, sludges, sediments, and other solid wastes for which total (acid-leachable) elements are requested. See SOP # CORP-IP-0002NC and SOP #CORP-IP-0003NC for preparation details.

1.4. The associated QuantIMs method codes are MH (6020) and QV (200.8).

1.5. This document accurately reflects current laboratory standard operating procedures (SOP) as of the date above. All facility SOPs are maintained and updated as necessary.

2. SUMMARY OF METHOD

2.1. Aqueous samples, digestates, or leachates are nebulized into a spray chamber where a stream of argon carries the sample aerosol through the quartz torch and injects it into an R.F. plasma. There the sample is decomposed and desolvated. The ions produced are entrained in the plasma gas and by means of a water-cooled, differentially pumped interface, introduced into a high-vacuum chamber that houses a quadrapole mass spectrometer capable of providing a resolution better than or equal to 0.9 AMU peak width at 10% of the peak height. For analysis by methods 200.8 the resolution requirement is 1.0 amu at 5% peak height. The ions are sorted according to their mass-to-charge ratio and measured with a channel electron multiplier. Interference 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 the constituents of the sample matrix. Recommended elemental equations which correct for many of these interferences are listed in Table I.

Use of the internal standard technique is required to compensate for suppressions and enhancements caused by sample matrices.

3. DEFINITIONS

3.1. Refer to the glossary in the Laboratory Quality Manual (LQM), latest version.

3.2. *Dissolved Metals* - Those elements which pass through a 0.45 µm membrane filter (sample is acidified after filtration).

3.3. *Suspended Metals* - Those elements which are retained by a 0.45 µm membrane filter.

3.4. *Total Metals* - The concentration determined on an unfiltered sample following vigorous acid digestion.

3.5. *Total Recoverable Metals* - The concentration determined on an unfiltered sample following treatment with hot, dilute mineral acids.

3.6. *Instrument Detection Limit (IDL)* - See Section 9.1.1.

3.7. *Sensitivity* - The slope of the analytical curve (i.e. the functional relationship between raw instrument signal and the concentration).

3.8. *Tuning Solution* - This is a multi-element solution containing analytes which are representative of the entire mass range capable of being scanned by the instrument. It is used to optimize the sensitivity of the instrument and to verify the mass resolution meets method criteria.

3.9. *Initial Calibration Verification/Quality Control Standard (ICV/QCS)* - A multi-element standard of known concentrations prepared to verify instrument calibration. This solution must be an independent standard prepared near the mid-point of the calibration curve, and at a concentration other than that used for instrument calibration.

3.10. *Continuing Calibration Verification (CCV).* - A multi-element standard of known concentrations prepared to monitor and verify the instrument daily continuing performance.

3.11. *Interference Check Standard (ICS)* - A solution containing both interfering and analyte elements of know concentration that is used to verify background and interelement correction factors.

3.12. *Laboratory Control Sample / Laboratory Fortified Blank (LCS/LFB)* - A multi-element

standard of known concentrations which is carried through the entire sample preparation and analysis procedure. This solution is used to verify the accuracy of the sample preparation.

3.13. *Reagent Blank* - High purity (> 18 megohm-cm) water carried through the entire digestion process.

3.14. *Calibration Blank* - High purity (> 18 megohm- cm) water acidified with the same acid concentrations present in the standards and samples Also referred to as the Initial Calibration Blank (ICB) and Continuing Calibration Blank (CCB).

3.15. *Method Detection Limit (MDL).* See Section 9.1.3

4. INTERFERENCES

4.1. Isobaric Interferences - Isobaric interferences in the ICPMS are caused by isotopes of different elements forming ions with the same nominal mass-to-charge ratio (m/z). Most interferences of this type are corrected for by the instrument software.

4.2. Isobaric Molecular and Doubly Charged Ion Interferences - Isobaric molecular interferences are caused by ions consisting of more than one atom or charge. Table II lists isobaric interferences which might possibly affect required analytes. When these interferences cannot be avoided by the use of another isotope with sufficient natural abundance, corrections must be applied and the data flagged to indicate the presence of interferences.

4.3. Physical Interferences - Physical interferences are associated with the transport and nebulization process. Internal standards are used to compensate for these types of interferences.

4.3.1. Internal standards should be added at a level to give approximately 100,000 – 1,000,000 counts of raw signal intensity. The mass of the internal standard should ideally be within 20 amu of the mass of the measured analyte.

4.3.2. Matrix effects will be monitored by comparing the internal standard intensity in the sample to the internal standard intensity of the calibration blank. When performing method 6020 the internal standard intensities must be between 30% and 120% of the intensities in the calibration blank. When performing method 200.8 the internal standards must be between 60% and 125% of the calibration blank If they fall outside this window, a dilution is performed on the sample to correct for matrix effects and the sample reanalyzed.

4.3.3. Memory effects are dependent on the relative concentration differences between samples and/or standards which are analyzed sequentially. The rinse period between samples must be long enough to eliminate significant memory interference.

4.3.4. Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus that lead to discrete artifacts. All of these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. Specific selection of reagents may be required to avoid introduction of contaminants.

5. SAFETY

5.1. Employees must abide by the policies and procedures in the Corporate Safety Manual, and this document.

5.2. Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Cut resistant gloves must be worn doing any other task that presents a strong possibility of getting cut. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.3. The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Hydrochloric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Nitric Acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

5.4. The RF Generator produces strong radio frequency waves, most of which are unshielded. People with pacemakers should not go near the instrument while in operation.

5.5. Exposure to chemicals must be maintained **as low as reasonably achievable**, therefore, unless they are known to be non-hazardous, all samples must be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. All samples with stickers that read "Caution/Use Hood!" **must** be opened in the hood. Contact the EH&S Coordinator if this is not possible. Solvent and waste containers will be kept closed unless transfers are being made.

5.6. It is recommended that neat standards be purchased only as a last resort. The preparation of standards from neat materials and reagents should be conducted in a fume hood with the sash closed as far as the operations will permit.

5.7. Standards in solution may be diluted in the open laboratory when syringes and the like are utilized.

5.8. The ICP plasma emits strong UV light and is harmful to vision. All analysts must avoid looking directly at the plasma.

5.9. All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica associate. The situation must be reported **immediately** to a laboratory supervisor and the EH&S Coordinator.

6. EQUIPMENT AND SUPPLIES

6.1. Argon gas: High purity grade (99.99%).

6.2. Inductively Coupled Plasma Mass Spectrometer capable of providing resolution, less than or equal to 0.9 AMU at 10% peak height from 6-253 AMU and 1.0AMU at 5% peak height from 6-253 AMU with a data system that allows corrections for isobaric interferences and the application of the internal standard technique.

6.3. A four channel peristaltic pump.

6.4. Appropriate water cooling device.

6.5. Calibrated automatic pipettes or Class A glass volumetric pipettes.

6.6. Autosampler with autosampler tubes.

7. REAGENTS AND STANDARDS

7.1. Calibration standards are purchased as custom multielement mixes or as single element solutions. All standards must be stored in FEP fluorocarbon or previously unused polyethylene or polypropylene bottles. Intermediate standard solutions must be replaced prior to the expiration date provided by the manufacturer. If no expiration date is provided, the intermediate solutions may be used for up to one year and must be replaced sooner if verification from an independent source indicates a problem. See Table XI.

7.2. Check Calibration Standard (ICV)

A quality control standard similar to the calibration standards and prepared in the same acid matrix. This solution must be made at a concentration near the midpoint of the calibration curve. This standard is composed of analytes from a different source from those used in the calibration of the instrument. See Table XI.

7.3. The tuning solution is purchased as custom multielement mixes or as single element solutions. All standards must be stored in FEP fluorocarbon or previously unused polyethylene or polypropylene bottles. The solution must be replaced prior to the expiration date provided by the manufacturer. If no expiration date is provided, the intermediate solutions may be used for up to one year.

7.4. The use of hydrochloric and sulfuric acids should be minimized due to higher incidence of molecular-ion interferences with the presence of these acids. Excessive amounts of nitric acid can also lead to molecular interferences.

7.5. Reagent water:

7.5.1. ASTM Type I or equivalent for the elements of interest, generated using an ion-exchange water polishing system capable of achieving 18.0 megohm-cm.

7.6. Rinse Solution: Carefully dilute 200 mL of concentrated HNO_3 and 40mL of concentrated HCl to 4.0 L with reagent water.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Aqueous samples are preserved with nitric acid to a pH of 2, and may be stored in plastic or glass. Preservation must be verified prior to analysis.

8.2. Soil samples do not require preservation, but must be stored at 4° ± 2°C until the time of preparation.

8.3. The analytical holding times for metals are six months from the time of collection.

8.4. Solid and aqueous samples must be digested prior to analysis by the appropriate method.

9. QUALITY CONTROL

9.1. Initial Demonstration of Capability

Table X provides a summary of quality control requirements including type, frequency, acceptance criteria and corrective action. Prior to analysis of any analyte the following requirements must be met.

9.1.1. Instrument Detection Limit (IDL). IDLs can be determined 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 a separate analytical sample. The IDL should be performed every three months. The IDL is calculated by multiplying by 3, the average of the standard deviations obtained on three nonconsecutive days.

9.1.1.1.IDL = (3) (s), where s = standard deviation.

9.1.2. Linear Calibration Ranges - Linear calibration ranges are primarily detector limited. The linear range must be determined at instrument setup, and the upper limit must be verified annually or whenever a change in instrument hardware or operating conditions, in the judgement of the analyst, may lower expected ranges.

Standards used to determine or verify linear ranges must be analyzed during a routine analytical run. The linear range is the concentration above which sample results cannot be reported.

9.1.2.1. For initial determination of the upper limit of the linear range, determine the signal responses from three different concentration standards across the estimated range. One standard must be at the upper limit of the estimated range. Results must recover within 10% of the expected value for the three standards. The Linear Range is then set at the concentration of the high standard.

9.1.2.2. For verification of the upper limit of the linear range, the high standard must recover within 10% of its expected value

9.1.3. Method Detection Limit (MDL) - The laboratory shall determine a method detection limit for all analytes of interest initially and annually thereafter. The MDL study is performed and calculated according to TestAmerica SOP S-Q-003 and NC-QA-0021, which are based on 40CFR Part 136 Appendix B.

9.2. Batch Definition

9.2.1. A batch is a group of no greater than 20 samples excluding QC samples (LCS, Method Blank, MS, MSD) which are processed similarly, with respect to the procedure. All sample setups must be initiated within a 24 hour period from the initial preparation or extraction and without interruption of the process. All samples within the batch must be treated with the same lots of reagents and the same processes.

9.3. Method Blank

9.3.1. One method blank (MB) must be processed with each preparation batch. The method blank consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. The method blank should not contain any analyte of interest at or above the reporting limit (exception: common laboratory contaminants, see below) or at or above 5% of the measured concentration of that analyte in associated samples, whichever is higher (sample result must be a minimum of 20x higher than the blank contamination level). **Note:** For Ohio VAP samples, all analytes must be less than the reporting limit.

- If the analyte is a common laboratory contaminant (copper, iron, lead, calcium, magnesium, potassium, sodium or zinc) the data may be reported with qualifiers if the concentration of the analyte in the method blank is less than two times the RL. Barium, Chromium and Manganese may also be considered common laboratory contaminants at ICPMS reporting limits. **Such action must be addressed in the project narrative.**

- Repreparation and reanalysis of all samples associated with an unacceptable method blank is required when reportable concentrations are determined in the samples (see exception noted above).

- If there is no analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. **Such action must be addressed in the project narrative.**

- If the above criteria are not met and reanalysis is not possible, then the sample data must be qualified. **This anomaly must be addressed in the project narrative.**

9.3.2. For dissolved metals samples which have not been digested, a CCB result is reported as the method blank. The CCB run immediately prior to the start of the dissolved sample analyses must be used for this purpose. No more than 20 samples can be associated with one CCB

9.4. Laboratory Control Sample (LCS)

9.4.1. One LCS from an independent source must be processed with each preparation batch. The LCS must be carried through the entire analytical procedure. The LCS is used to monitor the accuracy of the analytical process. On-going monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines. The historical limits for the LCS for each analyte are in the LIMS system. If the LCS exceeds these limits for any analyte, that analyte is judged to be out of control and must be corrected before the analysis can be reported

9.4.2. Corrective Action for LCS

9.4.2.1. If any analyte is outside established control limits the system is out of control and corrective action must occur.

9.4.2.2. The only exception is that if the LCS recoveries are biased high and the associated sample is ND for the parameter(s) of interest, the batch is acceptable. **This must be addressed in the project narrative.**

9.4.2.3. Corrective action will be repreparation and reanalysis of the batch unless the client agrees that other corrective action is acceptable. **Note:** For Ohio VAP samples, the batch must be redigested if the exception in Section 9.4.2.2 is not applicable.

9.5. Matrix Spike/Matrix Spike Duplicate (MS/MSD)

9.5.1. One MS/MSD pair must be processed for each batch. A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added. A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked identically as the MS) prepared and analyzed along with the sample and matrix spike. Some client specific data quality objectives (DQO's) may require the use of sample duplicates in place of or in addition to MS/MSD's. The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Due to the potential variability of the matrix of each sample, these results may have immediate bearing only on the specific sample spiked. Samples identified as field blanks cannot be used for MS/MSD analysis. The historical spike recovery acceptance limits for each analyte are in the LIMS system. If they are not in control and all other quality control criteria have been met, then a matrix interference is suspected.

9.5.2. Corrective action for MS/MSDs

9.5.2.1. If the analyte recovery or RPD falls outside the acceptance range, the recovery of that analyte must be in control for the LCS. If the LCS recovery is within limits, then the laboratory operation is in control and the results may be accepted. If the recovery of the LCS is outside limits, corrective action must be taken. Corrective action will include repreparation and reanalysis of the batch.

9.5.2.2. If the native analyte concentration in the MS/MSD exceeds 4x the spike level for that analyte, the recovery data is reported as NC (not calculated).

9.5.2.3. If an MS/MSD is not possible due to limited sample volume then a laboratory control sample duplicate (LCSD) should be analyzed. The RPD of the LCS and LCSD must be compared to the laboratory limits.

9.5.2.4. If client program requirements specify to confirm matrix interference's, repreparation and reanalysis of the MS/MSD may be necessary.

9.6. Sample Duplicate

9.6.1. A sample duplicate (DU) is a second aliquot of an environmental sample, taken from the same sample container when possible, that is processed with the first aliquot of that sample. That is, sample duplicates are processed as independent samples within the same QC batch. The sample and DU results are compared to determine the effect of the sample matrix on the precision of the analytical process. As with the MS/MSD results, the sample/DU precision results are not necessarily representative of the precision for other samples in the batch.

9.6.2. Sample duplicates may be performed in lieu of or in addition to MSDs.

9.7. Control Limits

9.7.1. Control limits are established by the laboratory as described in SOP NC-QA-0018.

9.7.2. Laboratory control limits are internally generated and updated periodically unless method specified. Control limits are easily accessible via the LIMs (QC Browser program).

9.8. Method Detection Limits (MDLs) and MDL Checks

9.8.1. MDLs and MDL Checks are established by the laboratory as described in SOP NC-QA-0021.

9.8.2. MDLs are easily accessible via the LIMs (QC Browser program).

9.9. ICV/CCV/QCS - Calibration accuracy is verified at the beginning of each analytical run by analyzing a second-source initial calibration verification (ICV) standard. A continuing calibration verification (CCV) standard is analyzed at a 10% frequency throughout the run. The ICV must be within 10% of the expected value, or the analysis is terminated. The CCV must be within 10% of the expected value for method 6020 or 15% of the expected value for method 200.8. Sample results may only be reported when bracketed by valid CCV's.

9.10. RL Verification Standard –An independent standard is analyzed after the ICV to monitor the lab's ability to produce reliable results at RL-level concentrations. There is no set acceptance criteria established for this standard, but generally results should be within 50% of the expected value.

9.11. ICB/CCB/CB - The initial calibration blank must be analyzed immediately following the ICV. The continuing calibration blank must be analyzed at a frequency of 10% throughout the remainder of the analytical run. The ICB/CCB must fall within +/- the

reporting limit from zero.

9.12. Interference Check Solutions (ICSA/ICSAB) ***Method 6020 only*** - The interference check solution is prepared with known concentrations of interfering elements so a determination may be made as to the magnitude of the interference on analytes of interest as well as a test of any software corrections. The required elements and their concentrations are listed in Table V. The interference check solutions must be analyzed at the beginning of every analytical run and every 12 hours thereafter. The results of solution "A" and solution "AB" should be monitored for possible interferences.

9.12.1. Control limits of spiked analytes in the ICSA/ICSAB solution are +/- 50% of true value. Some projects may require control limits of +/- 20% of true value. Control limits of non-spiked analytes are +/- 2x the reporting limit or less than 1 ug/L.

Note: It may not be possible to obtain absolutely clean ICSA/ICSAB standards. If contamination can be confirmed by another method (ICP/GFAA), acceptance criteria will be applied at that level and the data accepted.

9.13. Internal Standards

The intensities of all internal standards must be monitored throughout the run. The internal standard in the samples must be between 30% and 120% of the intensity of the calibration blank for Method 6020, and between 60% and 125% for Method 200.8. If the sample falls outside of this criteria, perform the following procedures. First, evaluate nearby CCVs and CCBs. If sample internal standard recoveries appear to be related to instrument drift, then rerun affected samples. If sample internal standard recoveries appear to be primarily sample or matrix related, then perform appropriate dilutions until the internal standard recoveries are within the method criteria. In no case, may Method 6020 sample results be reported with internal standard recoveries greater than 40% higher than recoveries in surrounding CCVs/CCBs. Alternately, the run may be reprocessed with an alternative internal standard that is not in the samples and at an appropriate mass for the masses being reported.

9.14. Serial Dilution ***Method 6020 only*** - One serial five-fold dilution should be analyzed per batch for each matrix. If the analyte concentration is within linear range of the instrument and sufficiently high (generally, a factor of 100 times above the reporting limit), the serial dilution must agree within 10% of the original analysis. If not, an interference effect must be suspected, the result is flagged and included in the final report narrative. Samples identified as blanks cannot be used for serial dilution.

9.15. Post-Digestion Spike Addition (PDS) ***Method 6020 only*** - If the serial dilution fails to meet the acceptance criteria, a PDS must be performed as follows. An analytical spike added to a portion of a prepared sample, or its dilution, should be recovered within 75 -

125% of the known value. If the PDS fails to meet this criterion, matrix interference should be suspected.

9.16. General Corrective Action Requirements - The general requirements for evaluation of QC results and corrective action for failures is described in TestAmerica Policy QA-003

9.17. Nonconformance and Corrective Action

9.17.1. Any deviations from QC procedures must be documented as a nonconformance, with applicable cause and corrective action approved by the facility QA Manager.

10. CALIBRATION AND STANDARDIZATION

10.1. Instrument StartUp

Set up the instrument according to manufacturers operating instructions. Allow the instrument to become thermally stable for at least 30 minutes before tuning.

10.2. Instrument Tuning / Mass Calibration / Daily Performance

10.2.1. Daily Performance – Refer to Appendix A for ICPM/MS Instrument Instructions. Instrument manuals are available as needed. Verify instrument performance daily with a solution containing elements representing all of the mass regions of interest. The relative standard deviations must be less than 5% after running the tuning solution a minimum of 4 times. For method 200.8, the tuning solution must be analyzed 5 times with a relative standard deviation less than 5%.

10.2.2. Check mass calibration and resolution daily.

10.2.2.1. Mass Calibration Check – The mass calibration results must be within 0.1 amu from the true value. If this criterion is not met, the mass calibration must be adjusted before running samples.

10.2.2.2. Mass Resolution Check - The resolution must be verified to be less than 0.9 amu full width at 10% peak height. Due to a limitation of the instrument software, the resolution requirement for method 200.8 of 1.0 amu full width at 5% peak height cannot be verified automatically. If the mass resolution requirement of 0.9AMU at 10% peak height is met the 200.8 requirement is also satisfied.

10.3. Calibrate the instrument for the analytes of interest according to manufacturer's instructions. Routine calibration and calibration verification levels are shown in Table

XI. The calibration should include a blank and three standards. For a linear multi-point calibration curve, the correlation coefficient must be >/= 0.995. Report the average of at least two integrations for both calibration and sample analysis. A calibration must be performed daily and each time the instrument is set up. Instrument run may be continued over periods exceeding 24 hours as long as calibration verification, interference check, and internal standard QC criteria are met.

11. PROCEDURE

11.1. One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and is approved by a Technical Specialist and QA Manager. The Nonconformance Memo shall be filed in the project file.

11.2. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

11.3. Sample Preparation

11.3.1. Preliminary acid digestion is required for groundwater, aqueous samples, sludges, sediments, and other solid wastes for which total (acid- leachable) elements are requested. See SOP CORP-IP-0002NC and SOP CORP-IP-0003NC for preparation details.

11.4. Sample Analysis

11.4.1. Flush the system with the rinse blank for at least 30 seconds between samples and standards during the analytical run.

11.4.2. Masses which would affect the data quality must be monitored during the analytical run to determine the potential effects of matrix on a given element.

11.4.3. Dilute and reanalyze samples that are more concentrated than the linear range for an analyte or specific isotope of interest. No analyte may be reported from an analysis of a diluted sample in which the analyte concentration is less than 5 times the IDL (the sample should be diluted to the approximate midrange of the analytical curve), unless the dilution is for internal standard recoveries.

11.4.4. The analytical run sequence should be performed as follows to meet all quality control criteria:

Warm-up

Verify instrument performance
Calibration blank
Calibration standards
ICV
ICB
RL verification standard
ICSA (6020 Only)
ICSAB (6020 Only)
CCV
CCB
10 Samples
CCV
CCB

11.5. Analytical Documentation

11.5.1. Record all analytical information in the analytical logbook/logsheet, which may be in an electronic format, including the analytical data from standards, blanks, LCSs, MS/MSDs, and any corrective actions or modifications to the method.

11.5.2. All standards are logged into a department standard logbook. All standards are assigned an unique number for identification. Logbooks are reviewed by the supervisor or designee.

11.5.3. Documentation such as all associated instrument printouts (final runs, screens, reruns, QC samples, etc.) and daily calibration data corresponding to all final runs is available for each data file.

11.5.4. Sample results and associated QC are entered into the LIMs after final technical review.

12. DATA ANALYSIS AND CALCULATIONS

Note: The mean of 2 exposures is used to derive the sample concentrations used in the calculations in this section.

12.1. ICV percent recoveries are calculated according to the equation:

$$\%R = \mathbf{100} \times \left(\frac{\textbf{Found (ICV)}}{\textbf{True (ICV)}} \right)$$

12.2. CCV percent recoveries are calculated according to the equation:

$$\%R = 100 \times \left(\frac{\text{Found (CCV)}}{\text{True (CCV)}} \right)$$

12.3. Matrix Spike Recoveries are calculated according to the following equation:

$$\%R = 100 \times \left(\frac{\text{SSR - SR}}{\text{SA}} \right)$$

Where:
SSR = Spike Sample Result
SR = Sample Result
SA = Spike Added

Note: When sample concentration is less than the method detection limit, use SR = 0 for purposes of calculating % Recovery.

12.4. The relative percent difference (RPD) of sample duplicates are calculated according to the following equation:

$$RPD = 100 \times \left[\frac{\text{(DU1 - DU2)}}{\text{(DU1 + DU2) / 2}} \right]$$

Where:
DU1 = Sample result
DU2 = Sample duplicate result

12.5. The final concentration for an aqueous sample is calculated as follows:

$$\text{Result (ug/L)} = \frac{\text{(C x V1 x D)}}{\text{V2}}$$

Where:
C = Concentration from instrument readout, ppb
D = Instrument dilution factor
V1 = Final volume in liters after sample preparation
V2 = Initial volume of sample digested in liters

12.6. The concentration determined in digested solid samples when reported on a wet weight

basis is as follows:

$$\text{Result (ug/kg)} = \frac{(C \times V \times D)}{W}$$

Where:

C = Concentration from instrument readout, ppb
D = Instrument dilution factor
V = Final volume in liters after sample preparation
W = Weight, in g, of wet sample digested

12.7. Sample results should be reported according to the following significant figure rules:

12.7.1. All uncorrected values less than the detection limit are reported as "less than" the detection limit.

12.7.2. Positive results for target analytes are reported to three significant figures if the method is used without dilution.

12.8. Positive results obtained after dilution and results for non-certified analytes are reported to two significant figures

13. METHOD PERFORMANCE

13.1. Each laboratory must have initial demonstration of performance data on file and corresponding method detection limit files.

13.2. Refer to Table I for the list of analytes that may be analyzed using this SOP for methods 6020 and 200.8. Additional analytes may be analyzed if all method required QC is acceptable.

13.3. Method performance is determined by the analysis of matrix spike and matrix spike duplicate samples as well as method blanks and laboratory control samples. The matrix spike recovery should fall within historical laboratory control limits and the matrix spike duplicates should compare within 20% RPD. Method blanks must meet the criteria specified in Section 9.3. The laboratory control samples should recover within 20% of the true value until in house control limits are established.

13.4. Training Qualifications:

13.4.1. The Group/Team Leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the

required experience.

14. POLLUTION PREVENTION

14.1. This method does not contain any specific modifications that serve to minimize or prevent pollution.

15. WASTE MANAGEMENT

15.1. All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in Section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

15.2. Solid materials (gloves, soiled paper products, etc.) are placed in the solid debris container. Do not put liquids in the solid waste container.

15.3. Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices of TestAmerica. They must have training on the hazardous waste disposal practices upon initial assignment to these tasks, followed by an annual refresher training.

15.4. Waste Streams Produced by the Method

15.4.1. Acid waste consisting of sample and rinse solution generated by this method.

15.4.1.1. Aqueous waste can be poured down the drain if the pH is between 4 and 10. Any sample waste generated that is not in this pH range must be collected and disposed of in the acid waste drum located in the metals lab.

16. REFERENCES

16.1. References

16.1.1. Test Methods For Evaluating Solid Waste, EPA SW-846, 3rd Edition, Final Update II, Method 6020: "Inductively Coupled Argon Plasma - Mass Spectrometry", Revision 0, September 1994.

16.1.2. Environmental Monitoring Systems Laboratory, EPA Method 200.8, "Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma - Mass Spectrometry", Revision 5.4, EMMC Version

16.1.3. Corporate Quality Management Plan (QMP), current version.

16.1.4. TestAmerica Laboratory Quality Manual (LQM), current version.

16.2. Associated SOPs and Policies, latest version

16.2.1. QA Policy, QA-003

16.2.2. CORP-IP-0002NC, Acid Digestion of Soils, SW846 Method 3050B, latest version.

16.2.3. CORP-IP-0003NC, Acid Digestion of Aqueous Samples by SW846 and MCAWW 200 Series Methods

16.2.4. Glassware Washing, NC-QA-0014

16.2.5. Statistical Evaluation of Data and Development of Control Charts, NC-QA-0018

16.2.6. Method Detection Limits and Instrument Detection Limits, NC-QA-0021 and S-Q-003.

16.2.7. Supplemental Practices for DoD Project Work, Navy/Army SOP, NC-QA-0016.

16.2.8. Standards and Reagents, NC-QA-0017.

17. MISCELLANEOUS (TABLES, APPENDICES, ETC.)

17.1. Reporting limits

17.1.1. Refer to Table XII for associated reporting limits

17.1.2. If samples require dilution or smaller volumes than specified in this method, the RL will be elevated.

17.2. Method deviations

17.2.1. Deviations from method 6020

17.2.1.1. Commercially available standards are purchased and verified at the laboratory rather than being prepared from the solid material. These verification records are kept in the laboratory.

17.2.1.2. The results of the calibration blank as well as all other blanks must be less than the reporting limit, not 3 times the instrument IDL.

17.2.1.3. Milli-Q or Nanopure water is substituted when reagent water is called for. This water is tested to be free of contaminants by conductivity (18megOhm) and by the analysis of blanks.

17.2.1.4. Internal standard recoveries may be less than 80% in CCV's and CCB's as long as QC criteria are met. Sample internal standard recoveries may never be greater than 40% higher than recoveries in associated CCV's/CCB's.

17.2.2. Deviations from method 200.8

17.2.2.1. Commercially available standards are purchased and verified at the laboratory rather than being prepared from the solid material. These verification records are kept in the laboratory.

17.2.2.2. The results of the calibration blank as well as all other blanks must be less than the reporting limit, not 3 times the instrument IDL.

17.2.2.3. Milli-Q or Nanopure water is substituted when reagent water is called for. This water is tested to be free of contaminants by conductivity (18 megOhm) and by the analysis of blanks.

17.2.2.4. Resolution criteria of the mass calibration is met if the resolution criteria for method 6020 is satisfied.

17.2.2.5.The concentration of most analytes in the LCS is 100 µg/L. This is made from a commercially available stock solution and has all analytes at the same level. Verification records for this solution are kept in the laboratory.

17.2.2.6. Results are reported up to the verified linear range, not up to only 90% of the linear range.

TABLE I: Recommended Elemental Interference Equations

Element	Isobaric Correction	Mathematical Equation
Al	none	(1.0000)(27M*)
Sb	none	(1.0000)(121M)
As	ArCl, Se	(1.0000)(75M) - (3.1278)(77M) + (1.0177)(78M)
Ba	none	(1.0000)(135M)
Be	none	(1.0000)(9M)
Cd	MoO, Sn	(1.0000)(114M) - (0.0268)(118M) - (1.0000)(135M)
Ca	none	(1.0000)(44M)
Cr	none	(1.0000)(52M)
Co	none	(1.0000)(59M)
Cu	none	(1.0000)(65M)
Fe	none	(1.0000)(57M)
Pb	none	(1.0000)(208M) + (1.0000)(207M) + (1.0000)(206M)
Mg	none	(1.0000)(25M)
Mn	none	(1.0000)(55M)
Ni	none	(1.0000)(60M)
K	none	(1.0000)(39M)
Se	Ar2	(1.0000)(78M) - (1.1869)(76M)
Ag	none	(1.0000)(107M)
Na	none	(1.0000)(23M)
Tl	none	(1.0000)(205M)
V	ClO, Cr	(1.0000)(51M) - (3.1081)(53M) + (0.3524)(52M)
Zn	none	(1.0000)(66M)
6Li	Li (natural)	(1.0000)(6M) - (0.0813)(7M)
Sc	none	(1.0000)(45M)
Y	none	(1.0000)(89M)
Rh	none	(1.0000)(103M)
In	Sn	(1.0000)(115M) - (0.0149)(118M)
Tb	none	(1.0000)(159M)
Ho	none	(1.0000)(165M)
Bi	none	(1.0000)(209M)

* M = Total ion count rate at the specified mass

TABLE II: Isobaric Molecular-Ion Interferences Which Could Affect the Analytes

Analyte	Interferences						
	Oxygen	Hydroxyl	Nitrogen	Chlorine	Sulfur	Carbon	Other
^{121}Sb	PdO		AgN			AgC	
^{123}Sb	AgO		AgN	SrCl	ZrS	CdC	
^{75}As	CoO	NiOH	NiN	ArCl	CaS	CuC	
^{138}Ba	SnO	SbOH					
^{137}Ba	SbO	SnOH		MoCl			
^{136}Ba	SnO	SnOH				SnC	
^{135}Ba	SnO	SnOH		MoCl			
^{134}Ba	SnO	SnOH	SnN	MoCl		SnC	
^{132}Ba	SnO, CdO	InOH	SnN	MoCl	MoS	SnC	
^{130}Ba	CdO	CdOH	SnN, CdN	MoCl	MoS	SnC	
^{9}Be							
^{114}Cd	MoO	MoOH	MoN	SeCl	SeS		
^{112}Cd	MoO, ZrO	MoOH	MoN	AsCl, SeCl	SeS	MoC	
^{111}Cd	MoO	MoOH	MoN	GeCl			
^{110}Cd	MoO, ZrO		MoN, ZrN	GeCl, AsCl	SeS	MoC	
^{113}Cd	MoO	MoOH		SeCl, AsCl			
^{116}Cd	MoO						
^{106}Cd	ZrO		MoN, ZrN		GeS	MoC, ZrC	
^{108}Cd	MoO, ZrO	ZrOH	MoN, ZrN	GeCl	SeS, GeS	MoC, ZrC	
^{52}Cr	ArO	ClOH				ArC	
^{53}Cr	ClO	ArOH	KN	NCl, OCl		KC	
^{50}Cr	SO		ArN		SO	ArC	Mo^{++}
^{54}Cr		ClOH	ArN, CaN			CaC	
^{59}Cr	CaO	CaOH	ScN	MgCl	AlS	TiC	Sn^{++}
^{63}Cu	TiO, PO_2	TiOH	TiN	SiCl, MgCl	PS	VC	ArNa
^{65}Cu	TiO	TiOH	VN	SiCl	SS,SO_2H	CrC	
^{208}Pb							
^{206}Pb							
^{207}Pb							
^{204}Pb							
^{55}Mn	KO	ArOH	KN		NaS	CaC	Cd^{++}

TABLE II: (cont.) Isobaric Molecular-Ion Interferences Which Could Affect the Analytes

Analyte	Interferences						
	Oxygen	Hydroxyl	Nitrogen	Chlorine	Sulfur	Carbon	Other
^{200}Hg	WO	WOH	WN				
^{199}Hg	WO	WOH					
^{201}Hg		WOH					
^{198}Hg	WO	TaOH	WN			WC	
^{204}Hg							
^{196}Hg			WN				
^{58}Ni	CaO	KOH	CaN	NaCl	MgS	TiC	Cd^{++}, Sn^{++}
^{60}Ni	CaO	CaOH	TiN	MgCl, NaCl	SiS	TiC	Sn^{++}
^{62}Ni	TiO	ScOH	TiN	AlCl, MgCl	SiS	TiC, CrC	Sn^{++}
^{61}Ni	SeO	CaOH	TiN	MgCl	SiS	TiC	
^{64}Ni	TiO	TiOH	TiN, CrN	SiCl, AlCl	SS	CrC	
^{80}Se	ZnO	CuOH	ZnN	ScCl, CaCl	TiS	ZnC	
^{78}Se	NiO	NiOH	ZnN	CaCl, KCl	TiS	ZnC	
^{82}Se	ZnO	CuOH	ZnN	TiCl, ScCl	TiS, CrS		
^{76}Se	NiO	CoOH	NiN	KCl	CaS	ZnC	
^{77}Se	NiO	CuN	CuN	CaCl, ArCl	ScS	CuC	
^{74}Se	NiO	NiN	NiN	ClCl, KCl	CaS	NiC	
^{107}Ag	ZrO	ZrOH		GeCl	AsS	MoC	
^{109}Ag		MoOH	MoN	GeCl	SeS	MoC	
^{205}Tl							
^{203}Tl		WOH					
^{51}V	ClO	SOH	ClN	ClO, ClN	FS	KC	
^{50}V	SO		ArN			ArC	Mo
^{64}Zn	TiO	TiOH	TiN, CrN	SiCl, AlCl	SS	CrC	
^{66}Zn	TiO	TiOH	CrN	PCl, SiCl	SS	FeC	
^{68}Zn	CrO	VOH	FeN	PCl	ArS	FeC	Ba^{++}
^{67}Zn	VO	TiOH, Cr	CrN	SCl	ClS	MnC	Ba^{++}
^{70}Zn	FeO	CrOH	GeN	ClCl	ArS	NiC	

Note: The information provided in this table does not indicate that all of the described interferences need to be tested. However, the table can be consulted for informational purposes if unusual samples are encountered.

Table III: Changes in Isobaric Molecular-Ion Interferences with Changing Plasma Conditions**

	Molecular Interference	Nebulizer		
		High	Average	Low
Oxides:	ScO/Sc	0.00326	0.00055	0.00116
	YO/Y	0.00568	0.00395	0.00353
	TbO/Tb	0.0156	0.00648	0.00614
	ClO, Cl	0.00725	0.00227	0.00233
Hydroxides:	ScOH/Sc	0.00040	0.00011	0.00000
	YOH/Y	0.00078	0.00044	0.00048
	TbOH/Tb	0.00034	0.00008	0.00011
	ClOH/Cl	0.00048	0.00031	0.00029
Chlorine:	ClO/Cl	0.00725	0.00227	0.00233
	ClOH/Cl	0.00048	0.00031	0.00029
	ArCl/Cl	0.00605	0.00091	0.00477

** Information for this table is being determined by the EPA.

Table IV: Recommended Internal Standards

Method 6020	Method 200.8
Li	Sc
Sc	Y
Y	In
Rh	Tb
In	Bi
Tb	
Ho	
Bi	
Ge	

Table V: Interference Check Sample Components and Concentrations

(ICSAB minors are suggested spike levels)

Interference Component	Solution A Concentration (mg/L)	Solution AB Concentration (mg/L)
Al	50	50
Ca	50	50
Fe	50	50
Mg	50	50
Na	50	50
P	50	50
K	50	50
S	50	50
C	100	100
Cl	500	500
Mo	1.0	1.0
Ti	1.0	1.0
As	0.0	0.1
Cd	0.0	0.1
Cr	0.0	0.1
Co	0.0	0.1
Cu	0.0	0.1
Mn	0.0	0.1
Ni	0.0	0.1
Se	0.0	0.1
Ag	0.0	0.1
V	0.0	0.1
Zn	0.0	0.1

Table VI: Sample Preservation and Holding Times

Measurement Parameter	Container (1)	Preservative (2)	Maximum Holding Time (3)
Waters:			
Metals (4)	P,G	HNO_3 to pH < 2	6 months
Soils/Sediments/Wastes:			
The preservation required for soil/sediment/waste samples is maintenance at 4°C (± 2°C) until digestion.			

Footnotes: (1) Polyethylene (P) or glass (G).

(2) Sample preservation is performed by the sampler immediately upon sample collection.

(3) Samples must be analyzed as soon as possible after collection. The times listed are the maximum times that sample may be held before analysis and still considered valid. Holding times are calculated from the date when the sample was collected.

(4) Samples are filtered immediately on-site by the sampler before adding preservative for dissolved elements.

Table VII: Suggested Mass Choices

Boldface masses indicate the masses which must have the most impact on data quality and the elemental equations used to collect the data. Suggested masses for method 200.8 are in "quotes".

Mass	Element of Interest
"**27**"	Aluminum
121, "**123**"	Antimony
"75"	Arsenic
138, "137", 136, **135**, 134, 132, 130	Barium
"**9**"	Beryllium
114, 112, "111", 110, 113, 116, 106	Cadmium
42, 43, **44**, 46, 48	Calcium
"**52**", **53**, **50**, 54	Chromium
"**59**"	Cobalt
"**63**", **65**	Copper
56, **54**, **57**, 58	Iron
"**208**", "**207**", "**206**", 204	Lead
24, **25**, **26**	Magnesium
"**55**"	Manganese
58, "**60**", 62, **61**, 64	Nickel
39	Potassium
80, **78**, "**82**", **76**, **77**, 74	Selenium
"**107**", **109**	Silver
23	Sodium
"**205**", 203	Thallium
"**51**", **50**	Vanadium
64, "**66**", **68**, **67**, 70	Zinc
72	Germanium
139	Lanthanum
118	Tin
35, 37	Chlorine
"98", 96, 92, **97**, 94	Molybdenum

Note: It is strongly recommended that elements other than those of interest be monitored to indicate other potential molecular interferences which could affect the data quality.

Table VIII: Tuning Solution

A tuning solution containing elements representing all of the mass regions of interest must be analyzed. Below are two groups of suggested solutions which cover a typical mass calibration range.

Method 6020

Element	Concentration (µg/L)
Solution A	
Mg	10.
Rh	10.
Pb	10.
Solution B	
Li	10.
Co	10.
In	10.
Tl	10.

Method 200.8

Element	Concentration (µg/L)
Be	10.
Mg	10.
Co	10.
In	10.
Pb	10.

Table IX: Suggested Tuning and Response Factor Criteria

Minimum Response from Tuning Solution

With a Peristalic Pump Speed of 12 RPM:

Be	>1,000
Mg	>10,000
Rh	>100,000
Pb	>50,000
Li	>2,000
Co	>20,000
In	>1,000
Tl	>1,000

Suggested Mass Calibration:

Be	9.0122
Mg	23.98
Rh	102.91
Pb	207.98
Li	7.016
Co	58.9332
In	114.904
Tl	204.9744

Table X: Summary of Quality Control Requirements

QC Parameter	Frequency*	Acceptance Criteria	Corrective Action
ICV/QCS	Beginning of every analytical run.	90 - 110% recovery.	Terminate analysis; correct the problem; recalibrate.
ICB/CB	Immediately after each ICV	The result must be < RL.	Terminate analysis; correct the problem; recalibrate.
CCV	Beginning and end of run and every 10 samples.	**6020-** 90 - 110% recovery **200.8-** 85-115% recovery	If unacceptable, correct the problem recalibrate the instrument, reverify calibration and rerun all samples associated with unacceptable CCV's.
CCB	Immediately following each CCV.	The result must be < RL	If unacceptable, correct the problem recalibrate the instrument, reverify calibration and rerun all samples associated with unacceptable CCB's.
ICSA (6020 Only)	Beginning and every 12 hours.	Monitor for possible interferences.	See Section 9.12
ICSAB (6020 Only)	Immediately following each ICSA.	Monitor for possible interferences.	See Section 9.12

Table X (cont'd): Summary of Quality Control Requirements

QC Parameter	Frequency*	Acceptance Criteria	Corrective Action
Method Blank/Laboratory Reagent Blank	One per lot of 20 field samples or fewer.	The result must be < RL. Sample results greater than 20x the blank concentration or samples for which the contaminant is < RL, do not require redigestion or reanalysis.	Redigest and reanalyze samples. See Section 9.3 for additional requirements.
Laboratory Control Sample/Laboratory Fortified Blank	One per lot of 20 field samples or fewer.	80-120%, or in-house limits (6020), 85-115% (200.8)	Redigest and reanalyze samples. See Section 9.4.
Serial Dilution (6020 Only)	One per lot of 20 field samples or fewer.	90 – 110% recovery	See section 9.14 for additional requirements.
Post-Digestion Spike (6020 Only)	See section 9.15	75-125% recovery	See section 9.15.
Matrix Spike/Matrix Spike Duplicate	One per lot of 20 field samples or fewer.	Must be within laboratory control limits	See section 9.5 for additional requirements.

Table XI: ICP/MS Calibration and Calibration Verification Checklist

Suggested Levels in µg/L

Element	Calibration			ICV	CCV
	1	2	3		
Aluminum	50	5000	10000	25	50
Antimony	2	50	100	25	50
Arsenic	2	50	100	25	50
Barium	1	50	100	25	50
Beryllium	1	50	100	25	50
Cadmium	0.5	50	100	25	50
Chromium	2	50	100	25	50
Cobalt	1	50	100	25	50
Copper	2	50	100	25	50
Iron	20	5000	10000	25	50
Lead	1	50	100	25	50
Manganese	1	50	100	25	50
Nickel	2	50	100	25	50
Selenium	2	50	100	25	50
Silver	0.5	50	100	25	50
Thallium	1	50	100	25	50
Vanadium	5	50	100	25	50
Zinc	10	50	100	25	50

This procedure has been developed for additional elements. Additional elements may be included in the calibration solution at the appropriate levels. Levels may be adjusted to meet specific regulatory or client programs.

Table XII: Suggested ICP/MS Reporting Limits

Water 6020 and 200.8 Solid 6020 (only)

Compound	RL	Units	RL	Units
Aluminum	50	ug/L	--	--
Antimony	2	ug/L	200	ug/kg
Arsenic	5	ug/L	500	ug/kg
Barium	5	ug/L	500	ug/kg
Beryllium	1	ug/L	100	ug/kg
Cadmium	1	ug/L	100	ug/kg
Chromium	2	ug/L	200	ug/kg
Cobalt	1	ug/L	100	ug/kg
Copper	5	ug/L	500	ug/kg
Iron	20	ug/L	--	--
Lead	1	ug/L	100	ug/kg
Manganese	5	ug/L	500	ug/kg
Molybdenum	2	ug/L	200	ug/kg
Nickel	2	ug/L	100	ug/kg
Selenium	5	ug/L	500	ug/kg
Silver	1	ug/L	100	ug/kg
Thallium	1	ug/L	100	ug/kg
Tin	10	ug/L	1000	ug/kg
Vanadium	5	ug/L	500	ug/kg
Zinc	10	ug/L	1000	ug/kg

APPENDIX A – OPERATION INSTRUCTIONS – P.E. 6100 ICP/MS INSTRUCTIONS

A. Light the plasma and start the peristaltic pump.

1. Allow the instrument to warm up approximately 30 minutes.

B. Daily Performance

1. Open Daily2_asx workplace.
2. Open the sampling tab in the method screen.
3. Select and initialize the autosampler. Click O.K.
4. Click on probe. Click go to rinse. Send probe to tube #8.
5. Allow solution to reach plasma and then click on analyze sample.
6. When analysis is complete, send probe back to rinse.

C. Analysis Setup

1. Open Analysis workspace.
2. Under the method window, open the report tab and type in your report filename. Save the method.
3. Highlight the dataset window. Go to file and select new. Type in the dataset name (normally the same as the filename).
4. Highlight autosampler window. Type in your autosampler locations and samples. Right click under measurement action and select what needs to be analyzed. Right click under method description and select method. Verify that all times and rpms on table are correct. Go to file and click save as. Type autosampler table name (normally the same as the filename).

D. Analyze samples

1. Highlight samples to be analyzed.
2. Left click on analyze batch.

APPENDIX B – OPTIMIZATIONS – P.E. 6100

X-Y Adjustment

Adjusts torch to achieve best intensities. This should be done whenever anything is done to the torch or the cones.

1. Open X-Y_asx.wrk.
2. Under the method window, go to the sampling tab and send the probe to tube #8.
3. Allow solution to reach plasma and hit analyze sample.
4. Adjust x and y while watching the signal on the realtime window. Adjust only until signal is at its highest.

NEB Lens

This also is done to get best intensities. It effects the shape and the depth of the plasma. This should be done if your oxides or doubly charged are >3%.

1. Open neb lens power oxides.wrk
2. Under the method window, go to the sampling tab and send the probe to tube #8.
3. Click on the Autooptimize tab. Select nebulizer gas flow.
4. Click get analyte list.
5. Make sure solution has reached the plasma and click optimize.
6. When done, save the optimization file.

Autolens

Each element done represents a section of the mass spectrum. Be is on the low end, CO is in the middle and Pb is on the higher end. If there is a problem with any particular section of the spectrum, it may be an indication that this needs done. This should probably be performed on a weekly basis.

1. Open Autolens_asx.wrk.
2. Under the method window, go to the sampling tab and send the probe to tube #8.
3. Click on the autolens tab.
4. Click on clear calibration.
5. Click on get analyte list.
6. Make sure the solution has reached the plasma and click on calibrate.

7. Save the optimization file.

8. In the interactive window, the optimization curve can be printed.

Dual Detector Calibration

This extends the dynamic range of the detector. This should be done on a weekly basis. All analytes of interest must be included in the solution.

1. Open dual detector2.wrk

2. Under the method window, go to the sampling tab and send the probe to tube #8.

3. Click on dual detector cal tab.

4. Click on clear calibration.

5. Click on get analyte list.

6. Make sure the solution has reached the plasma and click on calibrate.

7. When complete, check to make sure that all r values are at least .999.

8. Save the optimization file.

9. In the interactive window, the plots can be displayed.

Tuning

This adjusts the electronics to assure the accuracy of the mass spec. The resolution adjustment assures that the resolution of each mass of interest is within range. This should be done daily.

1. Open tuning_asx.wrk.

2. Under the method window, go to the sampling tab and send the probe to tube #8.

3. Allow sample to reach the plasma and click on tune mass spec.

4. Make sure measured mass and peak width is within range. If its not, resolution will need adjusted. Adding 30 units will decrease the amu by about 0.1. Subtracting 30 units will increase the amu about 0.1.

General Notes

1. All optimizations can be done with the tuning solution, except the dual detector cal needs the cross cal standard with all the elements of interest.

2. All optimizations can be run at 12 rpm, except the dual detector calibration should be at 24 rpm.

APPENDIX C – ICPMS MAINTENANCE SCHEDULE

Daily

Change sample and internal standard pump tubing and pump windings

Check argon gas supply level

Check rinse solution and fill if needed

Check waste containers and empty if needed

Check sample capillary tubing is clean and in good condition

Check sample flow for cross flow nebulizer

Check pressure for vacuum systems

Check daily performance

As Needed

Clean Sampler and skimmer cones

Clean plasma torch assembly to remove accumulated deposits

Clean nebulizer

Replace sample and internal standard capillary tubing and autosampler sipper probe

Replace drain tubing

Perform necessary optimizations

Clean autolens

Monthly

Inspect air filters; clean or replace as needed

Bi-Yearly

Change oil in vacuum pumps

Check water in coolflow

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Implementation Date: 7-18-07

TESTAMERICA NORTH CANTON STANDARD OPERATING PROCEDURE

TITLE: PREPARATION AND ANALYSIS OF MERCURY IN AQUEOUS SAMPLES BY COLD VAPOR ATOMIC ABSORPTION, SW846 7470A AND MCAWW 245.1

(SUPERSEDES: REVISION 2.5 DATED 01/08/04)

Approved by:	Roger R. Todd	7/17/07
	Technical Specialist	Date
Approved by:	Dorothy J. Reuss	7/17/07
	Quality Assurance Manager	Date
Approved by:	William J. Gerber	7-17-07
	Environmental, Health and Safety Coordinator	Date
Approved by:	[signature]	7/18/07
	Laboratory Director	Date

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1. SCOPE AND APPLICATION

1.1. This procedure describes the preparation and analysis of mercury (Hg, CAS # 7439-97-6) by Cold Vapor Atomic Absorption Spectroscopy (CVAA) using SW-846 Method 7470A and MCAWW Method 245.1.

1.2. The associated LIMs method codes are BL (Method 245.1) and O8 (Method 7470A).

1.3. CVAA analysis provides for the determination of total mercury (organic and inorganic). The combination of the oxidants, potassium permanganate and potassium persulfate, has been found to give 100% recovery with both types of compounds. Detection limits, sensitivity and optimum concentration ranges for mercury analysis will vary with the matrices, instrumentation and volume of sample used.

1.4. Method 7470A is applicable to the preparation and analysis of mercury in ground water, aqueous samples, TCLP, and other leachates/extracts. Certain solid and sludge type wastes may also be analyzed, however Method 7471A (see CORP-MT-0007NC) is usually the method of choice. All matrices require sample preparation prior to analysis.

1.5. Method 245.1 is applicable to the determination of mercury in drinking, surface and saline waters and domestic and industrial wastes. All matrices require sample preparation prior to analysis.

1.6. The TestAmerica North Canton reporting limit for mercury in aqueous matrices is 0.0002 mg/L except for TCLP or SPLP leachates for which the reporting limit is 0.002 mg/L.

1.7. This document accurately reflects current laboratory standard operating procedures (SOP) as of the date above. All facility SOPs are maintained and updated as necessary.

2. SUMMARY OF METHOD

2.1. This SOP describes a technique for the determination of mercury in solution. The procedure is a physical method based on the absorption of radiation at 253.7 nm by mercury vapor. A representative portion of the sample is digested in sulfuric and nitric acids. Organic mercury compounds are oxidized with potassium permanganate and potassium persulfate and the mercury reduced to its elemental state with stannous chloride 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 is measured as a function of mercury concentration. Concentration of

the analyte in the sample is determined by comparison of the sample absorbance to the calibration curve (absorbance vs. concentration).

3. DEFINITIONS

3.1. Dissolved Metals: Those elements which pass through a 0.45 um membrane. (Sample is acidified after filtration).

3.2. Suspended Metals: Those elements which are retained by a 0.45 um membrane.

3.3. Total Metals: The concentration determined on an unfiltered sample following digestion.

3.4. Refer to the glossary in the Laboratory Quality Manual (LQM), latest version.

4. INTERFERENCES

4.1. Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus that lead to discrete artifacts. All of these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. Specific selection of reagents may be required to avoid introduction of contaminants.

4.2. Potassium permanganate, which is used to breakdown organic mercury compounds also eliminates possible interferences from sulfide. Concentrations as high as 20 mg/L of sulfide as sodium sulfide do not interfere with the recovery of inorganic mercury from reagent water.

4.3. Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/L had no effect on the recovery of mercury from spiked samples.

4.4. Chlorides can cause a positive interference. Sea waters, 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 at 253.7 nm. Care must be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. This is accomplished by adding excess hydroxylamine reagent (25 mL) and purging the sample headspace before stannous chloride is added. Both inorganic and organic mercury spikes have been quantitatively recovered from seawater using this technique.

Note: Sufficient addition of permanganate is apparent when the purple color persists

at least 15 minutes. Some samples may require dilution prior to digestion due to extremely high concentrations of chloride.

4.5. Interference from certain volatile organic materials that absorb at this wavelength may also occur. While the possibility of absorption from certain organic substances present in the sample does exist, this problem is not routinely encountered. This is mentioned only to caution the analyst of the possibility.

4.6. Samples containing high concentrations of oxidizing organic materials, as evidenced by high COD levels, may not be completely oxidized by this procedure. When this occurs the recovery of mercury will be low.

4.7. The most common interference is laboratory contamination, which may arise from impure reagents, dirty glassware, improper sample transfers, dirty work areas, etc. Be aware of potential sources of contamination and take appropriate measures to minimize or avoid them.

5. SAFETY

5.1. Employees must abide by the policies and procedures in the Corporate Safety Manual, and this document.

5.2. The following is a list of the materials used in this method, which have a serious or significant hazard rating. NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table. A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Sulfuric Acid	Corrosive Oxidizer Dehydrator Poison	1 Mg/M3-TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.
Nitric Acid	Corrosive	2 ppm-TWA	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause

	Oxidizer Poison	4 ppm-STEL	breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Hydrochloric Acid	Corrosive Poison	5 PPM-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Potassium Permanganate	Oxidizer	5 Mg/M3 for Mn Compounds	Causes irritation to the respiratory tract. Symptoms may include coughing, shortness of breath. Dry crystals and concentrated solutions are caustic causing redness, pain, severe burns, brown stains in the contact area and possible hardening of outer skin layer. Diluted solutions are only mildly irritating to the skin. Eye contact with crystals (dusts) and concentrated solutions causes severe irritation, redness, and blurred vision and can cause severe damage, possibly permanent.
Mercury (1,000 ppm in Reagent)	Oxidizer Corrosive Poison	0.1 Mg/M3 Ceiling (Mercury Compounds)	Extremely toxic. Causes irritation to the respiratory tract. Causes irritation. Symptoms include redness and pain. May cause burns. May cause sensitization. Can be absorbed through the skin with symptoms to parallel ingestion. May affect the central nervous system. Causes irritation and burns to eyes. Symptoms include redness, pain, and blurred vision; may cause serious and permanent eye damage.
Potassium Persulfate	Oxidizer	None	Causes irritation to the respiratory tract. Symptoms may include coughing, shortness of breath. Causes irritation to skin and eyes. Symptoms include redness, itching, and pain. May cause dermatitis, burns, and moderate skin necrosis.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

5.3. Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Cut resistant gloves must be worn doing any other task that presents a strong possibility of getting cut. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.4. Exposure to chemicals must be maintained **as low as reasonably achievable.** Therefore, unless they are known to be non-hazardous, all samples should be opened,

transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made. All samples with stickers that read "Caution/Use Hood!" **must** be opened in the hood.

5.5. All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica North Canton associate. The situation must be reported **immediately** to a Laboratory Supervisor and the EH&S Coordinator.

5.6. Do not look directly into the beam of the Hg lamp. The UV light that these lamps radiate is harmful to the eyes.

5.7. Cylinders of compressed gas must be handled with caution, in accordance with local regulations. It is recommended that, wherever possible, cylinders are located outside the laboratory and the gas led to the instrument through approved lines.

5.8. The CVAA apparatus must be properly vented to remove potentially harmful fumes generated during sample analysis.

6. EQUIPMENT AND SUPPLIES

6.1. Temperature controlled water bath capable of maintaining a temperature of 90-95 °C.

6.2. Atomic Absorption Spectrophotometer equipped with:

6.2.1 Absorption Cell with quartz end windows perpendicular to the longitudinal axis. Dimensions of the cell must result in sufficient sensitivity to meet the SOP defined reporting limit. The quartz windows must be maintained to provide accurate measurements. Any scratches or fingerprints can alter the absorption of UV radiation.

6.2.2 Mercury specific hollow cathode lamp (HCL) or electrodeless discharge lamp (EDL).

6.2.3 Peristaltic pump, which can deliver 1 L/min, air.

6.2.4 Flowmeter capable of measuring an airflow of 1 L/min.

6.2.5 Recorder or Printer.

6.2.6 Aeration Tubing: A straight glass frit having a course porosity and Tygon tubing is used for the transfer of mercury vapor from the sample bottle to the

absorption cell and return. The tubing must be inert and mercury-free.

6.2.7 Drying device to prevent condensation in cell. The lamp is positioned to shine on the absorption cell maintaining the air temperature in the cell about 10 °C above room temperature. Other drying devices that achieve the same purpose are also acceptable (i.e., Gortex filter).

6.3. 8oz. HDPE Plastic bottles.

6.4. Nitrogen or argon gas supply, welding grade, or equivalent.

6.5. Calibrated automatic pipettes or Class A glass volumetric pipettes.

6.6. Class A volumetric flasks.

6.7. Thermometer (capable of accurate readings at 95 °C).

6.8. Disposable cups or tubes.

7. REAGENTS AND STANDARDS

7.1. Reagent water must be produced by a Millipore DI system or equivalent. Reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks.

7.2. Stock (10 ppm) mercury standards (in 10% HNO_3) are purchased as custom solutions. All standards must be stored in FEP fluorocarbon or previously unused polyethylene or polypropylene bottles. Stock standard solutions must be replaced prior to the expiration date provided by the manufacturer. If no expiration date is provided, the stock solutions may be used for up to one year and must be replaced sooner if verification from an independent source indicates a problem.

7.3. Working mercury standard (0.1 ppm): Take 1 mL of the stock mercury standard (7.2) and dilute to 100 mL with reagent water. The working mercury standard must be made daily and must be prepared in a matrix of 0.15% HNO_3. This acid (150 uL of concentrated HNO_3) must be added to the flask/bottle before the addition of the stock standard aliquot.

7.4. The calibration standards listed in Table I must be prepared fresh daily from the working standard (7.3) by transferring 0, 0.2, 0.5, 1.0, 5.0 and 10.0 mL aliquots of the working mercury standard into 100 mL flasks and diluting to volume with reagent water.

7.5. The initial calibration verification standard must be made from a different stock solution than that of the calibration standards.

7.6. Refer to Table I (Appendix A) for details regarding the working standard concentrations for calibration, calibration verification and spiking solutions. All standards must be processed through the entire analytical procedure including sample preparation.

7.7. Nitric acid (HNO_3), concentrated, traces metal grade or better.

7.8. Sulfuric acid (H_2SO_4), concentrated, traces metal grade or better.

7.9. Stannous chloride solution: Add 50 g of stannous chloride and 25 mL of concentrated hydrochloric acid to a 500mL volumetric flask and bring to volume with deionized water.

7.10. Sodium chloride-hydroxylamine hydrochloride solution: Add 240 g of sodium chloride and 240 g of hydroxylamine hydrochloride to every 2000 mL of reagent water.

7.11. Potassium permanganate, 5% solution (w/v): Dissolve 100 g of potassium permanganate for every 2000 mL of reagent water.

7.12. Potassium persulfate, 5% solution (w/v): Dissolve 100 g of potassium persulfate for every 2000 mL of reagent water.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Sample holding time for mercury is 28 days from time of collection to the time of analysis.

8.2. Aqueous samples are preserved with nitric acid to a pH of <2 and may be stored in either plastic or glass. Refrigeration is not required. Preservation must be verified prior to analysis.

9. QUALITY CONTROL

9.1. Table II (Appendix A) provides a summary of quality control requirements including type, frequency, acceptance criteria and corrective action.

9.2. Initial Demonstration of Capability

9.2.1 Prior to the analysis of any analyte using 7470A or the 245.1, the following requirements must be met.

9.2.1.1 Method Detection Limit (MDL) - An MDL must be determined for each analyte/matrix prior to the analysis of any samples. The MDL is determined using seven replicates of reagent water, spiked with all the analytes of interest, that have been carried through the entire analytical procedure. MDLs must be predetermined on an annual basis in accordance with 40 CFR Part 136 Appendix B requirements. The spike level must be between the calculated MDL and 10X the MDL to be valid. The result of the MDL determination must be below the TestAmerica North Canton reporting limit.

9.2.2 Initial Demonstration Study - This requires the analysis of four QC check samples. The QC check sample is a well-characterized laboratory generated sample used to monitor method performance. The results of the initial demonstration study must be acceptable before analysis of samples may begin.

9.2.2.1 Four aliquots of the check sample (LCS) are prepared and analyzed using the procedures detailed in this SOP and the determinative SOPs.

9.3. Preparation Batch - A batch is a group of no greater than 20 samples excuding QC Samples (LCS, Method Blank, MS, MSD) which are processed similarly, with respect to the procedure. All sample setups must be initiated within a 24 hour period from the initial preparation or extraction and without interruption of the process. All samples within the batch must be treated with the same lots of reagents and the same processes. In some cases, at client request, it may be appropriate to process a matrix spike and sample duplicate in place of the MS/MSD. If clients specify specific samples for MS/MSD, the batch may contain multiple MS/MSD pairs.

9.4. Method Blank (MB) - One method blank must be processed with each preparation batch. The method blank consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. The method blank should not contain any analyte of interest at or above the reporting limit or at or above 5% of the measured concentration of that analyte in associated samples, whichever is higher (sample result must be a minimum of 20 times higher than the blank contamination level).

- Re-preparation and re-analysis of all samples associated with an unacceptable method blank is required when reportable concentrations are determined in the samples (see exception noted above).

- If there is no analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported. **Such action must be addressed in the project narrative.**

- If the above criteria are not met and reanalysis is not possible, then the sample data must be qualified. **This anomaly must be addressed in the project narrative.**

9.5. Laboratory Control Sample (LCS) - One aqueous LCS must be processed with each preparation batch. The LCS is used to monitor the accuracy of the analytical process. On going monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines. The LCS must be carried through the entire analytical procedure. If the LCS is outside established control limits the system is out of control and corrective action must occur.

- In the instance where the LCS recovery is greater than the upper control limit and the sample results are less than RL, the data may be reported. Such action must be addressed in the project narrative.

- In the event that an MS/MSD analysis is not possible, a Laboratory Control Sample Duplicate (LCSD) must be analyzed. The RPD of the LCS and LCSD must be compared to the matrix spike RPD limits.

- Corrective action will be repreparation and reanalysis of the batch unless the client agrees that other corrective action is acceptable.

9.6. Matrix Spike/Matrix Spike Duplicate (MS/MSD) - One MS/MSD pair must be processed for each preparation batch. A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added. A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked identically as the MS) prepared and analyzed along with the sample and matrix spike. Some client specific data quality objectives (DQO's) may require the use of sample duplicates in place of or in addition to MS/MSD's. The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Due to the potential variability of the matrix of each sample, these results may have immediate bearing only on the specific sample spiked. Samples identified as field blanks cannot be used for MS/MSD analysis. Spiking levels are provided in Table I (Appendix A).

- If analyte recovery or RPD falls outside the acceptance range, the recovery of

that analyte must be in control for the LCS. Until in-house control limits are established, a control limit of 75 - 125 % recovery for Method 7470A, 70 – 130% for Method 245.1, and 20% RPD must be applied to the MS/MSD. If the LCS recovery is within limits, then the laboratory operation is in control and the results may be accepted. If the recovery of the LCS is outside limits, corrective action must be taken. Corrective action will include repreparation and reanalysis of the batch. MS/MSD results, which fall outside the control limits, must be addressed in the narrative.

- If the native analyte concentration in the MS/MSD exceeds 4x the spike level for that analyte, the recovery data is reported as "amount" MSB. The Exception Code is changed to NC. The following two footnotes will appear on the report page—"NC: The recovery and/or RPD were not calculated.", and "MSB: The recovery and RPD were not calculated, because the sample amount was greater than four times the spike amount."

- If an MS/MSD is not possible due to limited sample volume, then a laboratory control sample duplicate (LCSD) should be analyzed. The RPD of the LCS and LCSD must be compared to the matrix spike RPD limits.

9.7. Initial Calibration Verification (ICV/ICB) - Calibration accuracy is verified by analyzing a second source standard (ICV). For Method 7470A, the ICV result must fall within 10% of the true value for that solution. An ICB is analyzed immediately following the ICV to monitor low level accuracy and system cleanliness. The ICB result must fall within +/- the reporting limit (RL) from zero. If either the ICV or ICB fail to meet criteria, the analysis should be terminated, the problem corrected and the instrument re-calibrated. (See Section 11.2.8 for required run sequence). If the cause of the ICV or ICB failure was not directly instrument related the corrective action will include re-preparation of the ICV, ICB, CRA, CCV, and CCB with the calibration curve.

9.8. Continuing Calibration Verification (CCV/CCB) - Calibration accuracy is monitored throughout the analytical run through the analysis of a known standard after every 10 samples. The CCV must be a mid-range standard at a concentration other than that of the ICV. For Method 245.1, the CCV must be 5% immediately following the calibration. All other CCVs must be 80 – 120%. A CCB is analyzed immediately following each CCV. (See Section 11.2.8 for required run sequence.) The CCB result must fall within +/- RL from zero. Each CCV and CCB analyzed must reflect the conditions of analysis of all associated samples. If the CCV/CCB is biased high and the sample results associated with the CCV/CCB are below the requested reporting limit then the results can be reported. Sample results may only be reported when bracketed by valid ICV/CCV and ICB/CCB pairs.

9.9. Detection Limit Standard (CRA)-To verify linearity at the reporting limit, a CRA standard is run at the beginning of each sample analysis run after the ICV/ICB. The CRA standard mercury concentration is 0.2 ug/L. Recovery must be ± 50% of the true value, or the standard is either rerun or the problem corrected and the instrument re-calibrated. The CRA is only required when requested. (See Section 11.2.8 for the required run sequence.)

9.10. Method of Standard Addition (MSA) -This technique involves adding known amounts of standard to one or more aliquots of the sample prior to preparation. This technique compensates for a sample interferent that may enhance or depress the analyte signal, thus producing a different slope from that of the calibration standards. It will not correct for additive interferences, which cause a baseline shift. Refer to Section 11.2.9 for additional information on when full 4 point MSA is required as well as Appendix B for specific MSA requirements.

10. CALIBRATION AND STANDARDIZATION

10.1. Calibration standards must be processed through the preparation procedure as described in Section 11.1.

10.2. Calibration must be performed daily (every 24 hours) and each time the instrument is set up. The instrument calibration date and time must be included in the raw data.

10.3. Set up the instrument with the operating parameters recommended by the manufacturer and listed in Appendix F. Allow the instrument to become thermally stable before beginning calibration (approximately 30 minutes of warm-up is required).

10.4. Calibrate the instrument according to instrument manufacturer's instructions, using a minimum of five standards and a blank. One standard must be at the TestAmerica North Canton reporting limit. Analyze standards in ascending order beginning with the blank. Refer to Section 7 and Table I for additional information on preparing calibration standards and calibration levels.

10.5. The calibration curve must have a correlation coefficient of ≥0.995 or the instrument shall be stopped and recalibrated prior to running samples. Sample results can not be reported from a curve with an unacceptable correlation coefficient. NOTE: If any digested standard does not meet criteria, all Ohio VAP samples associated with that curve will be re-digested.

10.6. Refer to Section 9.0 for calibration verification procedures, acceptance criteria and corrective actions.

11. PROCEDURE

11.1. Sample Preparation:

11.1.1 All calibration and calibration verification standards (ICV, ICB, CCV, CCB) are processed through the digestion procedure as well as the field samples. Transfer 0, 0.2, 0.5, 1.0, 5.0 and 10.0 mL aliquots of the working standard (7.3) into a series of 100 ml class A volumetrics, then dilute to volume . For the ICV, use a 2.5 ml aliquot of the working standard. The ICV working standard must be made from a source other than that used for the calibration standards.

11.1.2 Transfer 100 mL of well-mixed sample or standard to a clean sample digestion bottle.

Note: Reduced sample volumes can be used as long as a representative sample can be obtained and the reagent levels are adjusted to maintain the same sample to reagent ratio. All samples and standards must be processed similarly.

Note: Spiking is done before the addition of acids or reagents.

11.1.3 Add 5 mL of concentrated H_2SO_4 and 2.5 mL of concentrated HNO_3 mixing after each addition.

11.1.4 Add 15 mL of potassium permanganate solution. For samples high in organic materials or chlorides, additional permanganate may be added. Shake and add additional portions of permanganate solution until a purple color persists for at least 15 minutes. If after the addition of up to 25-mL additional permanganate the color does not persist, sample dilution prior to reanalysis may be required.

Note: When performing analyses using automated vs. manual techniques the sample dilution resultant from the addition of more than the original aliquot of permanganate solution must be compensated for by the addition of the same volume of permanganate to all other associated samples and standards in the run. In instances, where this is not feasible, the addition of excess reagent can be addressed through mathematical correction of the results to account for the resultant dilution effect.

11.1.5 Add 8 mL of potassium persulfate solution and heat for two hours in a water bath at 90 - 95 °C.

11.1.6 Cool samples.

11.2. Sample Analysis:

11.2.1 Refer to the Appendix F of this SOP for detailed setup and operation protocols.

11.2.2 When ready to begin analysis, add 6 mL of sodium chloride-hydroxylamine hydrochloride solution to the samples to reduce the excess permanganate (the permanganate has been reduced when no purple color remains).

11.2.3 Automated determination: Follow instructions provided by instrument manufacturer.

11.2.4 Perform a linear regression analysis of the calibration standards by plotting maximum response of the standards vs. concentration of mercury. Determine the mercury concentration in the samples from the linear regression fit of the calibration curve. Calibration using computer or calculation based regression curve fitting techniques on concentration/response data is acceptable.

11.2.5 All measurements must fall within the defined calibration range to be valid. Dilute and reanalyze all samples for analytes that exceed the highest calibration standard.

11.2.6 If the sample results are negative and the absolute value of the negative result is greater than the reporting limit, the sample must be diluted and reanalyzed.

11.2.7 The samples must be allowed to cool to room temperature prior to analysis or a decrease in the response signal can occur.

11.2.8 The following run sequence is consistent with 7470A and 245.1.

Instrument Calibration
ICV
ICB
CRA
CCV
CCB
10 samples
CCV
CCB

Repeat sequence of 10 samples between CCV/CCB pairs as required to complete run.
CCV
CCB

Refer to Quality Control Section 9.0 and Table II (Appendix A) for Quality Control criteria to apply to Methods 7470A and 245.1.

11.2.9 For TCLP samples, full four point MSA will be required if all of the following conditions are met:

1) recovery of the analyte in the matrix spike is not at least 50%,

2) the concentration of the analyte does not exceed the regulatory level, and,

3) the concentration of the analyte is within 20% of the regulatory level.

The reporting and matrix spike levels for TCLP analyses are detailed in Table I (Appendix A). Appendix B provides guidance on performing MSA analyses. For TCLP mercury determinations, MSA spikes must be added prior to sample preparation.

11.3. To facilitate the early identification of QC failures and samples requiring rerun it is strongly recommended that sample data are reviewed periodically throughout the run.

11.4. Guidelines are provided in the appendices on procedures to minimize contamination of samples and standards, preventive maintenance and troubleshooting.

11.5. Analytical Documentation

11.5.1 Record all analytical information in the analytical logbook/logsheet which may be in an electronic format, including the analytical data from standards, blanks, LCSs, MS/MSDs, and any corrective actions or modifications to the method.

11.5.2 All standards are logged into a department standard logbook. All standards are assigned an unique number for identification. Logbooks are reviewed by the supervisor or designee.

11.5.3 Documentation such as all associated instrument printouts (final runs, screens, reruns, QC samples, etc.) and daily calibration data corresponding to all final runs is available for each data file.

11.5.4 Sample results and associated QC are entered into the LIMs after final technical review.

11.6. One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and is approved by a Technical Specialist and QA Manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file.

11.7. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

12. DATA ANALYSIS AND CALCULATIONS

12.1. ICV percent recoveries are calculated according to the equation:

$$\%R = 100\left(\frac{Found(ICV)}{True(ICV)}\right)$$

12.2. CCV percent recoveries are calculated according to the equation:

$$\%R = 100\left(\frac{Found(CCV)}{True(CCV)}\right)$$

12.3. Matrix spike recoveries are calculated according to the following equation:

$$\%\,R\; = 100\left(\frac{SSR - SR}{SA}\right)$$

Where:

SSR = Spike Sample Result
SR = Sample Result
SA = Spike Added

12.4. The relative percent difference (RPD) of matrix spike/matrix spike duplicates or sample duplicates are calculated according to the following equations:

$$RPD = 100\left[\frac{|MSD - MS|}{\left(\frac{MSD + MS}{2}\right)}\right]$$

Where:
MS = determined spiked sample concentration
MSD = determined matrix spike duplicate concentration

$$RPD = 100\left[\frac{|DU1 - DU2|}{\left(\frac{DU1 + DU2}{2}\right)}\right]$$

Where:
DU1 = Sample result
DU2 = Sample duplicate result

12.5. The final concentration for an aqueous sample is calculated as follows:

$$mg/L = C \times D$$

Where:
C = Concentration (mg/L) from instrument readout
D = Instrument dilution factor

12.6. The LCS percent recovery is calculated according to the following equation:

$$\%R = 100\left(\frac{Found(LCS)}{True(LCS)}\right)$$

12.7. Appropriate factors must be applied to sample values if dilutions are performed.

12.8. Sample results should be reported with up to three significant figures in accordance with the TestAmerica North Canton significant figure policy.

13. METHOD PERFORMANCE

13.1. Each laboratory must have initial demonstration of performance data on file for each analyte of interest as described in Section 9.0.

13.2. Method performance is determined by the analysis of method blanks, laboratory control samples, matrix spike and matrix spike duplicate samples. The matrix spike recovery should fall within +/- 25 % and the matrix spike duplicates should compare within 20% RPD. The method blanks must meet the criteria in Section 9.3. The laboratory control sample should recover within 20% of the true value until in house limits are established.

13.3. Training Qualification:

13.3.1 The group/team leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience.

14. POLLUTION PREVENTION

14.1. This method allows for the proportional reduction of sample and reagent volumes to decrease waste generation.

15. WASTE MANAGEMENT

15.1. All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

15.2. Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices of TestAmerica. They must have training on the hazardous waste disposal practices upon initial assignment to these tasks, followed by an annual refresher training.

15.3. Waste Streams Produced by the Method

15.3.1 **Acid Waste- Aqueous waste generated by the analysis.** Samples are disposed of in the acid waste drum located in the metals lab. The contents of the drum are neutralized and released to the POTW.

16. REFERENCES

16.1. References

16.1.1 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods,

SW846, 3rd Edition, Final Update II, Revision I, September 1994, Method 7470A (Mercury).

16.1.2 "Methods for the Chemical Analysis of Water and Wastes", Rev. 3.0 (1994).

16.1.3 Corporate Quality Management Plan (QMP), current version.

16.1.4 TestAmerica Laboratory Quality Manual (LQM), current version.

16.2. Associated SOPs and Policies, latest version

16.2.1 QA Policy, QA-003.

16.2.2 Glassware Washing, NC-QA-0014.

16.2.3 Statistical Evaluation of Data and Development of Control Charts, NC-QA-0018.

16.2.4 Method Detection Limits and Instrument Detection Limits, NC-QA-0021.

16.2.5 Supplemental Practices for DoD Project Work, SOP, NC-QA-0016.

16.2.6 Preparation and Analysis of Mercury in Aqueous Samples by Cold Vapor Atomic Absorption, Method 245.1 and CORP-MT-0006NC, current version.

16.2.7 Standards and Reagents, Sop NC-QA-0017.

17. MISCELLANEOUS (TABLES, APPENDICES, ETC. . .)

17.1. Modifications/Interpretations from reference method.

17.1.1 Modifications from both 7470A and 245.1.

17.1.1.1 The 200 series methods and Chapter 1 of SW846 specify the use of reagent water with a purity equivalent to ASTM Type II water. This SOP specifies the use of a Millipore DI system or equivalent to produce reagent water. This SOP requires that reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks.

17.1.1.2 This SOP allows for the use of reduced sample volumes to decrease waste generation. Reagent levels are adjusted to maintain

the same ratios as stated in the source methods. According to a letter from Robert Booth of EPA EMSL-Cinn to David Payne of EPA Region V, "Reduction in sample size and appropriate corresponding reduction in sample volume is not considered a significant change in the methodology."

17.1.2 Modifications from Method 7470A

17.1.2.1 Chapter 1 of SW-846 states that the method blank should not contain any analyte of interest at or above the MDL. This SOP states that the method blank must not contain any analyte of interest at or above the reporting limit if the samples associated with the method blank are equal to or above the reporting limit.

17.1.3 Modifications from 245.1

17.1.3.1 Method 245.1 states that standards are not heated. TestAmerica North Canton prepares heated standards for this method.

APPENDIX A

TABLES

TABLE I . MERCURY REPORTING LIMITS, CALIBRATION STANDARD*, QC STANDARD AND SPIKING LEVELS (MG/L)

Standard Aqueous RL	0.0002
TCLP RL	0.002
Std 0	0
Std 1/CRA	0.0002
Std 2	0.0005
Std 3	0.001
Std 4	0.005
Std 5	0.010
ICV	0.0025
LCS/CCV	0.005
Aqueous MS	0.001
TCLP MS	0.005

TABLE II. Summary Of Quality Control Requirements

QC PARAMETER	FREQUENCY	ACCEPTANCE CRITERIA	CORRECTIVE ACTION
ICV	Beginning of every analytical run.	90-110 % recovery.	Terminate analysis; Correct the problem; Recalibrate or reprep with calibration curve. (See Section 9.6).
ICB	Beginning of every analytical run, immediately following the ICV.	The result must be within +/- RL from zero if the samples are at or above the reporting limit	Terminate analysis; Correct the problem; Recalibrate or reprep with calibration curve. (See Section 9.6).
CRA	Beginning of every analytical run following the ICB and prior to sample analyses at or near the end of a run required only when requested	50-150% recovery	Rerun to verify; or correct problem and recalibrate or reprep with the calibration curve (See Sec. 9.8)
CCV	Every 10 samples and at the end of the run.	Recovery for Method 245.1 = 95-105% following a calibration. All other CCV for 245.1 are 80-120%. Recovery for Method 7470A = 80-120% following a calibration. If the CCV is biased high and the samples are < RL the results are acceptable.	Terminate analysis; Correct the problem; Recalibrate and rerun all samples not bracketed by acceptable CCV or reprep with calibration curve. (See Section 9.7).

CCB	Immediately following each CCV.	The result must be within +/- RL from zero. If the CCB is biased high and the samples are < RL the results are acceptable.	Terminate analysis; Correct the problem; Recalibrate and rerun all samples not bracketed by acceptable CCB or reprep with calibration curve. (See Section 9.7).
Method Blank	One per sample preparation batch of up to 20 samples.	The result must be less than or equal to the RL. Sample results greater than 20x the blank concentration are acceptable. Samples for which the contaminant is < RL do not require re-digestion (See Section 9.3).	Re-digest and reanalyze samples. Note exceptions under criteria section. See Section 9.3 for additional requirements.

TABLE II. Summary of Quality Control Requirements (Continued)

QC PARAMETER	FREQUENCY	ACCEPTANCE CRITERIA	CORRECTIVE ACTION
Laboratory Control Sample (LCS)	One per sample preparation batch of up to 20 samples.	Aqueous LCS must be within 80 - 120% recovery or in-house control limits. For Method 245.1, the LCS must be 85-115%.	Terminate analysis; Correct the problem; Re-digest and reanalyze all samples associated with the LCS (see Section 9.4).
Matrix Spike	One per sample preparation batch of up to 20 samples.	75 - 125 % recovery or in-house control limits. If the MS/MSD is out for an analyte, it must be in control in the LCS.	In the absence of client specific requirements, flag the data; no flag required if the sample level is > 4x the spike added. (see Section 9.5) For TCLP see Section 11.2.9
Matrix Spike Duplicate	See Matrix Spike	75 - 125 % recovery or in-house control limits; RPD ≤ 20%. (See MS)	See Corrective Action for Matrix Spike.

APPENDIX B

MSA GUIDANCE

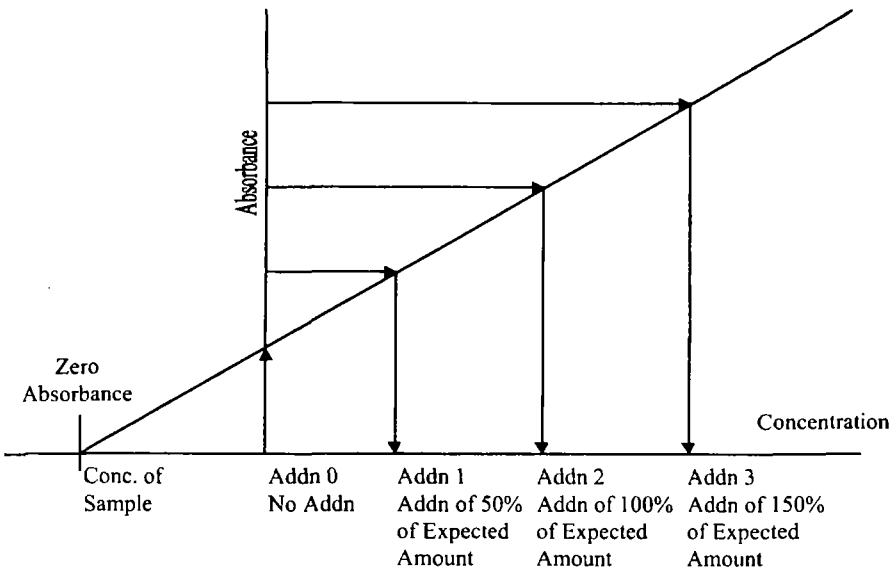
APPENDIX B. MSA GUIDANCE

Method of Standard Addition

Four equal volume aliquots of sample are measured and known amounts of standards are added to three aliquots. The fourth aliquot is the unknown and no standard is added to it. The concentration of standard added to the first aliquot should be 50% of the expected concentration. The concentration of standard added to the second aliquot should be 100% of the expected concentration and the concentration of standard added to the third aliquot should be 150% of the expected concentration. The volume of the unspiked and spiked aliquots should be the same (i.e., the volume of the spike added should be negligible in relation to the volume of sample).

To determine the concentration of analyte in the sample, the absorbance (or response) of each solution is determined and a linear regression performed. On the vertical axis the absorbance (or response) is plotted versus the concentrations of the standards on the horizontal axis using 0 as the concentration of the unspiked aliquot. An example plot is shown in Figure 1. When the resulting line is extrapolated back to zero absorbance, the point of interception of the horizontal axis is the concentration of the unknown. Calculate the correlation coefficient (r) and the x-intercept (where y=0) of the curve. The concentration in the digestate is equal to the negative x-intercept.

Figure 1



- For the method of standard additions to be correctly applied, the following limitations must be taken into consideration.

- The plot of the sample and standards must be linear over the concentration range of concern. For best results, the slope of the curve should be similar to that of a plot of the aqueous standard curve.

- The effect of the interference should not vary as the ratio of the standard added to the sample matrix changes.

APPENDIX C

TROUBLESHOOTING GUIDE

APPENDIX C. TROUBLESHOOTING GUIDE

Problem	Possible Cause
Poor or No Absorbance or Sensitivity Check failed	Incorrect wavelength Dirty windows Window loose Etched or dirty optics Wrong lamp Bad lamp Not enough or no sample introduced Empty sample cup Incorrectly made standards Gas leak Tubing blockage
Erratic Readings	Source lamp not aligned properly Lamp not prewarmed Injection tip partially clogged Contaminated reagents Contaminated glassware Drying tube saturated Bad lamp Injection tip hitting outside of tube Injection tip coated or not set properly Leak in sample tubing Power fluctuations Air bubbles in tubing
Lamp Won't Light	Lamp cable not plugged in Lamp power set at 0 Lamp is dead Power supply fuse is blown Short in cord
Standards reading twice or half normal absorbance or concentration	Incorrect standard used Incorrect dilution performed Dirty cell
Background Correction Light Blinking	Background screen or attenuator faulty

APPENDIX D

CONTAMINATION CONTROL GUIDELINES

APPENDIX D. CONTAMINATION CONTROL GUIDELINES

The following procedures are strongly recommended to prevent contamination:

All work areas used to prepare standards and spikes should be cleaned before and after each use.

All glassware should be washed with detergent and tap water and rinsed with 1:1 nitric acid followed by deionized water.

Proper laboratory housekeeping is essential in the reduction of contamination in the metals laboratory. All work areas must be kept scrupulously clean.

Powdered gloves must not be used in the metals laboratory since the powder contains silica and zinc, as well as other metallic analytes. Alternatively, vinyl or nitrile gloves should be used in the metals laboratory.

Glassware should be periodically checked for cracks and etches and discarded if found. Etched glassware can cause cross contamination of any metallic analytes.

The following are helpful hints in the identification of the source of contaminants:

Reagents or standards can contain contaminants or be contaminated with the improper use of a pipette.

Improper cleaning of glassware can cause contamination.

Separate glassware if an unusually high sample is analyzed and soak with sulfuric acid prior to routine cleaning.

APPENDIX E

PREVENTIVE MAINTENANCE

APPENDIX E. PREVENTIVE MAINTENANCE

A maintenance log is used to record when maintenance is performed on instruments. When an instrument problem occurs indicate the date, time and instrument number, then identify the problem and corrective action in the maintenance log.

The following procedures are required to ensure that that the instrument is fully operational.

Cold Vapor Atomic Absorption (Leeman PS 200II)

Daily	As Needed
Check nitrogen flow.	Check Hg lamp intensity.
Check tubing.	Clean lens.
Check drain.	Check aperture.
	Replace drying tube.
	Change Hg lamp.
	Check liquid/gas separator.

APPENDIX F

INSTRUMENT SET UP

Hg Analysis (Leeman PS200II)

SYSTEM INITIALIZATION AND WARM UP

1. F1 Menu

2. Instrument

a. TASKMASTER

b. #4 Wake System Up Enter

The warming up period takes approximately 10 minutes.

TO SET UP INSTRUMENT FOR ANALYSIS

1. F1 Menu

2. Autosampler

   A. Rack Entry

   B. Edit (ex. Rack 1), Enter

   C. Cup ID - Enter (clears sample #'s)

   D. Extended ID- type in matrix of sample (water or solid), Enter.

   E. Press Insert Key and move cursor with arrows to cup ID and begin typing labels.

   F. F3 Print Screen

3. Press F2 Macro key and type in analyst's first name - Enter

   A. Enter folder name - ex. HG10306, Enter. If folder does not exist, type Y - Enter.

   B. Type in - "Rack 1", "Rack 2" etc., Enter.

   C. Type in : FROM CUP TO CUP

   Ex. = 1 30

Do the same for position 2 if needed. If not needed, you must press Enter 3 times to begin analysis.

Title: PREPARATION AND ANALYSIS OF MERCURY IN SOLID SAMPLES BY COLD VAPOR ATOMIC ABSORPTION SPECTROSCOPY

[Method: SW846 7471A]

Approvals (Signature/Date):

Roger Jobs 12-5-07
Technology Specialist Date

12-6-07
Health & Safety Coordinator Date

Dorothy J. Leeson 12/6/07
Quality Assurance Manager Date

12/7/07
Laboratory Director Date

Mark E Brown 12/6/07
Technical Director Date

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1. SCOPE AND APPLICATION

1.1. This procedure describes the preparation and analysis of mercury (Hg, CAS # 7439-97-6) by Cold Vapor Atomic Absorption Spectroscopy (CVAA) using SW-846 Method 7471A.

1.2. The associated LIMs method code is O9.

1.3. CVAA analysis provides for the determination of total mercury (organic and inorganic). The combination of the oxidants, potassium permanganate and potassium persulfate, has been found to give 100% recovery with both types of compounds. Detection limits, sensitivity and optimum concentration ranges for mercury analysis will vary with the matrices, instrumentation and volume of sample used.

1.4. Method 7471A is applicable to the preparation and analysis of mercury in soils, sediments, bottom deposits, wastes, wipes and sludge-type materials. All matrices require sample preparation prior to analysis.

1.5. The TestAmerica North Canton reporting limit for mercury in solid matrices is 0.033 mg/kg based on a 0.6 g sample aliquot (wet weight).

2. SUMMARY OF METHOD

2.1. This SOP describes a technique for the determination of mercury in solution. The procedure is a physical method based on the absorption of radiation at 253.7 nm by mercury vapor. A representative portion of the sample is digested in hydrochloric and nitric acids. Organic mercury compounds are oxidized with potassium permanganate and the mercury reduced to its elemental state with stannous chloride 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 is measured as a function of mercury concentration. Concentration of the analyte in the sample is determined by comparison of the sample absorbance to the calibration curve (absorbance vs. concentration).

3. DEFINITIONS

3.1. Total Metals: The concentration determined on an unfiltered sample following digestion.

4. INTERFERENCES

Chemical and physical interferences may be encountered when analyzing samples using this method.

4.1. Potassium permanganate which is used to breakdown organic mercury compounds also

eliminates possible interferences from sulfide. Concentrations as high as 20 mg/L of sulfide as sodium sulfide do not interfere with the recovery of inorganic mercury from reagent water.

4.2. Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/L had no effect on the recovery of mercury from spiked samples.

4.3. Chlorides can cause a positive interference. Samples 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 at 253.7 nm. Care must be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. This is accomplished by adding excess hydroxylamine reagent (25 mL) and purging the sample headspace before stannous chloride is added. Both inorganic and organic mercury spikes have been quantitatively recovered from seawater using this technique.

Note: Sufficient addition of permanganate is apparent when the purple color persists at least 15 minutes. Some samples may require dilution prior to digestion due to extremely high concentrations of chloride.

4.4. Interference from certain volatile organic materials that absorb at this wavelength may also occur. If suspected, a preliminary run without stannous chloride can determine if this type of interference is present. While the possibility of absorption from certain organic substances present in the sample does exist, this problem is not routinely encountered. This is mentioned only to caution the analyst of the possibility. If this condition is found to exist, the mercury concentration in the sample can be determined by subtracting the result of the sample run without the reducing reagent (stannous chloride) from that obtained with the reducing reagent.

4.5. Samples containing high concentrations of oxidizable organic materials, as evidenced by high COD levels, may not be completely oxidized by this procedure. When this occurs the recovery of mercury will be low. The problem can be eliminated by reducing the volume of original sample used.

4.6. The most common interference is laboratory contamination which may arise from impure reagents, dirty glassware, improper sample transfers, dirty work areas, etc. Be aware of potential sources of contamination and take appropriate measures to minimize or avoid them.

5. SAFETY

5.1. Employees must abide by the policies and procedures in the Corporate Safety Manual and this document.

5.2. Samples that contain high concentrations of carbonates or organic material or samples that

are at elevated pH can react violently when acids are added.

5.3. The following is a list of the materials used in this method, which have a serious or significant hazard rating. NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table. A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Mercury (1,000 PPM in Reagent)	Oxidizer Corrosive Poison	0.1 Mg/M3 Ceiling (Mercury Compounds)	Extremely toxic. Causes irritation to the respiratory tract. Causes irritation. Symptoms include redness and pain. May cause burns. May cause sensitization. Can be absorbed through the skin with symptoms to parallel ingestion. May affect the central nervous system. Causes irritation and burns to eyes. Symptoms include redness, pain, and blurred vision; may cause serious and permanent eye damage.
Nitric Acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Hydrochloric Acid	Corrosive Poison	5 PPM-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.

Potassium Permanganate	Oxidizer	5 Mg/M3 for Mn Compounds	Causes irritation to the respiratory tract. Symptoms may include coughing, shortness of breath. Dry crystals and concentrated solutions are caustic causing redness, pain, severe burns, brown stains in the contact area and possible hardening of outer skin layer. Diluted solutions are only mildly irritating to the skin. Eye contact with crystals (dusts) and concentrated solutions causes severe irritation, redness, and blurred vision and can cause severe damage, possibly permanent.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

5.4. Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Cut resistant gloves must be worn doing any other task that presents a strong possibility of getting cut. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.5. Exposure to chemicals must be maintained **as low as reasonably achievable.** Therefore, unless they are known to be non-hazardous, all samples should be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. All samples with stickers that read "Caution/Use Hood!" **must** be opened in the hood. Contact the EH&S Coordinator if this is not possible. Solvent and waste containers will be kept closed unless transfers are being made.

5.6. All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica North Canton associate. The situation must be reported **immediately** to the EH&S Coordinator and the Laboratory Supervisor.

5.7. Do not look directly into the beam of the Hg lamp. The UV light that these lamps radiate is harmful to the eyes.

5.8. Cylinders of compressed gas must be handled with caution, in accordance with local regulations. It is recommended that, wherever possible, cylinders be located outside the laboratory and the gas led to the instrument through approved lines.

5.9. The CVAA apparatus must be properly vented to remove potentially harmful fumes generated during sample analysis.

6. EQUIPMENT AND SUPPLIES

6.1. Temperature controlled water bath (capable of maintaining temperature of 90- 95 °C).

6.2. Atomic Absorption Spectrophotometer equipped with:

6.2.1. Absorption Cell with quartz end windows perpendicular to the longitudinal axis. Dimensions of the cell must result in sufficient sensitivity to meet the SOP defined reporting limit. The quartz windows must be maintained to provide accurate measurements. Any scratches or fingerprints can alter the absorption of UV radiation.

6.2.2. Mercury specific hollow cathode lamp (HCL) or electrodeless discharge lamp (EDL).

6.2.3. Peristaltic pump which can deliver 1 L/min air.

6.2.4. Flowmeter capable of measuring an airflow of 1 L/min.

6.2.5. Recorder or Printer.

6.2.6. Aeration Tubing: A straight glass frit having a course porosity and Tygon tubing is used for the transfer of mercury vapor from the sample bottle to the absorption cell and return.

6.2.7. Drying device (a drying tube containing magnesium perchlorate or magnesium sulfate and/or a lamp with a 60 W bulb) to prevent condensation in cell. The lamp is positioned to shine on the absorption cell maintaining the air temperature in the cell about 10 °C above room temperature. Other drying devices that acheive the same purpose are also acceptable (i.e., Gortex filter).

Note: Instruments designed specifically for the measurement of mercury using the cold vapor technique may be substituted for the atomic absorption spectrophotometer.

6.3. BOD bottles or equivalent

6.4. Nitrogen or argon gas supply, welding grade or equivalent

6.5. Calibrated automatic pipettes or Class A glass volumetric pipettes

6.6. Class A volumetric flasks

6.7. Top-loading balance, capable of reading up to two decimal places

6.8. Thermometer (capable of accurate readings at 95 °C)

6.9. Disposable cups or tubes

7. REAGENTS AND STANDARDS

7.1. Reagent water must be produced by a Millipore DI system or equivalent. Reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks.

7.2. Stock (10 ppm) mercury standards (in 10% HNO_3) are purchased as custom solutions. All standards must be stored in FEP fluorocarbon or previously unused polyethylene or polypropylene bottles. Stock standard solutions must be replaced prior to the expiration date provided by the manufacturer. If no expiration date is provided, the stock solutions may be used for up to one year and must be replaced sooner if verification from an independent source indicates a problem.

7.3. Working mercury standard (0.1 ppm): Take 1 mL of the stock mercury standard (7.2) and dilute to 100 mL with reagent water. The working mercury standard must be made daily and must be prepared in a matrix of 0.15% HNO_3. This acid (150 uL of concentrated HNO_3) must be added to the flask/bottle before the addition of the stock standard aliquot.

7.4. The calibration standards must be prepared fresh daily from the working standard (7.3) by transferring 0, 0.2, 0.5, 1.0, 5.0 and 10.0 mL aliquots of the working mercury standard into sample preparation bottles and proceeding as specified in Section 11.1

Note: Alternate approaches to standard preparation may be taken and alternate volumes of standard may be prepared as long as the accuracy and final standard concentrations as detailed in Table I are maintained. For example, automated mercury systems do not require 100 mL of standard and therefore smaller volumes may be generated to reduce waste generation.

7.5. The initial calibration verification standard must be made from a different stock solution than that of the calibration standards.

7.6. Refer to Table I (Appendix A) for details regarding the working standard concentrations for calibration, calibration verification and spiking solutions. All standards must be processed through the entire analytical procedure including sample preparation.

7.7. Nitric acid (HNO_3), concentrated, trace metal grade or better.

Note: If a high reagent blank is obtained, it may be necessary to distill the nitric acid.

7.8. Sulfuric acid (H_2SO_4), concentrated, trace metal grade or better.

7.9. Hydrochloric acid (HCl), concentrated, trace metal grade or better.

7.10. Aqua Regia: Prepare immediately before use by carefully adding three volumes of concentrated HCl to one volume of concentrated HNO_3.

7.11. Stannous chloride solution: Add 50 g of stannous chloride and 25 mL of concentrated HCl, and bring to a final volume of 500 mL with DI water.

Note: Stannous sulfate may be used in place of stannous chloride. Prepare the stannous sulfate solution according to the recommendations provided by the instrument manufacturer.

7.12. Sodium chloride-hydroxylamine hydrochloride solution: Add 12 g of sodium chloride and 12 g of hydroxylamine hydrochloride to every 100 mL of reagent water.

Note: Hydroxylamine sulfate may be used in place of hydroxylamine hydrochloride.

7.13. Potassium permanganate, 5% solution (w/v): Dissolve 5 g of potassium permanganate for every 100 mL of reagent water.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Sample holding time for mercury is 28 days from time of collection to the time of sample analysis.

8.2. Soil samples do not require preservation but must be stored at 4° C ± 2° C until the time of analysis.

9. QUALITY CONTROL

Table II (Appendix A) provides a summary of quality control requirements including type, frequency, acceptance criteria and corrective action.

9.1. Initial Demonstration of Capability

Prior to the analysis of any analyte using 7471A, the following requirements must be met.

9.1.1. Method Detection Limit (MDL) - An MDL must be determined for each analyte/matrix prior to the analysis of any samples. The MDL is determined using seven replicates of reagent water, spiked with all the analytes of interest, that have been carried through the entire analytical procedure. MDLs must be redetermined on an annual basis in accordance with 40 CFR Part 136 Appendix B requirements. The result of the MDL determination must be below the TestAmerica North Canton reporting limit.

9.1.2. Initial Demonstration Study - This requires the analysis of four QC check samples. The QC check sample is a well characterized laboratory generated sample used to monitor method performance. The results of the initial demonstration study must be acceptable before analysis of samples may begin.

9.1.2.1. Four aliquots of the check sample (LCS) are prepared and analyzed using the procedures detailed in this SOP and the determinative SOPs.

9.2. Preparation Batch - A group of up to 20 samples that are of the same matrix and are processed together using the same procedures and reagents. The preparation batch must contain a method blank, a LCS and a matrix spike/matrix spike duplicate. In some cases, at client request, it may be appropriate to process a matrix spike and sample duplicate in place of the MS/MSD. If clients specify specific samples for MS/MSD, the batch may contain multiple MS/MSD pairs.

9.3. Sample Count - Laboratory generated QC samples (method blanks, LCS, MS/MSD) are not included in the sample count for determining the size of a preparation batch.

9.4. Method Blank (MB) - One method blank must be processed with each preparation batch. The method blank consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. The method blank should not contain any analyte of interest at or above the reporting or at or above 5% of the measured concentration of that analyte in associated samples, whichever is higher (sample result must be a minimum of 20 times higher than the blank contamination level). Note: For Ohio VAP projects, the result must be below the reporting limit or samples must be redigested.

- Repreparation and reanalysis of all samples associated with an unacceptable method blank is required when reportable concentrations are determined in the samples (see exception noted above).

- If there is no analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. **Such action must be addressed in the project narrative.**

- If the above criteria are not met and reanalysis is not possible, then the sample data must be qualified. **This anomaly must be addressed in the project narrative.**

9.5. Laboratory Control Sample (LCS) - One aqueous LCS must be processed with each preparation batch. The LCS is used to monitor the accuracy of the analytical process. On-going monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines. The LCS must be carried

through the entire analytical procedure. If the LCS is outside established control limits the system is out of control and corrective action must occur. Until in-house control limits are established, a control limit of 70-130% recovery must be applied.

- In the instance where the LCS recovery is greater than the upper control limit and the sample results are less than RL, the data may be reported. Such action must be addressed in the project narrative.

- In the event that an MS/MSD analysis is not possible, a Laboratory Control Sample Duplicate (LCSD) must be analyzed. The LCSD recovery is evaluated using the same control limits as the LCS. The RPD of the LCS and LCSD must be compared to the matrix spike RPD limits.

- Corrective action will be repreparation and reanalysis of the batch unless the client agrees that other corrective action is acceptable.

9.6. Matrix Spike/Matrix Spike Duplicate (MS/MSD) - One MS/MSD pair must be processed for each preparation batch. A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added. A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked identically as the MS) prepared and analyzed along with the sample and matrix spike. Some client specific data quality objectives (DQO's) may require the use of sample duplicates in place of or in addition to MS/MSD's. The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Due to the potential variability of the matrix of each sample, these results may have immediate bearing only on the specific sample spiked. Samples identified as field blanks cannot be used for MS/MSD analysis. Spiking levels are provided in Table I (Appendix A).

- If analyte recovery or RPD falls outside the acceptance range, the recovery of that analyte must be in control for the LCS. Until in-house control limits are established, a control limit of 70 - 130 % recovery and 20% RPD must be applied to the MS/MSD. If the LCS recovery is within limits, then the laboratory operation is in control and the results may be accepted. If the recovery of the LCS is outside limits, corrective action must be taken. Corrective action will include repreparation and reanalysis of the batch. MS/MSD results which fall outside the control limits must be addressed in the narrative.

- If the native analyte concentration in the MS/MSD exceeds 4 times the spike level for that analyte, the recovery data are reported as NC (i.e., not calculated). If the reporting software does not have the ability to report NC then the actual recovery must be reported and narrated as follows: "Results outside of limits do not necessarily reflect poor method performance in the matrix due to high analyte concentrations in the sample relative to the spike level."

- If an MS/MSD is not possible due to limited sample volume, then a laboratory control sample duplicate (LCSD) should be analyzed. The RPD of the LCS and LCSD must be compared to the matrix spike RPD limits.

9.7. Initial Calibration Verification (ICV/ICB) - Calibration accuracy is verified by analyzing a second source standard (ICV). The ICV result must fall within 10% of the true value for that solution. An ICB is analyzed immediately following the ICV to monitor low level accuracy and system cleanliness. The ICB result must fall within +/- the reporting limit (RL) from zero. If either the ICV or ICB fail to meet criteria, the analysis should be terminated, the problem corrected and the instrument recalibrated. (See Section 11.2.10 and Section 11.2.11 for required run sequence). If the cause of the ICV or ICB failure was not directly instrument related the corrective action will include repreparation of the ICV, ICB, CRA, CCV and CCB with the calibration curve.

9.8. Continuing Calibration Verification (CCV/CCB) - Calibration accuracy is monitored throughout the analytical run through the analysis of a known standard after every 10 samples. The CCV must be a mid-range standard at a concentration other than that of the ICV. The CCV result must fall within 20% of the true value for that solution. A CCB is analyzed immediately following each CCV. (See Section 11.2.10 and 11.2.11 for required run sequence.) The CCB result must fall within +/- RL from zero. Each CCV and CCB analyzed must reflect the conditions of analysis of all associated samples. If the CCV/CCB is biased high and the sample results associated with the CCV/CCB are below the requested reporting limit, then the results can be reported. Sample results may only be reported when bracketed by valid ICV/CCV and ICB/CCB pairs.

9.9. Detection Limit Standard (CRA)-To verify linearity at the reporting limit, a CRA standard is run at the beginning of each sample analysis run after the ICV/ICB. The CRA standard mercury concentration is 0.2 ug/L. Recovery must be ± 50% of the true value, or the standard is either rerun or the problem corrected and the instrument re-calibrated. The CRA is only required when requested. (See Section 11.2.8 for the required run sequence.)

9.10. Method of Standard Addition (MSA) -This technique involves adding known amounts of standard to one or more aliquots of the sample prior to preparation. This technique compensates for a sample interferent that may enhance or depress the analyte signal, thus producing a different slope from that of the calibration standards. It will not correct for additive interferences which cause a baseline shift. Refer to Section 11.2.12 for additional information on when full 4 point MSA is required as well as Appendix C for specific MSA requirements.

10. CALIBRATION AND STANDARDIZATION

10.1. Calibration standards must be processed through the preparation procedure as described in Section 11.1.

10.2. Due to the differences in preparation protocols separate calibration and calibration verification standards must be prepared for aqueous and solid matrices.

10.3. Calibration must be performed daily (every 24 hours) and each time the instrument is set up. The instrument calibration date and time must be included in the raw data.

10.4. Set up the instrument with the operating parameters recommended by the manufacturer. Allow the instrument to become thermally stable before beginning calibration (approximately 30 minutes of warm-up is required). Refer to the facility specific instrument SOP and CVAA instrument manual for detailed setup and operation protocols.

10.5. Calibrate the instrument according to instrument manufacturer's instructions, using a minimum of five standards and a blank. One standard must be at the TestAmerica North Canton reporting limit. Analyze standards in ascending order beginning with the blank. Refer to Section 7.4 and Table I for additional information on preparing calibration standards and calibration levels.

10.6. The calibration curve must have a correlation coefficient of ≥0.995 or the instrument shall be stopped and recalibrated prior to running samples. Sample results can not be reported from a curve with an unacceptable correlation coefficient. NOTE: If any digested standard does not meet SW846 criteria, all associated Ohio VAP samples must be redigested.

10.7. Refer to Section 9.0 for calibration verification procedures, acceptance criteria and corrective actions.

11. PROCEDURE

11.1. Standard and Sample Preparation:

11.1.1. All calibration and calibration verification standards (ICV, ICB, CCV, CCB) are processed through the digestion procedure as well as the field samples.

11.1.2. Transfer 0, 0.2, 0.5, 1.0, 5.0 and 10.0 mL aliquots of the working standard (7.3) into a series of sample digestion bottles. For the ICV, transfer a 2.5 ml aliquot of the working standard. The ICV working standard must be made from a source other than that used for the calibration standards.

Note: Alternate volumes of standard may be prepared as long as the accuracy and final standard concentrations as detailed in Table I are maintained.

11.1.3. Add reagent water to each standard bottle to make a total volume of 10 mL. Continue preparation as described under Section 11.1.5 below.

11.1.4. Transfer 0.6 g of a well mixed sample into a clean sample digestion bottle. Continue preparation as described under Section 11.1.5.

11.1.5. Water Bath protocol

11.1.5.1. To each **standard** bottle: Add 5 mL of aqua regia.

11.1.5.2. To each **sample** bottle: Add *10* mL of reagent water and 5 mLof aqua regia.

11.1.5.3. Heat for two minutes in a water bath at 90 - 95 ° C.

11.1.5.4. Add *40* mL of distilled water.

11.1.5.5. Add 15 mL of potassium permanganate solution.

11.1.5.6. Heat for 30 minutes in the water bath at 90 - 95 °C.

11.1.5.7. Cool.

11.1.5.8. Add 6 mL of sodium chloride-hydroxylamine sulfate solution to reduce the excess permanganate.

11.1.5.9. To each **standard** bottle: Add 50 mL of reagent water.
To each **sample** bottle: Add 50 mL of reagent water.

11.1.5.10. Continue as described under Section 11.2.

11.2. Sample Analysis

11.2.1. Because of differences between various makes and models of CVAA instrumentation, no detailed operating instructions can be provided. Refer to the facility specific instrument operating SOP and the CVAA instrument manual for detailed setup and operation protocols.

11.2.2. All labs are required to detail the conditions/programs utilized for each instrument within the facility specific instrument operation SOP.

11.2.3. Manual determination:

11.2.3.1. Treating each sample individually, purge the headspace of the sample bottle for at least one minute.

11.2.3.2. Add 5 mL of stannous chloride solution and immediately attach the bottle to the aeration apparatus.

11.2.3.3. Allow the sample to stand quietly without manual agitation while the sample is aerated (1 L/min flow). Monitor the sample absorbance during aeration. When the absorbance reaches a maximum and the signal levels off, open the bypass valve and continue aeration until the absorbance returns to its baseline level. Close the bypass valve and remove the aeration device.

11.2.3.4. Place the aeration device into 100 mLs of 1% HNO_3 and allow to bubble rinse until the next sample is analyzed.

11.2.4. Automated determination: Refer to Appendix G for instrument setup and operation.

11.2.5. Perform a linear regression analysis of the calibration standards by plotting maximum response of the standards vs. micrograms (ug) of mercury. Determine the mercury concentration in the samples from the linear regression fit of the calibration curve. Calibration using computer or calculation based regression curve fitting techniques on concentration/response data is acceptable.

11.2.6. All measurements must fall within the defined calibration range to be valid. Dilute and reanalyze all samples for analytes that exceed the highest calibration standard.

11.2.7. If the sample results are negative and the absolute value of the negative result is greater than the reporting limit, the sample must be diluted and reanalyzed.

11.2.8. The samples must be allowed to cool to room temperature prior to analysis or a decrease in the response signal can occur.

11.2.9. Baseline correction is acceptable as long as it is performed after every sample or after the CCV and CCB; resloping is acceptable as long as it is immediately preceded and followed by a compliant CCV and CCB.

11.2.10. The following analytical sequence must be used with Method 7471A:

Instrument Calibration
ICV
ICB
Maximum 10 samples
CCV
CCB

Repeat sequence of 10 samples between CCV/CCB pairs as required to complete run
CCV
CCB

Refer to Quality Control Section 9.0 and Table II (Appendix A) for quality control criteria to apply to Method 7471A.

Note: Samples include the method blank, LCS, MS, MSD, duplicate, field samples and sample dilutions.

11.2.11. The following run sequence is consistent with Method 7471A and may be used as an alternate to the sequence in 11.2.10. This run sequence is recommended if multiple method requirements must be accommodated in one analytical run:

Instrument Calibration
ICV
ICB
CRA
CCV
CCB
10 samples
CCV
CCB
Repeat sequence of 10 samples between CCV/CCB pairs as required to complete run.
CCV
CCB

11.2.12. For TCLP samples, full four point MSA will be required if all of the following conditions are met:

1) Recovery of the analyte in the matrix spike is not at least 50%,

2) The concentration of the analyte does not exceed the regulatory level, and,

3) The concentration of the analyte is within 20% of the regulatory level.

Appendix E provides guidance on performing MSA analyses. For TCLP mercury determinations, MSA spikes must be added prior to sample preparation.

11.3. To facilitate the early identification of QC failures and samples requiring rerun it is strongly recommended that sample data be reviewed periodically throughout the run.

11.4. Guidelines are provided in the appendices on procedures to minimize contamination of

samples and standards, preventive maintenance and troubleshooting.

11.5. One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo. The Nonconformance Memo shall be filed in the project file.

11.6. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

12. DATA ANALYSIS AND CALCULATIONS

12.1. ICV percent recoveries are calculated according to the equation:

$$\%R = 100\left(\frac{Found(ICV)}{True(ICV)}\right)$$

12.2. CCV percent recoveries are calculated according to the equation:

$$\%R = 100\left(\frac{Found(CCV)}{True(CCV)}\right)$$

12.3. Matrix spike recoveries are calculated according to the following equation:

$$\%R = 100\left(\frac{SSR - SR}{SA}\right)$$

Where:

SSR = Spike Sample Result
SR = Sample Result
SA = Spike Added

12.4. The relative percent difference (RPD) of matrix spike/matrix spike duplicates or sample duplicates are calculated according to the following equations:

$$RPD = 100\left[\frac{|MSD - MS|}{\left(\frac{MSD + MS}{2}\right)}\right]$$

Where:

MS = determined spiked sample concentration
MSD = determined matrix spike duplicate concentration

$$RPD = 100\left[\frac{|DU1 - DU2|}{\left(\frac{DU1 + DU2}{2}\right)}\right]$$

Where:

DU1 = Sample result
DU2 = Sample duplicate result

12.5. For automated determinations, the final concentration determined in solid samples when reported on a dry weight basis is calculated as follows:

$$mg/kg,\ dry\ weight = (C \times V \times D)/(W \times S)$$

Where:

C = Concentration (ug/L) from instrument readout
V = Volume of digestate (L)
D = Instrument dilution factor
W = Weight in g of wet sample digested
S = Percent solids/100

Note: A Percent Solids determination must be performed on a separate aliquot when dry weight concentrations are to be reported. If the results are to be reported on a wet weight basis, the "S" factor should be omitted from the above equation.

12.6. For manual (total) determinations, the final concentration determined in solid samples when reported on a dry weight basis is calculated as follows:

$$mg/kg,\ dry\ weight = (C)/(W \times S)$$

Where:

C = Concentration (ug) from instrument readout
W = Weight in g of wet sample digested
S = Percent solids/100

Note: A Percent Solids determination must be performed on a separate aliquot when dry weight concentrations are to be reported. If the results are to be reported on a wet weight basis, the "S" factor should be omitted from the above equation.

12.7. The LCS percent recovery is calculated according to the following equation:

$$\%R = 100\left(\frac{Found(LCS)}{True(LCS)}\right)$$

12.8. Sample results should be reported with up to three significant figures in accordance with the TestAmerica North Canton significant figure policy.

13. METHOD PERFORMANCE

13.1. Each laboratory must have initial demonstration of performance data on file for each analyte of interest as described in Section 9.1.

13.2. Method performance is determined by the analysis of method blank, laboratory control sample, matrix spike and matrix spike duplicate samples. The matrix spike recovery should fall within +/- 30 % and the matrix spike duplicates should compare within 20% RPD. The method blanks must meet the criteria in Section 9.4. The laboratory control sample should recover within 20% of the true value until in house limits are established.

13.3. Training Qualification:

The Group/Team Leader has the responsibility to ensure this procedure is performed by an associate who has been properly trained in its use and has the required experience.

14. POLLUTION PREVENTION

14.1. This method does not contain any specific modifications that serve to minimize or prevent pollution.

15. WASTE MANAGEMENT

15.1. All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in Section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

15.2. Waste Streams Produced by this Method

15.2.1. The following waste streams are generated by this method.

15.2.1.1. Acid Waste. This waste disposed of in the designated container labeled "Acid Waste".

16. REFERENCES

16.1. References

16.1.1. Test Methods for Evaluating Solid Waste , Physical/Chemical Methods, SW-846, 3rd Edition, Final Update II, Revision I, September 1994, Method 7471A (Mercury).

16.1.2. Corporate Quality Management Plan (QMP), current version.

16.1.3. TestAmerica Laboratory Quality Manual (LQM), current version. Associated SOPs and Policies, latest version

16.1.4. TestAmerica Corporate Safety Manual, M-E-0001 and TestAmerica North Canton Facility Addendum and Contingency Plan, current version.

16.2. Associated SOPs and Policies, latest version.

16.2.1. QA Policy, QA-003

16.2.2. Glassware Washing, NC-QA-0014

16.2.3. Statistical Evaluation of Data and Development of Control Charts, NC-QA-0018

16.2.4. Method Detection Limits and Instrument Detection Limits, NC-QA-0021 and S-Q-003.

16.2.5. Supplemental Practice for DoD Project Work, SOP NC-QA-0016

16.2.6. Standards and Reagents, SOP NC-QA-0017.

17. MISCELLANEOUS (TABLES, APPENDICES, ETC.)

17.1. Modifications/Interpretations from reference method.

17.1.1. Modifications from Method 7471A

17.1.1.1. A potassium persulfate oxidation step has been included to facilitate the breakdown of organic mercurials which are not completely oxidized by potassium permanganate. Use of potassium persulfate in combination

with the permanganate improves the recovery of mercury from organo-mercury compounds. The use of persulfate has been incorporated in several recent EPA mercury protocols.

17.1.1.2. The alternate run sequence presented in Section 11.2.11 is consistent with method requirements. An additional QC analysis (CRA) was added to accommodate the CLP protocol requirements.

17.1.2. Modifications from Method 7471A

17.1.2.1. Chapter 1 of SW846 specify the use of reagent water with a purity equivalent to ASTM Type II water. This SOP specifies the use of a Millipore DI system or equivalent to produce reagent water. This SOP requires that reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks.

17.1.2.2. Chapter 1 of SW-846 states that the method blank should not contain any analyte of interest at or above the MDL. This SOP states that the method blank must not contain any analyte of interest at or above the reporting limit.

17.2. Documentation and Record Management

The following documentation comprises a complete CVAA raw data package:

- Raw data (direct instrument printout)
- Run log printout from instrument software where this option is available or manually generated run log. (A bench sheet may be substituted for the run log as long as it contains an accurate representation of the analytical sequence).
- Data review checklist - See Appendix B
- Standards Documentation (source, lot, date).
- Copy of digestion log.
- Nonconformance summary (if applicable).

Figure 1. Solid Sample Preparation for Mercury - Water Bath Procedure

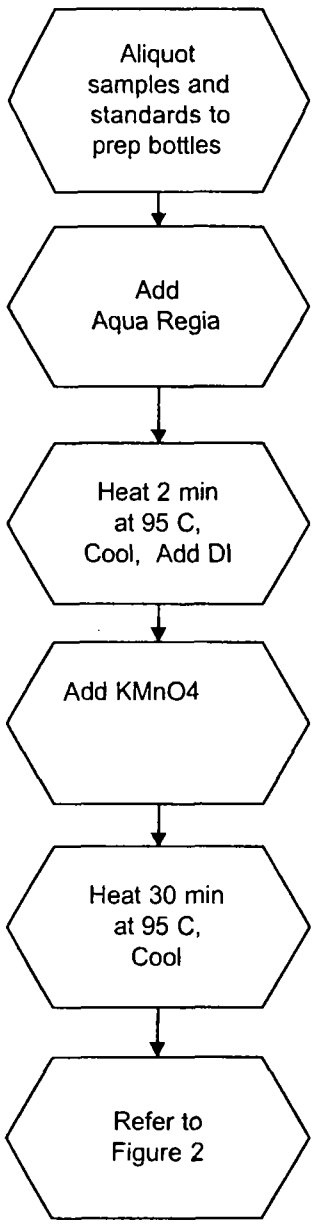
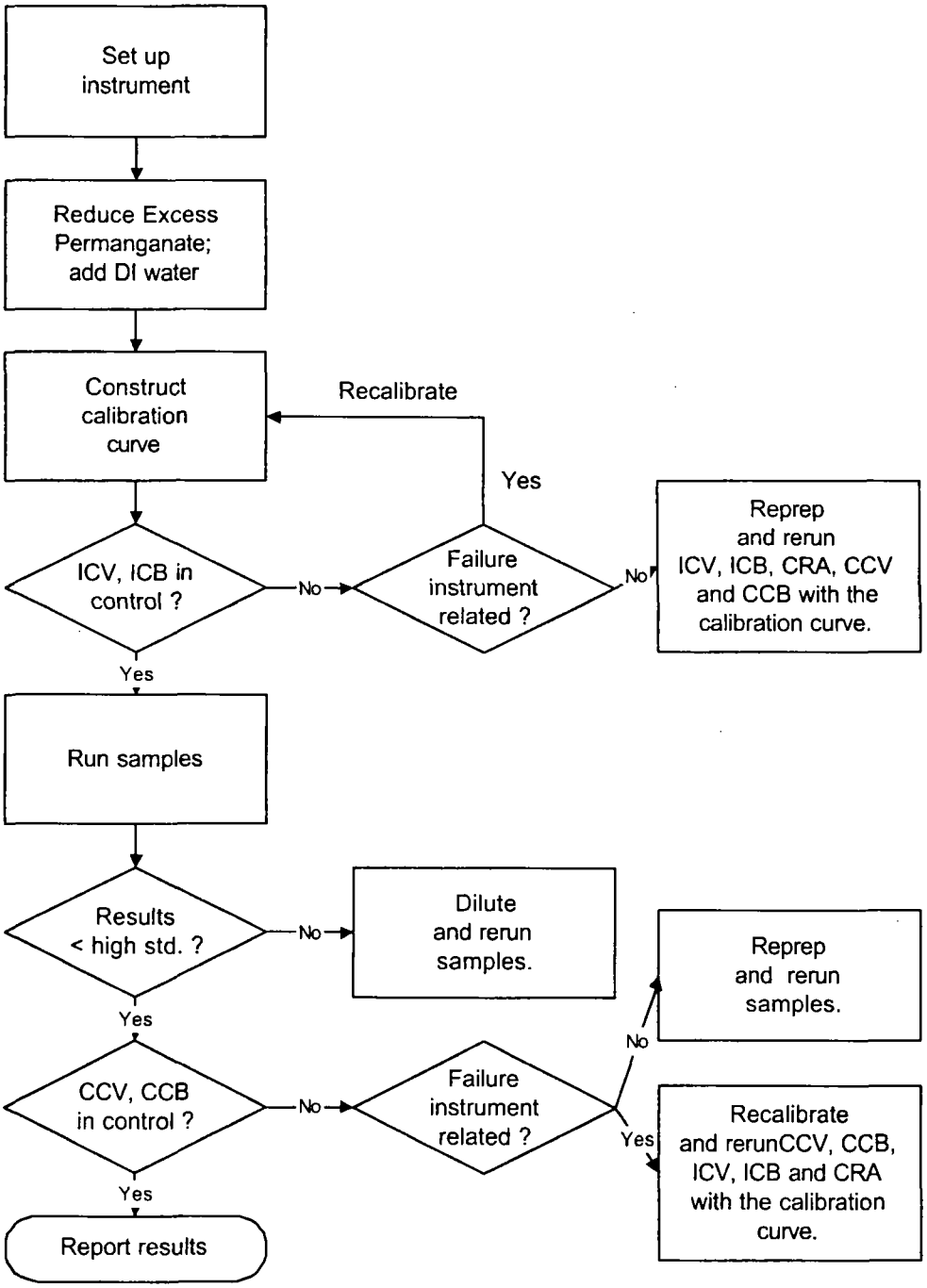


Figure 2. CVAA Mercury Analysis



APPENDIX A

TABLES

TABLE I. MERCURY REPORTING LIMITS, CALIBRATION STANDARD*, QC STANDARD AND SPIKING LEVELS

Soil RL (mg/kg)	0.1
Std 0 (mg/L)	0
Std 1 (mg/L)	0.0002
Std 2 (mg/L)	0.0005
Std 3 (mg/L)	0.001
Std 4 (mg/L)	0.005
Std 5 (mg/L) **	0.010
ICV (mg/L)	0.001 or 0.0025 ***
CCV/LCS/LCSD (mg/L)	0.0025 or 0.005 ***
MS (mg/L)	0.001

* SOP specified calibration levels must be used unless prevented by the instrument configuration or client specific requirements. Deviations from specified calibration levels must be documented in the facility specific instrument operation SOP and must be approved by the facility technical manager and Quality Assurance Manager.

** Optional standard which may be used to extend the calibration range as allowed by the instrument configuration. If the instrument configuration prevents the use of 6 standards, the 2 ppb standard may be eliminated in favor of the 10 ppb standard.

*** Concentration level dependent on high calibration standard used. CCV must be 50% of the high standard concentration and the ICV must be 20-25% of the high standard concentration.

TABLE II. Summary Of Quality Control Requirements

QC Parameter	Frequency *	Acceptance Criteria	Corrective Action
ICV	Beginning of every analytical run	90 - 110 % recovery	Terminate analysis; Correct the problem; Recalibrate or reprep with calibration curve (see Section 9.7)
ICB	Beginning of every analytical run, immediately following the ICV	The result must be within +/- RL from zero	Terminate analysis, correct the problem, recalibrate or reprep with calibration curve (see Section 9.7)
CCV	Every 10 samples and at the end of the run	80 - 120 % recovery	Terminate analysis, correct the problem, recalibrate and rerun all samples not bracketed by acceptable CCV or reprep with calibration curve. If CCV is biased high and samples are ND, results can be reported (see Sections 9.8 and 10.6).
CCB	Immediately following each CCV	The result must be within +/- RL from zero	Terminate analysis, correct the problem, recalibrate and rerun all samples not bracketed by acceptable CCB or reprep with calibration curve. If CCB is biased high and samples are ND, results can be reported (see Section 9.8).
Method Blank	One per sample preparation batch of up to 20 samples	The result must be less than or equal to the RL Sample results greater than 20x the blank concentration are acceptable Samples for which the contaminant is < RL do not require redigestion (see Section 9.4)	Redigest and reanalyze samples Note exceptions under criteria section See Section 9.4 for additional requirements

*See Sections 11.2.10 and 11.2.11 for exact run sequence to be followed.

TABLE II. Summary of Quality Control Requirements (Cont'd)

QC Parameter	Frequency *	Acceptance Criteria	Corrective Action
Laboratory Control Sample/Laboratory Control Sample Duplicate(LCS/LCSD)	One per sample preparation batch of up to 20 samples	Aqueous LCS/LCSD must be within 80 - 120% recovery or in-house control limits	Terminate analysis, correct the problem, redigest and reanalyze all samples associated with the LCS (see Section 9.5)
Matrix Spike	One per sample preparation batch of up to 20 samples	75 - 125 % recovery or in-house control limits If the MS/MSD is out for an analyte, it must be in control in the LCS	In the absence of client specific requirements, flag the data No flag required if the sample level is > 4x the spike added. (see Section 9.6) For TCLP see Section 11.3.12
Matrix Spike Duplicate	See Matrix Spike	75 - 125 % recovery or in-house control limits RPD ≤ 20% (see MS)	See Corrective Action for Matrix Spike

APPENDIX B

EXAMPLE
TESTAMERICA NORTH CANTON Hg DATA REVIEW CHECKLIST

Example
TestAmerica North Canton Hg Data Review Checklist

Run/Project Information

Run Date: _____ **Analyst:**_____ **Instrument:**_____
Prep Batches Run:_____

Circle Methods used: **7470A / 245.1 :** CORP-MT-0005 Rev 1 **7471 :** CORP-MT-0007 Rev 1

Review Items

A. Calibration/Instrument Run QC	Yes	No	N/A	2ndLevel
1. Instrument calibrated per manufacturer's instructions and at SOP specified levels ?				
2. ICV/CCV analyzed at appropriate frequency and within control limits?				
3. ICB/CCB analyzed at appropriate frequency and within +/- RL or +/- CRDL (CLP)?				
4. CRA run (CLP only)?				
B. Sample Results				
1. Were samples with concentrations > the high calibration standard diluted and reanalyzed?				
2. All reported results bracketed by in control QC ?				
3. Sample analyses done within holding time?				
C. Preparation/Matrix QC				
1. LCS done per prep batch and within QC limits ?				
2. Method blank done per prep batch and < RL or CRDL (CLP) ?				
3. MS run at required frequency and within limits ?				
4. MSD or DU run at required frequency and RPD within SOP limits?				
D. Other				
1. Are all nonconformances documented appropriately ?				
2. Current IDL/MDL data on file?				
3. Calculations and Transcriptions checked for error ?				
4. All client/ project specific requirements met?				
5. Date of analysis verified as correct ?				

Analyst: _____ **Date:**_____
Comments:

_____
_____

2nd Level Reviewer : _____ **Date:**_____

_____
_____

APPENDIX C

MSA GUIDANCE

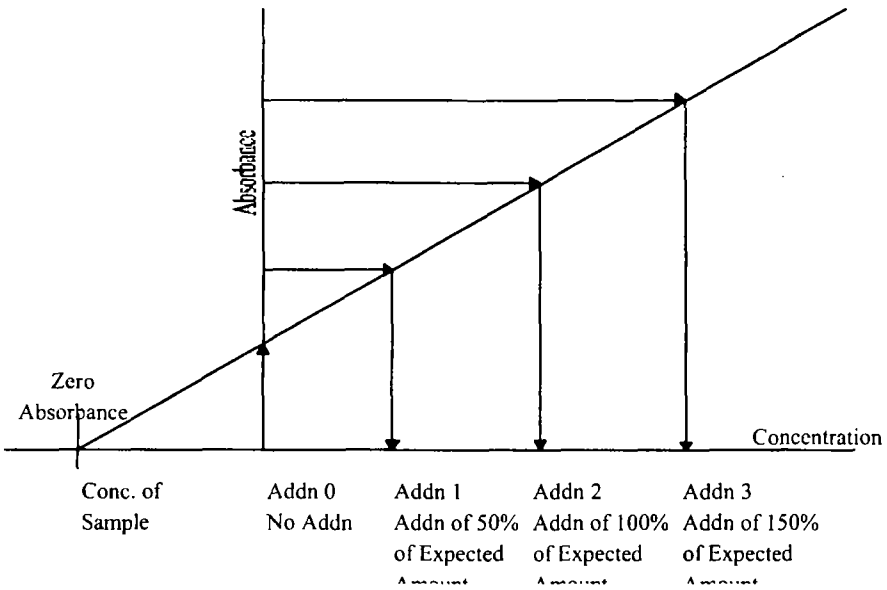
APPENDIX C. MSA GUIDANCE

Method of Standard Addition

Four equal volume aliquots of sample are measured and known amounts of standards are added to three aliquots. The fourth aliquot is the unknown and no standard is added to it. The concentration of standard added to the first aliquot should be 50% of the expected concentration. The concentration of standard added to the second aliquot should be 100% of the expected concentration and the concentration of standard added to the third aliquot should be 150% of the expected concentration. The volume of the unspiked and spiked aliquots should be the same (i.e., the volume of the spike added should be negligible in relation to the volume of sample).

To determine the concentration of analyte in the sample, the absorbance (or response) of each solution is determined and a linear regression performed. On the vertical axis the absorbance (or response) is plotted versus the concentrations of the standards on the horizontal axis using 0 as the concentration of the unspiked aliquot. An example plot is shown in Figure 1. When the resulting line is extrapolated back to zero absorbance, the point of interception of the horizontal axis is the concentration of the unknown. Calculate the correlation coefficient (r) and the x-intercept (where y=0) of the curve. The concentration in the digestate is equal to the negative x-intercept.

Figure 1



- For the method of standard additions to be correctly applied, the following limitations must be taken into consideration.
- The plot of the sample and standards must be linear over the concentration range of concern. For best results, the slope of the curve should be similar to that of a plot of the aqueous standard curve.
- The effect of the interference should not vary as the ratio of the standard added to the sample matrix changes.

APPENDIX D

TROUBLESHOOTING GUIDE

APPENDIX D. TROUBLESHOOTING GUIDE

Problem	Possible Cause
Poor or No Absorbance or Sensitivity Check failed	Incorrect wavelength Dirty windows Window loose Etched or dirty optics Wrong lamp Bad lamp Not enough or no sample introduced Empty sample cup Incorrectly made standards Gas leak EDL power supply set on "Continuous"
Erratic Readings	Source lamp not aligned properly Lamp not prewarmed Injection tip partially clogged Contaminated reagents Contaminated glassware Drying tube saturated Bad lamp Injection tip hitting outside of tube Injection tip coated or not set properly Leak in sample tubing Power fluctuations Air bubbles in tubing
EDL Won't Light	Lamp cable not plugged in Lamp power set at 0 Lamp is dead Power supply fuse is blown Short in cord
Standards reading twice or half normal absorbance or concentration	Incorrect standard used Incorrect dilution performed Dirty cell
Background Correction Light Blinking	Background screen or attenuator faulty

APPENDIX E

CONTAMINATION CONTROL GUIDELINES

APPENDIX E. CONTAMINATION CONTROL GUIDELINES

The following procedures are strongly recommended to prevent contamination:

All work areas used to prepare standards and spikes should be cleaned before and after each use.

All glassware should be washed with detergent and tap water and rinsed with 1:1 nitric acid followed by deionized water.

Proper laboratory housekeeping is essential in the reduction of contamination in the metals laboratory. All work areas must be kept scrupulously clean.

Powdered or Latex Gloves must not be used in the metals laboratory since the powder contains silica and zinc, as well as other metallic analytes. Only vinyl or nitrile gloves should be used in the metals laboratory.

Glassware should be periodically checked for cracks and etches and discarded if found. Etched glassware can cause cross contamination of any metallic analytes.

Autosampler trays should be covered to reduce the possibility of contamination. Trace levels of elements being analyzed in the samples can be easily contaminated by dust particles in the laboratory.

The following are helpful hints in the identification of the source of contaminants:

Reagents or standards can contain contaminants or be contaminated with the improper use of a pipette.

Improper cleaning of glassware can cause contamination.

Separate glassware if an unusually high sample is analyzed and soak with sulfuric acid prior to routine cleaning.

APPENDIX F

PREVENTIVE MAINTENANCE

APPENDIX F. PREVENTIVE MAINTENANCE

A maintenance log is used to record when maintenance is performed on instruments. When an instrument problem occurs indicate the date, time and instrument number, then identify the problem and corrective action in the maintenance log.

The following procedures are required to ensure that that the instrument is fully operational.

Cold Vapor Atomic Absorption (Leeman PS 200) [1]

Daily	Semi-annually	Annually
Clean lens	Check Hg lamp intensity	Change Hg lamp
Check aperture		Check liquid/gas separator
Check argon flow		
Check tubing		
Check drain		
Replace drying tube		

Cold Vapor Atomic Absorption (PE 5000) [1]

Daily	Monthly
Clean aspirator by flushing with DI water	Clean cell in aqua regia
Check tubing and replace if needed	Clean aspirator in aqua regia
Clean windows with methanol	
Change silica gel in drying tube	
Check argon gas supply	
Adjust lamp	

APPENDIX G

INSTRUMENT SET UP

Hg Analysis (Leeman PS200II)

SYSTEM INITIALIZATION AND WARM UP

1. F1 Menu
2. Instrument
   a. Taskmaster
   b. #4 Wake System Up - Enter

The warming up period takes approximately ten minutes.

TO SET UP INSTRUMENT FOR ANALYSIS

1. F1 Menu
2. Autosampler
   A. Rack Entry
   B. Edit (ex. Rack 1), Enter
   C. Cup ID - Enter (clears sample #'s)
   D. Extended ID- type in matrix of sample (water or solid), Enter.
   E. Press Insert Key and move cursor with arrows to cup ID and begin typing labels.
   F. F3 Print Screen
3. Press F2 Macro key and type in analyst's first name - Enter
   A. Enter folder name - ex. HG0306, Enter. If folder does not exist, type Y - Enter.
   B. Type in - "Rack 1", "Rack 2" etc. , Enter.
   C. Type in : FROM CUP TO CUP

      Ex. = 1 30

Do the same for position 2 if needed. If not needed, you must press "Enter" three times to begin analysis.

TestAmerica

THE LEADER IN ENVIRONMENTAL TESTING

TestAmerica North Canton

SOP No. NC-WC-0032, Rev. 8.4
Effective Date: 12/08/04
Cover Page

Title: Cyanide, Preparation Method
[Methods: SW9012A, EPA335.1, 335.2, SM4500CN-I, SM4500CN-E, CLP ILM03.0]

Approvals (Signature/Date):

Technology Specialist	Date	Health & Safety Coordinator	Date
Quality Assurance Manager	Date	Laboratory Director	Date

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STL STANDARD OPERATING PROCEDURE

TITLE: CYANIDE PREPARATION METHOD

(SUPERSEDES: REVISION 8.3, DATED 06/17/03)

Prepared by:	Rebecca L. Nolan	12/28/04 Date
Reviewed by:	Technology Specialist	12/28/04 Date
Approved by:	Quality Assurance Manager	12/30/04 Date
Approved by:	Environmental Health and Safety Coordinator	12-16-04 Date
Approved by:	Laboratory Director	12/29/04 Date

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1. SCOPE AND APPLICATION

1.1. This method is applicable to the determination of Total, Amenable, and Free Cyanide in solids, liquids, and waters. It is based on CLP ILM03.3, CLP ILM04.0, SW 846 Method 9012A, EPA 335.1, 335.2, 335.4, Standard Method 4500-CN-I and ASTM D 4282-83. The working linear range is 0.005 - 0.2 mg/L for waters and 0.25 to 10 mg/kg for solids.

1.2. The associated method codes are CLP ILM03.0 (DV), CLP ILM04.0 (OU), SW846 Method 9012A (QP), EPA 335.1 and 335.2 (CG), EPA 335.4 (O2), Standard Method 4500-CN-E (A4), Free Cyanide 4500CN-I (HF) and Amenable Cyanide 9012A (N4).

1.3. This document accurately reflects current laboratory standard operating procedures (SOP) as of the date above. All facility SOPs are maintained and updated as necessary by the laboratory QA department.

2. SUMMARY OF METHOD

2.1. The Cyanide, as HCN, is released by distilling/refluxing the sample with strong acid and is trapped in a sodium hydroxide solution.

3. DEFINITIONS

3.1. Refer to the glossary in the Laboratory Quality Manual (LQM), latest version.

4. INTERFERENCES

4.1. Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus that lead to discrete artifacts. All of these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. Specific selection of reagents may be required to avoid introduction of contaminants.

4.2. Oxyidizing agents such as chlorine will decompose most cyanides. Sulfide will distill over with the cyanide and could affect colorimetric, titrimetirc, and electrode procedures. Refer to the preparation section on how to screen and treat samples appropriately.

4.3. Aldehydes convert cyanide to cyanohydrin which could result in the lost of cyanide. If the presence of aldehydes are suspected, stabilize the sample with NaOH at the time of collection and add 2 mL 3.5% ethylenediamine solution per 100 mL of sample.

4.4. Refer to Standard Methods for further information on possible interferences and associated treatments.

5. SAFETY

5.1. Employees must abide by the policies and procedures in the Corporate Safety Manual the Waste Management SOP, and this document.

5.2. In the event the sample begins to react unexpectedly during distillation, remove entire apparatus from heat source, set aside, and allow to cool. DO NOT ATTEMPT TO DISASSEMBLE GLASSWARE. Doing so may result in a sudden release of pressure with spraying of the sample.

5.3. Ensure cooling water is turned on to the distillation unit. Otherwise the samples may boil over and come into contact with the heating plates.

5.4. Latex, vinyl, Nitrile or similar gloves may be used.

5.5. Preparation of sodium hydroxide solutions produces considerable amounts of heat. Use plastic containers to mix this solution if possible. If glass containers are used, they must be free of any cracks or irregularities.

5.6. The acidification of samples prior to extraction/preparation can result in the release of a highly toxic gas, hydrogen cyanide.

5.7. If samples are identified with cyanide concentrations equal to or greater than 200 mg/L, immediately notify the department manager and personnel responsible for hazardous waste shipping. Those samples must be identified as extremely hazardous for other chemists and must receive special attention during disposal. **Potassium cyanide and sodium cyanide will give off Hyrdogen Cyanide (HCN) gas if combined with strong acids. Inhalation of CN gas can cause irritation, dizziness, nausea, unconsciousness and potentially death.**

5.8. Cyanide and cyanide salts are extremely toxic. Addition of acid can generate Hydrogen Cyanide gas, which can be extremely dangerous.

5.9. The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in

the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Potassium Cyanide	Poison Corrosive	5 Mg/M3 TWA as CN	**This material will form Hydrogen Cyanide (HCN) gas when combined with strong acids. Breathing HCN gas may result in death.** Corrosive to the respiratory tract. May cause headache, weakness, dizziness, labored breathing nausea and vomiting, which can be followed by weak and irregular heart beat, unconsciousness, convulsions, coma and death. Solutions are corrosive to the skin and eyes, and may cause deep ulcers, which heal slowly. May be absorbed through the skin, with symptoms similar to those noted for inhalation. Symptoms may include redness, pain, blurred vision, and eye damage.
Pyridine	Flammable Irritant	5 ppm-TWA	Inhalation causes severe irritation to the respiratory tract. Symptoms of overexposure include headache, dizziness, nausea, and shortness of breath. Causes severe irritation possibly burns, to the skin. Symptoms include redness and severe pain. Absorption through the skin may occur, resulting in toxic effects similar to inhalation. May act as a photosensitizer. Vapors cause eye irritation. Splashes cause severe irritation, possible corneal burns and eye damage.
Acetic Acid (1)	Corrosive Poison Flammable	10 ppm-TWA	Contact with concentrated solution may cause serious damage to the skin and eyes. Inhalation of concentrated vapors may cause serious damage to the lining of the nose, throat, and lungs. Breathing difficulties may occur.
Acetone	Flammable	1000 ppm-TWA	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.
Bismuth Nitrate	Oxidizer	None	May cause irritation to the respiratory tract, skin and eyes.

Sodium Hydroxide	Corrosive Poison	2 ppm, 5 mg/m^3 2 Mg/M3-Ceiling	This material will cause burns if comes into contact with the skin or eyes. Severe irritant. Effects from inhalation of dust or mist vary from mild irritation to serious damage of the upper respiratory tract, depending on severity of exposure. Symptoms may include sneezing, sore throat or runny nose. Contact with skin can cause irritation or severe burns and scarring with greater exposures. Causes irritation of eyes, and with greater exposures it can cause burns that may result in permanent impairment of vision, even blindness.
Potassium Phosphate	Flammable	None	Inhalation causes severe irritation to the respiratory tract. Causes severe irritation possibly burns, to the skin. Symptoms include redness and severe pain. .
Hydrochloric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Lead Carbonate	Poison Neurotoxin Irritant Probable carcinogen Reproduc-tive hazard	0.05mg/m3 TWA as Lead	Inhalation can cause local irritation of bronchia and lungs and can cause symptoms such as metallic taste in the mouth, chest and abdominal pain. Skin contact can cause local irritation, redness and pain. Can be absorbed through the skin.

Sulfuric Acid	Corrosive Oxidizer Dehydrator Poison Carcinogen	1 Mg/M3-TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.
Phosphoric Acid	Corrosive	1 mg/m^3 TWA	Inhalation is not an expected hazard unless misted or heated to high temperatures. May cause redness, pain, and severe skin burns. May cause redness, pain, blurred vision, eye burns, and permanent eye damage.
Barbituric Acid	Irritant	Not established	Limited information. Inhalation may irritate respiratory tract. Causes skin and eye irritation. Should be treated as potential health hazard; do not ingest.
Potassium Hydroxide	Poison Corrosive Reactive	2 mg/m^3 – Ceiling	Inhalation symptoms may include coughing, sneezing, damage to the nasal or respiratory tract. High concentrations can cause lung damage. Swallowing may cause severe burns of mouth, throat and stomach. Other symptoms may include vomiting, diarrhea. Severe scarring of tissue and death may result. Contact with skin can cause irritation or severe burns and scarring. Causes irritation of eyes with tearing, redness, swelling. Greater exposures cause severe burns with possible blindness.
Sodium Cyanide	Poison Corrosive	5 mg/m^3 TWA as CN (skin)	**This material will form Hydrogen Cyanide (HCN) gas when combined with strong acids. Breathing HCN gas may result in death.** Corrosive to the respiratory tract. May cause headache, weakness, dizziness, labored breathing nausea and vomiting, which can be followed by weak and irregular heartbeat, unconsciousness, convulsions, coma and death. Solutions are corrosive to the skin and eyes, and may cause deep ulcers, which heal slowly. May be absorbed through the skin, with symptoms similar to those noted for inhalation. Symptoms may include redness, pain, blurred vision, and eye damage.

Chloramine T Hydrate	Poison		May be harmful by inhalation, ingestion, or skin absorption. This material is irritating to mucous membranes and upper respiratory tract. Avoid contact and inhalation.
Zinc Acetate	Irritant	None Listed	Symptoms of skin or eye contact include redness, itching and pain.
Silver Nitrate	Corrosive Poison Oxidizer	$0.01 mg/m^3$ (TWA) for silver metal dust and fume as 0.02 Ag	This is a corrosive, poisonous material. It will cause burns to any area of contact and is harmful if inhaled. Ingestion may cause death. Contact with other material may cause fire. Inhalation symptoms may include burning sensation, coughing, wheezing, laryngitis, shortness of breath, headache, nausea, and vomiting. May be absorbed into the body following inhalation. Swallowing can cause severe burns of the mouth, throat and stomach. Can cause sore throat, vomiting, and diarrhea. Poison. Symptoms include pain and burning in the mouth, blackening of the skin and mucous membranes, throat, and abdomen, salivation, vomiting of black material, diarrhea, collapse, shock, coma and death. Skin contact can cause redness, pain and severe burns. Eye contact can cause blurred vision, redness, pain, severe tissue burns and eye damage.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

5.10 Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Cut resistant gloves must be worn doing any other task that presents a strong possibility of getting cut. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.11 Exposure to chemicals must be maintained **as low as reasonably achievable,** therefore, unless they are known to be non-hazardous, all samples must be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. All samples with pink stickers that read "Caution/Use Hood!" **must** be opened in the hood. Contact the EH&S Coordinator if this is not possible. Solvent and waste containers will be kept closed unless transfers are being made.

5.12 The preparation of standards and reagents will be conducted in a fume hood with the sash closed as far as the operation will permit.

5.13 All work must be stopped in the event of a known or potential compromise to the health and safety of a STL associate. The situation must be reported **immediately** to the EH&S Coordinator and the Laboratory Supervisor.

6. EQUIPMENT AND SUPPLIES

6.1. Cyanide Distillation Apparatus

6.2. Analytical balance, capable of accurately weighing ± 0.0001 g

6.3. Vacuum pump

6.4. Graduated cylinders: various

6.5. Volumetric flasks: various

6.6. Volumetric pipets: various

6.7. Balance: Top loading, capable of accurately weighing ± 0.01 g

6.8. Lead Acetate Indicator Paper

6.9. Potassium Iodide (KI) Indicator Paper

6.10. Erlenmeyer flasks: various

6.11. Buret: Class A 10 mL

6.12. pH strips

6.13. Boiling stones or chips

6.14. Beakers: various

6.15. Snap seal containers: 120 mL

6.16. Plastic bottles with lids: 250mL or 500mL

7. REAGENTS AND STANDARDS

7.1. Reagents

7.1.1. Sulfamic Acid: reagent grade (not used for CLP ILM03.0)

7.1.2. Sulfamic Acid Solution: Add 100 g of sulfamic acid to 800 mL reagent water and dilute to 1 liter with reagent water (not used for CLP ILM03.0)

7.1.3. Ascorbic Acid: reagent grade

7.1.4. Sodium Hydroxide: (NaOH), high purity grade.

7.1.5. Sodium Hydroxide, 1.25 N: Add 50 g of NaOH to 900 mL and dilute to 1 liter with reagent water.

7.1.6. Sodium Hydroxide, 0.25 N: Add 10 g of NaOH to 900 mL reagent water and dilute to 1 liter with reagent water. Purchased reagent may also be used.

7.1.7. Sulfuric Acid: (H_2SO_4), concentrated

7.1.8. Acetic Acid Solution: Add 10 mL of glacial acetic acid to 90 mL of reagent water.

7.1.9. Magnesium Chloride: ($MgCl_2 \bullet 6H_2O$), reagent grade

7.1.10. Magnesium Chloride Solution: Add 510 g $MgCl_2 \bullet 6H_2O$ to 500 mL reagent water and dilute to 1 liter with reagent water. Purchased reagent may also be used.

7.1.11. Calcium Hypochlorite: [Ca $(OCl)_2$], reagent grade

7.1.12. Calcium Hypochlorite Solution: Add 5 g of $Ca(OCl)_2$ to 100 mL of reagent water.

7.1.13. Methyl Red Indicator: Add 0.05 g of methyl red to 50 mL of glacial acetic acid and dilute to 100 mL with reagent water.

7.1.14. Methyl red reagent grade glacial

7.1.15. Acetic Acid: (CH_3COOH), glacial reagent grade

7.1.16. Zinc Acetate: [$Zn(C_2H_3O_2)$], reagent grade

7.1.17. Zinc Acetate Solution: Add 100 g zinc acetate to 800 mL reagent water and dilute to 1 liter with reagent water.

7.1.18. Sodium Acetate: [$NaC_2H_3O_2 \bullet 3H_2O$] reagent grade

7.1.19. Sodium Acetate Buffer: Add 410 g of sodium acetate to 500 mL of reagent water. Adjust the pH to 4.5 using glacial acetic acid and dilute to 1 liter with reagent water.

7.1.20. Rhodanine: reagent grade

7.1.21. 0.0192 N Silver Nitrate: reagent grade

7.1.22. Bismuth nitrate [$Bi(NO_3)_3$]: Dissolve 30 g of $Bi(NO_3)_3$ in 100 mL of reagent water. While stirring, add 250 mL of glacial acetic acid. Stir until dissolved. Dilute to 1 L with reagent water.

7.1.23. Cadmium chloride [$CdCl_2$] – anhydrous : Dissolve 1.0 g $CdCl_2$ in 90 mL of reagent water. Dilute to 100 mL with reagent water to produce a 10 g/L $CdCl_2$ solution.

7.2. Standards

7.2.1. Primary Source Cyanide Stock Standard, 1000 mg/L: Add 2.51 g of potassium cyanide (KCN) and 2.0 g of potassium hydroxide (KOH) to a 1000 mL volumetric flask and dilute to volume with reagent water. Mix well and store in glass amber container. Stable for 1-3 months.

Note: This stock standard may also be purchased.

Note: This stock standard must be standardized prior to use. See SOP NC-WC-0031 Appendix I

7.2.2. Secondary Source Cyanide Standard, 1000 mg/L: Follow 7.2.1 using an alternate source of Potassium Cyanide (KCN).

Note: This stock standard may also be purchased.

Note: This stock standard must be standardized prior to use. See SOP NC-WC-0031 Appendix I.

7.2.3. Calibration Standards (Water and Solid Matrices)

7.2.3.1. If using the 1.25 N NaOH: pipet the appropriate amount of cyanide standard into 100 mL volumetric and add 20 mL 1.25N NaOH to each calibration standard (except the 1.0 mg/L) and bring to volume with reagent water.

If using the purchased 0.25N NaOH: pipet the appropriate amount of cyanide standard into 100 mL volumetric and bring to volume with 0.25N NaOH. Prepare weekly.

Concentration CN-	mL CN-	Final Volume
100 mg/L	10 mL of 1000 mg/L	100 mL
10 mg/L	10 mL of 100 mg/L	100 mL
1.0 mg/L	10 mL of 10 mg/L	100 mL
*0.2 mg/L	20 mL of 1 mg/L	100 mL
*0.1 mg/L	10 mL of 1 mg/L	100 mL
*0.05 mg/L	5 mL of 1 mg/L	100 mL
*0.025 mg/L	25 mL of 0.1 mg/L	100 mL
*0.01 mg/L	10 mL of 0.1 mg/L	100 mL
*0.005 mg/L	10 mL of 0.05 mg/L	100 mL

*Denotes calibration standards

8. SAMPLE PRESERVATION AND STORAGE

8.1. Solid and liquid samples are not chemically preserved. Water samples are preserved with NaOH to a pH>12. All samples are stored at 4° C ± 2°C in plastic or glass containers.

8.2. The holding time for **non-CLP** samples is fourteen days from sampling to analysis.

8.3. The holding time for **CLP** samples holding time is twelve days from receipt to analysis.

9. QUALITY CONTROL

9.1. Batch Definition

9.1.1. **Non-CLP**

A batch is a group of no greater than 20 samples excluding QC samples (LCS, Method Blank, MS, MSD) which are processed similarly, with respect to the procedure. All sample setups must be initiated within a 24 hour period from the initial preparation or extraction and without interruption of the process. All samples within the batch must be treated with the same lots of reagents and the same process.

9.1.2. **CLP**:

A batch is a group of no greater than 20 samples excluding QC samples (LCS/ICV, Method Blank, Sample Duplicate and Matrix Spike) which are processed similarly, with respect to the procedure. All sample setups must be initiated within a 24 hour period from the initial preparation or extraction and without interruption of the process. All samples within the batch must be treated with the same lots of reagents and the same processes.

9.2. Method Blank (MB)

9.2.1. **Non-CLP**

One method blank (MB) must be processed with each preparation batch. The method blank consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. The method blank should not contain any analyte of interest at or above the reporting limit.

9.2.1.1. A method blank consists of 50 mL 0.25N NaOH for Total Cyanide analysis or 50 mL reagent water for Free and Amenable Cyanide analysis. The blank must be distilled and analyzed with each analytical batch of samples.

9.2.2. CLP:

Each SDG (sample delivery group) must have one method blank processed per matrix and per twenty samples. If the SDG is distilled over multiple "racks", the method blanks must be distilled with the samples. If more than one SDG is on one rack, process one method blank per SDG and per matrix. The solid method blank is called "PBS" (prep blank solid) and the water method blank is called "PBW" (prep blank water).

9.2.2.1. A method blank (PBW/PBS) consisting of 50 mL 0.25N NaOH must be distilled and analyzed with each analytical batch of samples.

9.2.3. Corrective Action for Blanks

9.2.3.1. If the analyte level in the method blank exceeds the reporting limit for the analytes of interest in the sample, all associated samples are reprepared and reanalyzed. If this is not possible due to limited sample quantity or other considerations, the corresponding sample data **must be addressed in the project narrative.**

9.2.3.2. If there is no analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. **Such action must be taken in consultation with the client and must be addressed in the project narrative.**

9.3. Laboratory Control Sample (LCS)

9.3.1. One LCS must be processed with each preparation batch. The LCS must be carried through the entire analytical procedure. The LCS is used to monitor the accuracy of the analytical process. On-going monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines.

9.3.2. **Non-CLP**:

A midrange LCS consisting of a 0.04 mg/L (2.0 mL of 1.0 mg/L secondary source to 50 mL) must be distilled and analyzed with each analytical batch of samples for Total, Amenable, and Free cyanide analysis.

NOTE: A purchased complex cyanide solution may be used instead as the midrange LCS for **Total Cyanide** analysis only.

9.3.2.1.The acceptance limits for drinking water samples is 90 – 110%.

9.3.3. **CLP:**

9.3.3.1. A LCS (which doubles as an ICV) is processed with each batch or each SDG,which ever is more frequent. Even if multiple SDG's are on the "rack", only one LCS (ICV) needs to be distilled for up to a maximum of 20 samples.

NOTE: A "rack" is one setup of cyanide samples and QC, and can encompass 1 – 3 of the midi-distillation units.

9.3.3.2. For CLP waters: the LCS is 4.0 mL of 1.0 ppm secondary source in 50 mL (TV = 80ug/L).

9.3.3.3. For CLP solids: a solid LCS must be processed per SDG or per batch, which ever is more frequent. If more than one batch is processed on a "rack", process a solid LCS for each one. If a SDG has solid samples distilled on a different "rack", then additional solid LCSs will need to be distilled. The value for the LCS changes as the solid lot numbers change each time a new one is ordered. The value is noted on the product certification.

9.3.3.4. If more than one SDG is distilled on one rack, they may be analyzed together (however, it is **preferred** that each SDG be **analyzed separately**). It is also **preferred** that each SDG have its own method blank(s), its own ICV (LCS), its own LCS-S (if samples are solids), and its own sample duplicate and matrix spike. If the SDG has been split over multiple distillation "racks", then you may not have a sample duplicate and matrix spike for each rack. However, an ICV (LCS) is distilled with each "rack". If more than one SDG is distilled on a "rack", then the ICV (LCS) distilled with that rack must be analyzed with each SDG.

9.3.4. Corrective Action for Laboratory Control Samples

9.3.4.1. If any analyte is outside established control limits the system is out of control and corrective action must occur.

9.3.4.2. Corrective action will be repreparation and reanalysis of the batch unless the client agrees that other corrective action is acceptable.

9.4. Matrix Spike/Matrix Spike Duplicate (MS/MSD)

9.3.1. **Non-CLP**

One MS/MSD pair must be processed for each batch. A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added. A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked identically as the MS) prepared and analyzed along with the sample and matrix spike. Some client specific data quality objectives (DQO's) may require the use of sample duplicates in place of or in addition to MS/MSD's. The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Due to the potential variability of the matrix of each sample, these results may have immediate bearing only on the specific sample spiked. Samples identified as field blanks cannot be used for MS/MSD analysis.

9.4.1.1. A MS/MSD consisting of 50 mL or 1.0 g of sample brought up to 50 mL with reagent water and 2.0 mL of the 1.0 mg/L standard (either source) must be distilled with each analytical batch of samples.

9.4.1.2. The acceptance limits for drinking water samples is 90 – 110%.

9.4.2. **CLP:**

Each SDG must have a sample duplicate and a matrix spike processed per matrix. Sometimes this requirement is waived by the client or PM but, if uncertain, make sure that these are done. Usually , the sample to be spiked is assigned, but not always. If a MS/MSD is created in receiving, either batch the MSD and "N/A" the result or have the MSD deleted. In either case, create a sample duplicate for the sample that is spiked when batching. If processing a SDG over more than one "rack", then there is no need to process additional matrix spikes and sample duplicates (unless specifically requested). Typically, only one sample duplicate and matrix spike is required per SDG.

9.4.2.1. Matrix spike for CLP consists of 50 mL or 1.0 g of sample and 100 µg/L spike (5.0 mL of 1.0 mg/L secondary standard).

NOTE: see corrective action section 9.4.3.4 for A-spike

9.4.3. Corrective action for MS/MSDs

9.4.3.1. If the analyte recovery or RPD falls outside the acceptance range, the recovery of that analyte must be in control for the LCS. If the LCS recovery is within limits, then the laboratory operation is in control and the results may be accepted. If the recovery of the LCS is outside limits, corrective action must be taken. Corrective action will include repreparation and reanalysis of the batch.

9.4.3.2. If the native analyte concentration in the MS/MSD exceeds 4x the spike level for that analyte, the recovery data is reported as MSB and NC for the exception code. The A-spike is not needed in this case.

9.4.3.3. If an MS/MSD is not possible due to limited sample volume then a laboratory control sample duplicate (LCSD) should be analyzed. The RPD of the LCS and LCSD must be compared to the matrix spike RPD limits.

9.4.3.4. A-spike corrective action: if spike recovery fails criteria, then spike the sample at two times the reporting limit or 2 times the sample concentration, which ever is greater. Examples are shown below.

*A-spike = 2 mL of sample + 2mL of A-spike solution

A-spike solution = 0.8 mL .25N NaOH, +3.2 mL 0.05 ppm 1° standard.

9.5 Control Limits

9.5.1 Control limits are established by the laboratory as described in SOP, NC-QA-0018.

9.5.2 Laboratory control limits are internally generated and updated periodically unless method specified. Control limits are listed in the Laboratory Quality Manual (LQM) and the latest is version easily accessible via the LIMs (QC Browser program).

9.6 Method Detection Limits (MDLs) and MDL Checks

9.6.1 MDLs and MDL Checks are established by the laboratory as described in SOP, NC-QA-0021 and S-Q-003.

9.6.2 MDLs are listed in the Laboratory Quality Manual (LQM) and the latest version is easily accessible via the LIMs (QC Browser program).

9.7 Nonconformance and Corrective Action

9.7.1 Any deviations from QC procedures must be documented as a nonconformance, with applicable cause and corrective action approved by the facility QA Manager.

10. CALIBRATION AND STANDARDIZATION

10.1. **Non-CLP**:

A Low and High standard are distilled from the same source as the calibration curve each day. Prepare the Low standard (0.025mg/L) by diluting 0.125 mL of 10 ppm standard with reagent water to a final volume of 50 mL. Prepare the High standard (0.075 mg/L) by diluting 0.375 mL of 10 ppm standard with reagent water to a final volume of 50 mL. The distilled standards are evaluated against all applicable batch QC.

10.2. **CLP**:

The Low and High standards do not have to be evaluated for CLP.

11. PROCEDURE

11.1. One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and is approved by a Technical Specialist and QA Manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file.

11.2. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described

11.3Summary

11.3.1 Non-CLP

For all non-CLP methods, the sample is distilled/refluxed under acidic conditions for one hour. The released HCN is trapped in 50 mL of 0.25 N NaOH solution.

11.3.2 For CLP and Drinking Water (EPA 335.4) methods, the samples are distilled for one and a half hours. The released HCN is trapped in 0.25 N NaOH solution.

11.4. Sample Preparation Procedure applicable for use with the Midi distillation unit.

11.4.1. Checking for Interferences (For non-CLP samples)

11.4.1.1. Using pH paper strips, check the pH of the sample and record it as >12 or <12 on the analytical logsheet. If pH is <12, the deviation **must be addressed in the project narrative.**

11.4.1.2.For **ALL samples** (non-CLP and CLP samples): Test each sample for the presence of sulfides using lead acetate paper. If sulfides are present, treat the sample with powdered cadmium carbonate. Yellow cadmium sulfide precipitates if the sample contains sulfide. Repeat this operation until a drop of the treated sample solution does not darken the lead acetate test paper. Filter the solution. Avoid a large excess of cadmium carbonate and long contact time in order to minimize loss by complexation or occlusion of cyanide on the precipitated material.

11.4.1.3. **All Samples**: Test each sample for the presence of chlorine using potassium iodide test strips. Document this on the analytical logsheet.

11.4.2. Complex Cyanide Preparation Procedure [THIS PROCESS IS PERFORMED ONLY WHEN REQUESTED BY THE CLIENT]: Add 100 mL of water sample or 2.0 g of solid sample and 100 mL reagent water to a plastic, sealable container. Add 10 g NaOH pellets. Mix or tumble for 12-16 hours. Allow solids to settle out. Transfer 50 mL of the solution to the distillation tube. Distill sample (See section 11.4.4.1).

Note: If the sample requires an MS/MSD or MS/Dup, double or triple the volumes as stated above. A blank and LCS should be prepared and analyzed with samples using 10 g NaOH and 100 mL reagent water.

11.4.3. Amenable Cyanide (Chlorinated Aliquot) [THIS PROCESS IS PERFORMED ONLY WHEN REQUESTED BY THE CLIENT]

11.4.3.1.Place 50 mL (waters) or 1.0 g (solids/liquids) into a beaker. Add 50 mL of reagent water to non-waters. Place the beaker on a stir plate and begin mixing. Test the pH of the solution, if less than 12 add 1.25 N NaOH, drop by drop until pH $\geq$ 12. Drop by drop, add calcium hypochlorite until an excess of chlorine is reached. Test for chlorine excess using KI paper. Allow the sample to chlorinate for one hour. At the end of the chlorination period, add about 0.1 to 0.5 g of ascorbic acid to destroy excess chlorine. Test using KI paper. Keep the addition of ascorbic acid to a minimum. Pour the sample into a distillation flask and follow the total cyanide preparation method (Section 11.4.4). Also set up an unchlorinated aliquot of sample (50 mL or 1.0 g) following the total cyanide method.

11.4.4. Total Cyanide

11.4.4.1. Add 50 mL or 1.0 g of the sample and 2 - 3 boiling chips to the distillation tube. Bring the final volume to 50 mL with reagent water. Add 50 mL of 0.25 N NaOH solution to the absorber tube and assemble the scrubber. Assemble the cyanide distillation apparatus.

NOTE: If solid samples are being prepared under the Michigan program, the initial solid weight is 2.5 g

11.4.4.2. Turn on the cooling water to "60". Turn on the vacuum source and adjust the flow such that even stream of air bubbles are in the scrubber tube approximately $^1/_4$ " of foam or 1-2 bubbles per second. At this time add any spiking solutions to the LCS or MS/MSDs samples directly into the inlet tube.

11.4.4.3. In the order stated, add 2.0 mL sulfamic acid solution (not for CLP ILM03.0 samples), 2.5 mL of concentrated sulfuric acid and 2.0 mL of magnesium chloride solution to the distillation tube. Be sure to rinse the inlet tube sparingly with reagent water between and after reagent additions.

Note: Complex cyanide samples require an additional 2.5 mL of sulfuric acid. Be sure the pH is < 2.

11.4.4.4. Flip the heater switch to "on" and turn the dial to an appropriate setting (according to manufacturer's instructions) to allow the apparatus to warm up. Be sure to adjust the air flow and water as necessary. Heat for one hour. After the heating period, the heater will turn off automatically. Allow to cool for fifteen minutes. Keep the vacuum and cooling water on.

11.4.4.5. Disconnect the absorber. Pour solution into a 120 mL snap seal container. Do not rinse the scrubber tube or dilute NaOH in the snap seal. Be sure to properly label the bottles "total" or "amenable" along with sample ID, position and date.

11.4.5. Free Cyanide (Weak and Dissociable) [THIS PROCESS IS PERFORMED ONLY WHEN REQUESTED BY THE CLIENT]

11.4.5.1. Add 50 mL or 1.0 g of sample to the distillation tube. Bring all volumes up to 50 mL with reagent water. Add 50 mL of 0.25 N NaOH to the absorber tube and assemble.

11.4.5.2. Turn on cooling water to "60". Turn on the vacuum source. Add any spiking standards to the appropriate LCS or MS/MSDs at this time. Through the inlet tube, add 1.0 mL of sodium acetate buffer, 1.0 mL of zinc acetate, and 0.25 mL of methyl red indicator. Rinse the inlet tube sparingly with reagent water between and after reagent additions. If the sample is not red, carefully add 1:9 acetic acid dropwise until the sample

does turn red. Check the sample color periodically throughout the distillation hour to ensure the sample stays red.

Reminder: Do not use the complex purchased cyanide solution standard as the LCS for Free cyanide analysis.

11.4.5.3. Flip on the heater switch and turn the dial to "10.5" (This allows the apparatus to warm up). Adjust the air flow and water as needed. Heat for 1 hour. After the heating period, the heater will shut off automatically. Allow the sample to cool for fifteen minutes with the air and water on.

11.4.5.4. Pour the scrubber contents into a 120 mL snap seal bottle. Do not rinse the scrubber. Label the bottle well and be sure to denote that it is a "free" sample distillate.

11.4.6. CLP Cyanide distillation

11.4.6.1. Add 50 mL or 1.0 g of sample to the distillation tube. Bring all volumes up to 50 mL with reagent water. Add 50 mL of 0.25 N NaOH to the absorber tube and assemble.

11.4.6.2. Turn on cooling water to "60". Turn on the vacuum source and adjust the flow such that even stream of air bubbles are in the scrubber tube approximately ¼ " of foam or 1 –2 bubbles per second. At this time add any spiking solutions to the LCS or MS samples directly into the inlet tube.

11.4.6.3. In the order stated, add 2.5 mL of concentrated sulfuric acid and 2.0 mL of magnesium chloride solution to the distillation tube. Be sure to rinse the inlet tube sparingly with reagent water between and after reagent additions.

11.4.6.4. Flip the heater switch to "on" and turn the dial to an appropriate setting to allow the apparatus to warm up. Be sure to adjust the air flow and water as necessary. Heat for one and a half hours. After the heating period, allow to cool for fifteen minutes. Keep the vacuum and cooling water on.

11.4.6.5. Disconnect the absorber. Pour solution into a snap seal container. Do not rinse the scrubber tube or dilute NaOH in the snap seal. Be sure the properly label the snap seals with the sample ID.

11.4.7 Cyanide Unit Clean-up

11.4.7.1 Cyanide distillation unit glassware is very fragile and expensive. It must be handled with care at all times.

11.4.7.2 Disassemble each set-up and rinse the sample down the drain with large amounts of water. Be sure to collect the solids in a screen and dispose of properly.

11.4.7.3 Wash each set-up with soap and hot water. Rinse several times with reagent water. **After preparing samples found to be extremely high in cyanide, a subsequent rinse with 1.0N NaOH, followed by further rinsing with reagent water can help rinse away any residual cyanide. If contamination is suspected, distill 1.0N NaOH through the system.

11.4.7.4 Re-assemble the set-up.

11.4.7.5 Be sure to wash each set up as a separate unit and replace in the same position.

11.4.7.6 If a sample of known high cyanide concentration was distilled in a certain position, be sure to change the appropriate tubing on that position.

11.5 Analytical Documentation

11.5.1 Record all analytical information in the analytical logbook/logsheet, including the analytical data from standards, blanks, LCSs, MS/MSDs, and any corrective actions or modifications to the method.

11.5.2 All standards are logged into a department standard logbook. All standards are assigned an unique number for identification. Logbooks are reviewed by the supervisor or designee.

11.5.3 Documentation such as all associated instrument printouts (final runs, screens, reruns, QC samples, etc.) and daily calibration data corresponding to all final runs is available for each data file.

11.5.4 Sample results and associated QC are entered into the LIMs after final technical review.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Not applicable

13. METHOD PERFORMANCE

13.1. Each laboratory must have initial demonstration of performance data on file and corresponding method detection limit files.

13.2. Training Qualifications:

13.2.1. The group/team leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience.

13.2.2. Method validation information (where applicable) in the form of laboratory demonstrations of capabilities is maintained for this method in the laboratory QA files

14. POLLUTION PREVENTION

14.1. Using a Midi Cyanide distillation unit saves time and requires less sample and reagents for use.

15. WASTE MANAGEMENT

15.1 All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

15.2 Waste Streams Produced by the Method

15.2.1 The following waste streams are produced when this method is carried out.

15.2.1.1 Acidic waste. This waste is disposed of in the designated container labeled "Acid Waste".

15.2.1.2 Caustic waste containing Pyridine. This waste is disposed of in a designated container identified as "Pyridine Waste".

15.3. Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices of STL. They must have training on the hazardous waste disposal practices upon initial assignment to these tasks, followed by an annual refresher training.

16. REFERENCES

16.1. References.

16.1.1. SW846, Test Methods for Evaluating Solid Waste, Third Edition, Total and Amenable Cyanide, Automated UV; Method 9012A.

16.1.2. EPA 600; Cyanide, Total and Cyanide, Amenable to Chlorination; Methods 335.1, 335.4, and 335.2

16.1.3. Standard Methods for the Examination of Water and Wastewater, Eighteenth Edition; Weak and Dissociable Cyanide; Method 4500-CN-I

16.1.4. Standard Methods for the Examination of Water and Wastewater, Eighteenth Edition; Complex Cyanide; Method 4500-CN-E

16.1.5. USEPA CLP SOW ILM03.0 Section D-Cyanide Midi Distillation

16.1.6. Corporate Quality Management Plan (QMP), current version

16.1.7. STL Laboratory Quality Manual (LQM), current version

16.1.8 STL Corporate Safety Manual, M-E-0001 and STL North Canton Facility Addendum and Contingency Plan, current version.

16.2. Associated SOPs and Policies, latest version

16.2.1. QA Policy, QA-003

16.2.2 Glassware Washing, NC-QA-0014

16.2.3 Statistical Evaluation of Data and Development of Control Charts, NC-QA-0018

16.2.4 Method Detection Limits and Instrument Detection Limits, NC-QA-0021 and S-Q-003

16.2.5 Navy/Army SOP, NC-QA-0016

16.2.6 Cyanide, Automated Method NC-WC-0031

17. MISCELLANEOUS (TABLES, APPENDICES, ETC...)

17.1. BASF RFI Requirements

17.1.1. Amendments to this SOP to satisfy BASF RCRA Facility Investigation (RFI) requirements are based on comments from US EPA upon review of site requirements and laboratory procedures.

17.1.2. Amendment to the preparation of **all** samples

17.1.2.1. **Section 7.2.1**: Change 2.51 g of potassium cyanide to 2.11g potassium ferricyanide.

17.1.2.2. **Section 9.4**: The matrix spike/duplicate frequency has been increased from one per batch to one per 7 samples. Consult with the project manger for specific samples to be spiked. The goal is to spike each sampling area at the site at least once.

17.1.3. Amendment to the preparation of **Prussian blue area** samples

17.1.3.1. **Section 7.1.22**: Sodium thiocyanate (reagent grade): Prepare a spiking solution at a concentration 100X greater than the measured cyanide for the appropriate Prussian blue area samples.

17.1.3.2. **Section 9.5**: Three Prussian blue area samples will be spiked with 1 mL of the sodium thiocyanate solution (Section 17.1.3.1) in order to assess the potential impact of thiocyanate in the original samples on the measured cyanide concentration. These matrix spikes do not replace the cyanide matrix spikes mentioned above (Section 17.1.2.2). The increase (if any) in measured cyanide concentration relative to the original sample shall be reported as "percentage increase" using the following equation:

$$\%CN_{increase} = \frac{Conc_{SCN\_spike} - Conc_{unspiked}}{Conc_{unspiked}} \times 100$$

where

$Conc_{SCN\_spike}$ = *cyanide concentration measured in the thiocyanate spiked sample*

$Conc_{unspiked}$ = *cyanide concentration measured in the unspiked sample*

Note: Section 11.3.2.1 of NC-WC-0031 addresses sulfide testing and precipitation.

17.2. Method Deviation (9012A, 335.1, 335.2)

17.2.1. The reflux distillation apparatus used is the midi distillation.

17.2.2. The volume of sample used is reduced to 50 mL vs. 500 mL using the midi-distillation apparatus.

17.2.3. Method of Standard Addition is not performed for samples with matrix interference (sulfides)

TestAmerica

THE LEADER IN ENVIRONMENTAL TESTING

TestAmerica North Canton

SOP No. NC-WC-0031, Rev. 8
Effective Date: 11/08/04
Cover Page

Title: Cyanide, Automated Pyridine-Barbituric Acid
[Methods: SW9012A, EPA335.1, 335.2, SM4500CN-I CLP]

Approvals (Signature/Date):

Technology Specialist	12/14/07 Date	Health & Safety Coordinator	12-14-07 Date
Quality Assurance Manager	12/13/07 Date	Laboratory Director	12/14/07 Date

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STL NORTH CANTON STANDARD OPERATING PROCEDURE

TITLE: CYANIDE AUTOMATED, PYRIDINE-BARBITURIC ACID METHOD

(SUPERSEDES: REVISION 7 DATED 05/31/01)

Prepared by: _____ 11/16/04 Date

Reviewed by: _____ 11/16/04
Technology Specialist Date

Approved by: _____ 11/19/04
Quality Assurance Manager Date

Approved by: _____ 11-15-04
Environmental Health and Safety Coordinator Date

Approved by: _____ 11/22/04
Laboratory Director Date

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1. SCOPE AND APPLICATION

1.1. This method is applicable to the determination of Total, Amenable, and Free Inorganic Cyanide in solids, liquids, and waters. It is based on CLP ILM03.0, CLP ILM04.0, SW846 Method 9012A, 335.2, 335.4 and Standard Method 4500-CN-E. The working linear range is 0.005 - 0.2 mg/L for waters and 0.25 to 10 mg/kg for solids.

1.2. This document accurately reflects current laboratory standard operating procedures (SOP) as of the date above. All facility SOPs are maintained and updated as necessary.

1.3. The associated method codes are CLP ILM03.0 (DV), CLP ILM04.0 (OU), SW846 Method 9012A (QP), EPA 335.1(CF), 335.2 (CG), EPA 335.4 (O2), and Standard Method 4500-CN-E (A4).

2. SUMMARY OF METHOD

2.1. The Cyanide, as HCN, is released by distilling/refluxing the sample with strong acid and is trapped in a sodium hydroxide solution.

2.2. The sodium hydroxide solution is analyzed colormetrically on an autoanalyzer using the pyridine-barbituric acid method.

3. DEFINITIONS

3.1. Refer to the glossary in the Laboratory Quality Manual (LQM), latest version.

4. INTERFERENCES

4.1. Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus that lead to discrete artifacts. All of these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. Specific selection of reagents may be required to avoid introduction of contaminants.

4.2. Sulfides interfere, but can be eliminated by treating the sample with cadmium carbonate prior to analysis.

5. SAFETY

5.1. Employees must abide by the policies and procedures in the Corporate Safety Manual and this document.

5.2. Ensure cooling water is turned on to the distillation unit. Otherwise the samples may boil over and come into contact with the heating plates.

5.3. Preparation of sodium hydroxide solutions produces considerable amounts of heat. Use plastic containers to mix this solution if possible. If glass containers are used, they must be free of any cracks or irregularities.

5.4. The acidification of samples prior to extraction/preparation can result in the release of a highly toxic gas, hydrogen cyanide.

5.5. If samples are identified with cyanide concentrations equal to or greater than 200 mg/L, immediately notify the department manager and personnel responsible for hazardous waste shipping. Those samples must be identified as extremely hazardous for other chemists and must receive special attention during disposal.

5.6. Potassium cyanide and sodium cyanide will give off Hyrdogen Cyanide (HCN) gas if combined with strong acids. Inhalation of CN gas can cause irritation, dizziness, nausea, unconsciousness and potentially death.

5.7. Cyanide and cyanide salts are extremely toxic. Addition of acid can generate Hydrogen Cyanide gas, which can be extremely dangerous.

5.8. The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure

Potassium Cyanide	Poison Corrosive	5 Mg/M3 TWA as CN	**This material will form Hydrogen Cyanide (HCN) gas when combined with strong acids. Breathing HCN gas may result in death.** Corrosive to the respiratory tract. May cause headache, weakness, dizziness, labored breathing nausea and vomiting, which can be followed by weak and irregular heart beat, unconsciousness, convulsions, coma and death. Solutions are corrosive to the skin and eyes, and may cause deep ulcers, which heal slowly. May be absorbed through the skin, with symptoms similar to those noted for inhalation. Symptoms may include redness, pain, blurred vision, and eye damage.
Pyridine	Flammable Irritant	5 ppm-TWA	Inhalation causes severe irritation to the respiratory tract. Symptoms of overexposure include headache, dizziness, nausea, and shortness of breath. Causes severe irritation possibly burns, to the skin. Symptoms include redness and severe pain. Absorption through the skin may occur, resulting in toxic effects similar to inhalation. May act as a photosensitizer. Vapors cause eye irritation. Splashes cause severe irritation, possible corneal burns and eye damage.
Bismuth Nitrate	Oxidizer	None	May cause irritation to the respiratory tract, skin and eyes.
Sodium Hydroxide	Corrosive Poison	2 ppm, 5 mg/m^3 2 Mg/M3-Ceiling	This material will cause burns if comes into contact with the skin or eyes. Severe irritant. Effects from inhalation of dust or mist vary from mild irritation to serious damage of the upper respiratory tract, depending on severity of exposure. Symptoms may include sneezing, sore throat or runny nose. Contact with skin can cause irritation or severe burns and scarring with greater exposures. Causes irritation of eyes, and with greater exposures it can cause burns that may result in permanent impairment of vision, even blindness.
Potassium Phosphate	Flammable	None	Inhalation causes severe irritation to the respiratory tract. Causes severe irritation possibly burns, to the skin. Symptoms include redness and severe pain. .

Sodium Phosphate		None	Inhalation may cause respiratory tract irritation. Can produce delayed pulmonary edema. Causes mild skin and eye irritation. Injestion may cause gastrointestinal irritation.
Hydrochloric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Cadmimum Carbonate	Probable carcinogen	0.01 mg/ m^3 as Cd	Ingestion causes increated salivation, choking, vomiting, stomach pains and diahrrea. Inhalation may cause respiratory irritation, nausea and dyspnea.
Sulfuric Acid	Corrosive Oxidizer Dehydrator Poison Carcinogen	1 Mg/M3-TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.
Barbituric Acid	Irritant	Not established	Limited information. Inhalation may irritate respiratory tract. Causes skin and eye irritation. Should be treated as potential health hazard; do not ingest.
Potassium Hydroxide	Poison Corrosive Reactive	2 mg/m^3 – Ceiling	Inhalation symptoms may include coughing, sneezing, damage to the nasal or respiratory tract. High concentrations can cause lung damage. Swallowing may cause severe burns of mouth, throat and stomach. Other symptoms may include vomiting, diarrhea. Severe scarring of tissue and death may result. Contact with skin can cause irritation or severe burns and scarring. Causes irritation of eyes with tearing, redness, swelling. Greater exposures cause severe burns with possible blindness.

Sodium Cyanide	Poison Corrosive	5 mg/m^3 TWA as CN (skin)	**This material will form Hydrogen Cyanide (HCN) gas when combined with strong acids. Breathing HCN gas may result in death.** Corrosive to the respiratory tract. May cause headache, weakness, dizziness, labored breathing nausea and vomiting, which can be followed by weak and irregular heartbeat, unconsciousness, convulsions, coma and death. Solutions are corrosive to the skin and eyes, and may cause deep ulcers, which heal slowly. May be absorbed through the skin, with symptoms similar to those noted for inhalation. Symptoms may include redness, pain, blurred vision, and eye damage.
Chloramine T Hydrate	Poison		May be harmful by inhalation, ingestion, or skin absorption. This material is irritating to mucous membranes and upper respiratory tract. Avoid contact and inhalation.
Zinc Acetate	Irritant	None Listed	Symptoms of skin or eye contact include redness, itching and pain.
Silver Nitrate	Corrosive Poison Oxidizer	0.01 mg/m 3 (TWA) for silver metal dust and fume as 0.02 Ag	This is a corrosive, poisonous material. It will cause burns to any area of contact and is harmful if inhaled. Ingestion may cause death. Contact with other material may cause fire. Inhalation symptoms may include burning sensation, coughing, wheezing, laryngitis, shortness of breath, headache, nausea, and vomiting. May be absorbed into the body following inhalation. Swallowing can cause severe burns of the mouth, throat and stomach. Can cause sore throat, vomiting, and diarrhea. Poison. Symptoms include pain and burning in the mouth, blackening of the skin and mucous membranes, throat, and abdomen, salivation, vomiting of black material, diarrhea, collapse, shock, coma and death. Skin contact can cause redness, pain and severe burns. Eye contact can cause blurred vision, redness, pain, severe tissue burns and eye damage.

1 – Always add acid to water to prevent violent reactions.

2 – Exposure limit refers to the OSHA regulatory exposure limit.

5.9. Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Cut resistant gloves must be worn doing any other task that presents a strong possibility of getting cut. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned.

5.10. Exposure to chemicals must be maintained **as low as reasonably achievable**, therefore, unless they are known to be non-hazardous, all samples must be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

5.11. It is recommended that neat standards be purchased only as a last resort. The preparation of standards from neat materials and reagents {as well as glassware cleaning procedures that involved solvents such as methylene chloride} should be conducted in a fume hood with the sash closed as far as the operations will permit.

5.12. Standards in solution may be diluted in the open laboratory when syringes and the like are utilized.

5.13. All work must be stopped in the event of a known or potential compromise to the health and safety of a STL associate. The situation must be reported **immediately** to the EH&S Coordinator and to a laboratory supervisor.

6. EQUIPMENT AND SUPPLIES

6.1. Traacs 800 autoanalyzer or discrete autoanalyzer (Konelab)

6.2. Probe 0.016"

6.3. Flowcell 10mm

6.4. Wavelength cell 570nm

6.5. Manifold-Multitest cartridge with cyanide tubing

6.6. 4mL Cuvettes

6.7. 100 mL, 250 mL, 1000 mL volumetric flasks

6.8. Volumetric pipettes: various

6.9. Top loading balance: capable of accurately weighing ± 0.01g.

7. REAGENTS AND STANDARDS

7.1. Reagents

7.1.1. Cadmium carbonate: powder

7.1.2. 1.25 N sodium hydroxide: Add 50 g of sodium hydroxide pellets (NaOH) to a 1 liter volumetric flask and dilute to volume with reagent water.

7.1.3. Phosphate buffer: Add 136 g of potassium phosphate - monobasic (KH_2PO_4) and 2.8 g of sodium phosphate – dibasic anhydrous (Na_2HPO_4) to 800 mL of reagent water in a 1 liter volumetric flask. Mix, bring to volume with reagent water. Add 3-5 drops of Brij-35 to 100 mL of Buffer prior to using.

7.1.4. Chloramine-T reagent: Add 1.0 g of chloramine-T to a 250 mL volumetric flask and dilute to volume with reagent water. Prepare fresh daily.

7.1.5. Pyridine reagent: Add 15.0 g of barbituric acid to a 1 liter volumetric flask. Add 75 mL of pyridine and 15 mL of concentrated hydrochloric acid (HCl) and mix. Bring to volume with reagent water and store at 4°C ± 2°C in an amber glass bottle.

Note: the pyridine barbituric acid may be purchased commercially. Filter 50 ml of the pyridine barbituric acid and bring up to 250 ml with DI water.

7.1.6. 0.25 N sodium hydroxide: Add 200 mL of 1N NaOH to a 1 liter volumetric flask and dilute to volume with reagent water.

Note: 0.25 N NaOH may be purchased instead.

7.1.7. Brij-35

7.1.8. 30% Brij solution: Add 2 mL Brij-35 to 1000 mL reagent water.

7.1.9. Rhodanine indicator, purchased.

7.1.10. 0.0192 N silver nitrate, purchased

7.2. Standards

7.2.1. Primary Source Cyanide Stock Standard, 1000 mg/L: Add 2.51 g of potassium cyanide (KCN) and 2.0 g of potassium hydroxide (KOH) to a 1000 mL volumetric flask and dilute to volume with reagent water. Mix well and store in glass amber container. Stable for 1-3 months.

Note: This stock standard may also be purchased.

Note: This stock standard must be standardized prior to use. See Appendix I.

7.2.2. Secondary Source Cyanide Standard, 1000 mg/L: Follow 7.2.1 using an alternate source of Potassium Cyanide (KCN).

Note: This stock standard may also be purchased.

Note: This stock standard must be standardized prior to use. See Appendix I.

7.2.3. Calibration Standards (Water and Solid Matrices)

7.2.3.1. If using the 1.25 N NaOH: pipet the appropriate amount of cyanide standard into 100 mL volumetric and add 20 mL 1.25N NaOH to each calibration standard (except the 1.0 mg/L) and bring to volume with reagent water.

If using the purchased 0.25N NaOH: pipet the appropriate amount of cyanide standard into 100 mL volumetric and bring to volume with 0.25N NaOH.

Prepare weekly.

Concentration CN-	mL CN-	Final Volume
10 mg/L	1 mL of 1000 mg/L	100 mL
1.0 mg/L (secondary only)	10 mL of 10 mg/L	100 mL
*0.2 mg/L	2 mL of 10 mg/L	100 mL
*0.1 mg/L	1 mL of 10 mg/L	100 mL
*0.05 mg/L	0.5 mL of 10 mg/L	100 mL

*0.025 mg/L	0.25 mL of 10 mg/L	100 mL
*0.01 mg/L	0.1 mL of 10 mg/L	100 mL
*0.005 mg/L	0.05 mL of 10 mg/L	100 mL

*Denotes calibration standards

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Solid samples are not chemically preserved. Water samples are preserved with NaOH to a pH > 12. All samples are stored at 4°C ± 2°C in plastic or glass containers.

8.2. The holding time for **non-CLP** samples is fourteen days from sampling to analysis.

8.3. The holding time for **CLP** samples is twelve days from receipt to analysis.

9. QUALITY CONTROL

9.1. Batch Definition

9.1.1. **Non –CLP**:

9.1.1.1. A batch is a group of no greater than 20 samples excluding QC samples (LCS, Method Blank, MS, MSD) which are processed similarly, with respect to the procedure. All sample setups must be initiated within a 24 hour period from the initial preparation or extraction and without interruption of the process. All samples within the batch must be treated with the same lots of reagents and the same processes.

9.1.2. **CLP**

9.1.2.1. A batch is a group of no greater than 20 samples excluding QC samples (LCS/ICV, Method Blank, Sample Duplicate and Matrix Spike) which are processed similarly, with respect to the procedure. All sample setups must be initiated within a 24 hour period from the initial preparation or extraction and without interruption of the process. All samples within the batch must be treated with the same lots of reagents and the same processes.

9.1.2.2. A Chain of Custody (COC) is needed for each SDG.

9.2. Method Blank

9.2.1. Non-CLP

9.2.1.1. One method blank (MB) must be processed with each preparation batch. The method blank consists of reagent water or 0.25N NaOH containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. The method blank should not contain any analyte of interest at or above the reporting limit.

9.2.1.2. A method blank consists of 50 mL 0.25N NaOH for Total Cyanide analysis or 50 mL reagent water for Free and Amenable Cyanide analysis and must be distilled and analyzed with each analytical batch of samples. See SOP NC-WC-0032 for distillation instructions.

9.2.2. CLP

9.2.2.1. Each SDG (sample delivery group) must have one method blank (MB) processed per matrix and per twenty samples. If the SDG is distilled over multiple "racks", the method blanks must be distilled with the samples. If more than one SDG is on one rack, process one method blank per SDG and per matrix. The solid method blank is called "PBS" (prep blank solid) and the water method blank is called "PBW" (prep blank water).

NOTE: A "rack" is one setup of cyanide samples and QC, and can encompass 1-3 of the midi-distillation units.

9.2.2.2. A method blank (PBW/PS) consisting of 50 mL 0.25N NaOH must be distilled and analyzed with each analytical batch of samples. See SOP NC-WC-0032 for distillation instructions.

9.2.3. Corrective Action for Blanks

9.2.3.1. If the analyte level in the method blank exceeds the reporting limit for the analytes of interest in the sample, all associated samples are reprepared and reanalyzed. If this is not possible due to limited sample quantity or other

considerations, the corresponding sample data **must be addressed in the project narrative.**

9.2.3.2. If there is no analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. **Such action must be taken in consultation with the client and must be addressed in the project narrative.**

9.3. Laboratory Control Sample (LCS)

9.3.1. One LCS from an independent source must be processed with each preparation batch. The LCS must be carried through the entire analytical procedure. The LCS is used to monitor the accuracy of the analytical process. On-going monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines.

9.3.2. Non-CLP

9.3.2.1. A midrange LCS consisting of a 0.04 mg/L (2.0 mL of 1.0 mg/L to 50 mL) must be distilled and analyzed with each analytical batch of samples for Total, Amenable, and Free cyanide analysis. See SOP NC-WC-0032 for distillation instruction.

NOTE: A purchased complex cyanide solution may be used instead as the midrange LCS for **Total Cyanide** analysis only.

9.3.2.2. The acceptance limits for drinking water samples, Method 335.4, is 90 – 110%.

9.3.3. CLP

9.3.3.1. A LCS (which doubles as an ICV) is processed with each batch or each SDG, which ever is more frequent. Even if multiple SDG's are on the "rack", only one LCS (ICV) needs to be distilled for up to a maximum of 20 samples.

NOTE: A "rack" is one setup of cyanide samples and QC, and can encompass 1 – 3 of the midi-distillation units.

9.3.3.2. For CLP waters: the LCS is 4.0 mL of 1.0 ppm secondary source in 50 mL (TV = 80ug/L).

9.3.3.3. For CLP solids, a solid LCS must be processed per SDG or per batch, which ever is more frequent. Weigh out 0.05g of the solid LCS sample. If more than one SDG is processed on a "rack", process a solid LCS for each one. If a SDG has solid sample distilled on a different "rack", then additional solid LCS's will need to be distilled. The value for this LCS changes as the solid lot number changes each time a new one is ordered. The value is noted on the product certification.

9.3.3.4. If more than one SDG is distilled on one rack, they may be analyzed together (however, each SDG **must** be **analyzed separately with a separate PBW**). It is also **preferred** that each SDG have its own method blank(s), its own ICV (LCS), its own LCS-S (if samples are solids), and its own sample duplicate and matrix spike. If the SDG has been split over multiple distillation "racks", then you may not have a sample duplicate and matrix spike for each rack. However, an ICV (LCS) is distilled with each "rack". If more than one SDG is distilled on a "rack", then the ICV (LCS) distilled with that rack must be analyzed with each SDG.

9.3.4. Corrective Action for LCS

9.3.4.1. If any analyte is outside established control limits the system is out of control and corrective action must occur.

9.3.4.2. Corrective action will be repreparation and reanalysis of the batch unless the client agrees that other corrective action is acceptable.

9.4. Matrix Spike/Matrix Spike Duplicate (MS/MSD)

9.4.1. Non-CLP

9.4.1.1. One MS/MSD pair must be processed for each batch. A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added. A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked identically as the MS) prepared and analyzed along with the sample and matrix spike. Some client specific data quality objectives (DQO's) may require the use of sample duplicates in place of or in addition to MS/MSD's. The MS/MSD results are used to determine the effect of a matrix

on the precision and accuracy of the analytical process. Due to the potential variability of the matrix of each sample, these results may have immediate bearing only on the specific sample spiked. Samples identified as field blanks cannot be used for MS/MSD analysis.

9.4.1.2. A MS/MSD consisting of 50 mL or 1.0 g sample and 0.04 mg/L spike (2.0 mL of 1.0 mg/L to 50 mL) will be distilled and analyzed with every batch. See SOP NC-WC-0032 for distillation instructions. This is also the same value for CLP.

9.4.1.3. The acceptance limits for drinking water samples, Method 335.4, is 90 – 110%.

9.4.2. **CLP**

9.4.2.1. Each SDG must have a sample duplicate and a matrix spike processed per matrix. Sometimes this requirement is waived by the client or PM but, if uncertain, make sure that these are done. Usually , the sample to be spiked is assigned, but not always. If a MS/MSD is created in receiving, either batch the MSD and "N/A" the result or have the MSD deleted. In either case, create a sample duplicate for the sample that is spiked when batching. If processing a SDG over more than one "rack", then there is no need to process additional matrix spikes and sample duplicates (unless specifically requested). Typically, only one sample duplicate and matrix spike is required per SDG.

9.4.2.2. Matrix spike for CLP consists of 50 mL or 1.0 g of sample and 100 µg/L spike (5.0 mL of 1.0 mg/L secondary standard).

NOTE: see corrective action section 9.4.3.4 for A-spike

9.4.3. Corrective action for MS/MSDs

9.4.3.1. If the analyte recovery or RPD falls outside the acceptance range, the recovery of that analyte must be in control for the LCS. If the LCS recovery is within limits, then the laboratory operation is in control and the results may be accepted. If the recovery of the LCS is outside limits, corrective action must be taken. Corrective action will include repreparation and reanalysis of the batch.

9.4.3.2. If the native analyte concentration in the MS/MSD exceeds 4x the spike level for that analyte, the recovery data is reported as "amount" MSB. The Exception Code is changed to NC. The A-spike is not needed in this case.

9.4.3.3. If an MS/MSD is not possible due to limited sample volume then a laboratory control sample duplicate (LCSD) should be analyzed. The RPD of the LCS and LCSD must be compared to the matrix spike RPD limits.

9.4.3.4. A-spike corrective action: if matrix spike recovery fails criteria, then spike the sample at two times the reporting limit or 2 times the sample concentration, which ever is greater. Examples are shown below.

*A-spike = 2 mL of sample + 2mL of A-spike solution

A-spike solution = 0.8 mL .25N NaOH, +3.2 mL 0.05 ppm 1° standard

9.5. QC Acceptance Criteria

9.5.1. Control limits are established by the laboratory as described in NC-QA-0018.

9.5.2. Laboratory control limits are internally generated and updated periodically unless method specified. Control limits are listed in the Laboratory Quality Manual (LQM) and the latest is version easily accessible via the LIMs (QC Browser program.).

9.6. Method Detection Limits (MDLs) and MDL Checks

9.6.1. MDLs and MDL Checks are established by the laboratory as described in SOPs S-Q-003 and NC-QA-0021.

9.6.2. MDLs are listed in the Laboratory Quality Manual (LQM) and the latest version is easily accessible via the LIMs (QC Browser program).

9.7. Nonconformance and Corrective Action

9.7.1. Any deviations from QC procedures must be documented as a nonconformance, with applicable cause and corrective action approved by the facility QA Manager.

10. CALIBRATION AND STANDARDIZATION

10.1. Summary

10.1.1. The instrument is calibrated using six cyanide standards and a blank at the time of analysis. Non- CLP samples are processed in mg/L and CLP samples are in ug/L.

10.2. Initial Calibration

10.2.1. Non-CLP

10.2.1.1. The instrument is calibrated at the beginning of each run and is verified at the beginning of the run by using a midrange ICV. The ICV is composed of the 0.1 ppm secondary standard. The ICV must not vary from the original curve by more than ± 15% or recalibration is required. For drinking water samples, Method 335.4, the criteria is ± 10%. The correlation coefficient of the original curve must be ≥ 0.995 or recalibration is required.

10.2.2. CLP

10.2.2.1. The instrument is calibrated at the beginning of each run and is verified at the beginning of the run by analyzing the ICV/LCS. The ICV is composed of 4.0 mL of 1.0 ppm secondary standard (TV = 80 ug/L). The correlation coefficient of the original curve must be ≥ 0.995 or recalibration is required.

10.3. Continuing Calibration

10.3.1. The run is checked every ten samples and at the end of the run using a midrange CCV to verify continued linearity. It cannot vary from the original curve by more than ± 15% or recalibration is required. For drinking water samples, Method 335.4, the criteria is ± 10%. The previous 10 samples must be reanalyzed and bracketed by a CCV that passes criteria. The CCV is composed of the 0.1 mg/L primary standard for non-CLP runs and the 100 ug/L for CLP runs.

10.3.2. System cleanliness is checked every ten samples and at the end of the run using a CCB. It cannot contain the analyte of interest above the reporting limit or recalibration is required. The previous 10 samples must be reanalyzed and bracketed by a CCB that passes criteria. The CCB is 0.25N NaOH.

NOTE: Base and gain values may change with new reagents, standards, tubing changes, or board cleaning. These values are for reference only.

10.4. High and Low Standard

10.4.1. The distillation technique is checked by distilling a high and low standard and comparing the values obtained to the standard curve. The method recommends that the HI/LO standards be compared to the curve with a +/-10% agreement. The HI/LO standards are evaluated against all applicable batch QC.

11. PROCEDURE

11.1. One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and is approved by a Technical Specialist and QA Manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file.

11.2. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

11.3. Sample Preparation

11.3.1. See cyanide distillation SOP: NC-WC-0032.

11.3.1.1. Non-CLP

11.3.1.1.1. The sample is distilled/refluxed under acidic conditions for one hour. The released HCN is trapped in 50 mL of 0.25 N NaOH solution. EPA Method 335.4 says to reflux for one and a half hours.

11.3.1.2. CLP

11.3.1.2.1. The sample is distilled/refluxed under acidic conditions for one and a half hours. The released HCN is trapped in 50 mL of 0.25 N NaOH solution.

11.3.2. Sample Preparation Procedure

All Samples:Test each sample for the presence of sulfides using lead acetate paper. If sulfides are present, treat the sample with powdered cadmium carbonate. Yellow cadmium sulfide precipitates if the sample contains sulfide. Repeat this operation until a drop of the treated sample solution does not darken the lead acetate test paper. Filter the solution. Avoid a large excess of

cadmium carbonate and long contact time in order to minimize loss by complexation or occlusion of cyanide on the precipitated material.

NOTE: Water should be tested prior to distillation

11.4. Sample Analysis

11.4.1. Summary

11.4.1.1. The sample distillates are analyzed on the autoanalyzer for cyanide using the automated pyridine-barbituric method.

11.4.2. Recommended Instrument Conditions

11.4.2.1. See Manufacturer's information for operation instructions.

11.4.2.2. Start Up Solutions (and Wash Solutions)

11.4.2.2.1. All lines in 0.25N NaOH solution:

11.4.2.2.2. Then all lines in 30% Brij solution.

11.4.2.3. Running Solutions

11.4.2.3.1. Two DI water lines (orange/green) in 30% Brij solution

11.4.2.3.2. Red/Red in pyridine reagent

11.4.2.3.3. Orange/red in chloramine-T reagent

11.4.2.3.4. White/white in phosphate buffer solution

11.4.2.4. Base and Gain

11.4.2.4.1. Performed on the 0.2 mg/L standard

11.4.2.4.2. Approximate values: Base = 75 Gain = 150

*These values are for reference only and may change with new reagent or standard preparations.

11.4.2.5. Trouble shooting for poor Base and Gain or baseline noise

11.4.2.5.1. Place reagent lines 1-3 back in Brig solution and run on high for five minutes. Place all 5 lines (1-5) and probe line in 1.25 N NaOH solution and run on high for five minutes. Place lines back in appropriate "start-up" solutions and run on high for five minutes or make fresh new reagents.

Place lines back in reagents and perform another base and gain when the baseline has stabilized.

11.4.3. Sample Analysis Procedure

11.4.3.1. See Manufacturer's information for operating instructions.

11.4.3.2. A calibration curve is analyzed at the beginning of each run. The correlation coefficient must be > 0.995 to continue.

11.4.3.3. The ICV (from the secondary source) and the ICB is analyzed at the beginning of every run. CCV's (from the primary source) and CCB's are analyzed at the end and between every 10 samples.

11.4.3.4. Sample distillates higher than the highest calibration standard (0.2 mg/L) must be diluted with 0.25 N NaOH and re-analyzed.

11.4.3.5. Any samples analyzed after a high sample must be re-analyzed if carryover is suspected.

11.5. Tray Protocol (Run Order)

Normal Tray Protocol

1. Calibration
2. MRL
3. ICV (secondary source)
4. ICB (CCB)

5. Prep Blank
6. LCS
7. LOW
8. HI
9. UP to 6 more samples
10. MRL
11. CCV
12. CCB
13. Up to 10 samples
14. MRL
15. CCV
16. CCB

CLP Tray Protocol-Water

1. Calibration
2. Distilled ICV/LCS
3. ICB
4. CCV
5. CCB
6. PBW
7. Sample

8. Sample duplicate

9. Sample MS

10. Up to 6 more samples

11. CCV

12. CCB

13. Up to ten more samples

14. CCV

15. CCB

CLP Tray Protocol-Solid

1. Calibration standards

2. Distilled ICV

3. ICB

4. CCV

5. CCB

6. PBS

7. LCSS

8. Sample

9. Sample duplicate

10. Matrix Spike

11. Up to 5 more samples

12. CCV

13. CCB

14. Up to ten more samples

15. CCV

16. CCB

11.6. Analytical Documentation

11.6.1. Record all analytical information in the analytical logbook/logsheet, including the analytical data from standards, blanks, LCSs, MS/MSDs, and any corrective actions or modifications to the method.

11.6.2. All standards and reagents are logged into a department standard logbook. All standards are assigned an unique number for identification. Logbooks are reviewed by the supervisor or designee.

11.6.3. Documentation such as all associated instrument printouts (final runs, screens, reruns, QC samples, etc.) and daily calibration data corresponding to all final runs is available for each data file.

11.6.4. Sample results and associated QC are entered into the LIMs after final technical review.

12. DATA ANALYSIS AND CALCULATIONS

12.1. $$\textit{Total Cyanide, mg / L} = \frac{\textit{mg / L } CN^- \textit{ from printout x 50}}{\textit{mL of sample distilled}} \textit{ x D}$$

12.2. $$\textit{Total Cyanide, mg / kg} = \frac{\textit{mg / L } CN^- \textit{ from printout x 50}}{\textit{g of sample distilled.}} \textit{ x D}$$

12.3. $$\textit{Amenable Cyanide, mg / L} = \textit{Total } CN^- \textit{ (mg / L) - Chlorinated } CN^- \textit{ (mg / L)}$$

Where:

mg/L = ***can also be mg/kg***

$$D = \textit{Dilution Factor} = \frac{\textit{Final Volume of Dilution}}{\textit{Volume of Sample Distillate Used}}$$

NOTE: Free cyanide has the same calculations as Total cyanide

12.4. LCS Recovery:

$$\frac{\textit{Instrument Value}}{0.04(\textit{true})} \times 100 = \%\ \textit{Recovery}$$

12.5. CCV Recovery:

$$\frac{\textit{Instrument Value}}{0.025\ (\textit{true})} \times 100 = \%\ \textit{Recovery}$$

NOTE: CCV recovery must be between 85 - 115% for data to be acceptable. If CCV recovery is not within these limits, reanalysis is required 335.4 says 10%.

12.6. ***MS/MSD Recovery for Waters and solids:***

$$\frac{A - B}{0.040\ (\textit{true})} \times 100 = \%\ \textit{Recovery}$$

Where:

A = ***Instrument value MS/MSD***

B = ***Sample instrument value***

13. METHOD PERFORMANCE

13.1. Each laboratory must have initial demonstration of performance data on file and corresponding method detection limit files.

13.2. Training Qualifications:

13.2.1. The group/team leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience.

13.2.2. Method validation information (where applicable) in the form of laboratory demonstrations of capabilities is maintained for this method in the laboratory QA files.

14. POLLUTION PREVENTION

14.1. This method does not contain any specific modifications that serve to minimize or prevent pollution.

15. WASTE MANAGEMENT

15.1. All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

15.2. Waste Streams Produced by the Method

15.2.1. The following waste streams are produced when this method is carried out.

15.2.2. Alkaline material from the auto-analyzer. This waste is collected in the lab in a container labeled "Pyridine Waste".

15.2.3. Acidic waste This waste is collected in the lab in a container labeled "Acid Waste".

15.2.4. Caustic waste containing Pyridine. This waste is collected in the lab in a containers labeled "Pyridine Waste".

15.2.5. Wastewater contaminated with Pyridine. This waste is collected in the lab in a containers labeled "Pyridine Waste".

15.2.6. Wastewater containing 1.5% Pyridine This waste is collected in the lab in a containers labeled "Pyridine Waste".

15.2.7. Aqueous analytical waste, neutral to slightly basic, contaminated with 3% pyridine. This waste is collected in the lab in a container labeled "Pyridine Waste".

15.2.8. Filter paper contaminated with lead sulfideThis waste is placed in a container labeled "Solid Waste".

15.2.9. Aqueous rinsates from distillation tube clean upThis waste is collected in the lab and disposed of in a container labeled "Acid Waste".

15.2.10. Miscellaneous solid waste contaminated with sample residue, acids, caustics and reagents used in this SOP. A weigh tin is the only type of this waste generated. The tin is rinsed with water and disposed of in a container labeled "Solid Waste".

15.3. Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices of STL. They must have training on the hazardous waste disposal practices upon initial assignment to these tasks, followed by an annual refresher training.

16. REFERENCES

16.1. References

16.1.1. SW846, Test Methods for Evaluating Solid Waste Method 9012 A, and its updates

16.1.2. EPA 600; Cyanide, Total and Cyanide, Amenable to Chlorination; Methods 335.2, March 1983

16.1.3. EPA 600; Determination of Total Cyanide by Semi-Automated Colorimetry, 335.4, Revision 1.0, August 1993.

16.1.4. Standard Methods for the Examination of Water and Wastewater, Eighteenth Edition: Weak and Dissociable Cyanide; Method 4500-CN-E

16.1.5. USEPA CLP SOW ILM03.0 and ILM04.0, Section D - Cyanide Midi Distillation

16.1.6. Corporate Quality Management Plan (QMP), current version.

16.1.7. STL Laboratory Quality Manual (LQM), current version

16.1.8. STL Corporate Safety Manual, M-E-0001 and STL North Canton Facility Addendum and Contingency Plan, current version.

16.2. Associated SOPs and Policies, latest version

16.2.1. QA Policy, QA-003

16.2.2. Glassware Washing, NC-QA-0014

16.2.3. Statistical Evaluation of Data and Development of Control Charts, NC-QA-0018

16.2.4. Method Detection Limits and Instrument Detection Limits, S-Q-003 and NC-QA-0021

16.2.5. Navy/Army SOP, NC-QA-0016

16.2.6. NC-WC-0032, Cyanide Preparation Method

MISCELLANEOUS (TABLES, APPENDICES, ETC...)

17.1. Reporting limits

17.1.1. The reporting limit (RL) is 0.01 mg/L for waters (50 mL used) and 0.50 mg/kg for solids (1.0 g used). The reporting limit for solid samples performed only under the Michigan program is 200 µg/kg for solids (2.5 g used). The lowest level of the calibration curve can be used as the reporting limit upon request.

17.1.2. If samples require dilution or smaller volumes than specified in this method, the RL will be elevated.

17.2. Troubleshooting guide for poor Base and Gain or baseline noise

17.2.1. Place reagent lines 1-3 back in Brig solution and run on high for five minutes. Place all 5 lines (1-5) and probe line in 1.25 N NaOH solution and run on high for five minutes. Place lines back in appropriate "start-up" solutions and run on high for five minutes.

Place lines back in reagents and perform another base and gain when the baseline has been stabilized.

17.3. Method Deviation (9012A/335.2)

17.3.1. Method of Standard Addition is not performed for samples with matrix interference (sulfides).

Appendix I - Cyanide Standardization

1. Pipet 10.0 mL of the 1000 ppm stock cyanide standard into a 250 mL Erlenmeyer flask and add 90 mL of reagent water.
2. Add 0.5 mL (10 drops) of Rhodanine indicator.
3. Titrate with 0.0192 N silver nitrate (using a micro burette) until the color changes from yellow to pink/orange.
4. Titrate a blank (100 mL reagent water) following steps 2 and 3.
5. Calculation:

$$\textbf{Cyanide, mg / L} = \frac{\textbf{(A - B) (1000)}}{\textbf{mL Cyanide Solution (10)}}$$

Where:

A = mL titrant for standard

B = mL titrant for blank

6. If the cyanide concentration is not 1000 ppm, adjust concentration accordingly.

TestAmerica

THE LEADER IN ENVIRONMENTAL TESTING

TestAmerica North Canton

SOP No. NC-WC-0084, Rev. 5
Effective Date: 06/28/05
Cover Page

Title: Ion Chromatography, Determination of Inorganic Anions
[Method: **EPA300.0**]

Approvals (Signature/Date):

Technology Specialist	Date	Health & Safety Coordinator	Date
Quality Assurance Manager	Date	Laboratory Director	Date

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Revision No: 5
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Page 1 of 24

STL STANDARD OPERATING PROCEDURE

TITLE: DETERMINATION OF INORGANIC ANIONS BY ION CHROMATOGRAPHY

(SUPERSEDES: REVISION 4, REVISION DATE 11/06/04)

Prepared by: Rebecca L. Nolan 6/15/05
Date

Reviewed by: Angela Sura 6/15/05
Technology Specialist Date

Approved by: Bob Lambert 6-21-05
Quality Assurance Manager Date

Approved by: William J. Deibel 6-21-05
Environmental Health and Safety Coordinator Date

Approved by: 6/21/05
Laboratory Director Date

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1. SCOPE AND APPLICATION

1.1. This method covers the determination of fluoride, chloride, nitrite, bromide, nitrate, ortho-phosphate and sulfate in drinking water, surface water, mixed domestic and industrial wastewaters, groundwater, reagent waters, solids (after extraction 11.7) and leachates (when no acetic acid is used). This SOP is based on Method 300.0A and 9056A.

1.2. A listing of associated LIMs method codes is located in Section 8.2.

1.3. This document accurately reflects current laboratory standard operating procedures (SOP) as of the date above. All facility SOPs are maintained and updated as necessary.

2. SUMMARY OF METHOD

2.1. A 25 uL volume of sample is introduced into the ion chromatograph. The sample is pumped through three different ion exchange columns and into a conductivity detector. The first two columns, a precolumn or guard column and a separator column, are packed with low-capacity, strongly basic anion exchange resin. Ions are separated into discrete bands based on their affinity for the exchange sites of the resin. The last column is a suppresser column that reduces the background conductivity of the eluent to a low or negligible level and converts the anions in the sample to their corresponding acids. The separated anions in their acid form are measured using an electrical conductivity cell. Anions are identified based on their retention times compared to known standards. Quantitation is accomplished by measuring the peak height or area and comparing it to a calibration curve generated from known standards.

3. DEFINITIONS

3.1. Refer to the glossary in the Laboratory Quality Manual (LQM).

4. INTERFERENCES

4.1. Interferences can be caused by substances with retention times that are similar to and overlap those of the anion of interest. Large amounts of an anion can interfere with the peak resolution of an adjacent anion. Sample dilution and/or fortification can be used to solve most interference problems associated with retention times.

4.2. The water dip or negative peak that elutes near, and can interfere with, the fluoride peak can usually be eliminated by the addition of concentrated eluent to each standard and sample.

4.3. Method interferences may be caused by contaminants in the reagent water, reagents, glassware and other sample processing apparatus that lead to discrete artifacts or an elevated baseline in the ion chromatograms.

4.4. Any anion that is not retained by the column or only slightly retained will elute in the area of fluoride and interfere. Known coelution is caused by carbonate and other small organic anions. At concentrations of fluoride above 1.5 mg/L, this interference may not be significant; however, it is the responsibility of the user to generate precision and accuracy information in each sample matrix.

4.5. The acetate anion elutes early during the chromatographic run. The retention times of the anions also seem to differ when large amounts of acetate are present. Therefore, this method is not recommended for leachates of solid samples when acetic acid is used for pH adjustment.

5. SAFETY

5.1. Employees must abide by the policies and procedures in the Corporate Safety Manual and this document.

5.2. Exercise caution when using syringes with attached filter assemblies. Application of excessive force has, upon occasion, caused a filter disc to burst during the process.

5.3. The following is a list of the materials used in this method, which have a serious or significant hazard rating. NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table. A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Potassium Nitrate	Oxidizer	None	Causes irritation to the respiratory tract, skin and eyes. Symptoms may include coughing, shortness of breath. Symptoms include redness, itching, and pain.

Sodium Fluoride	Poison	2.5 Mg/M3-TWA as F	**Highly Toxic.** Causes severe irritation to the respiratory tract, symptoms may include coughing, sore throat, and labored breathing. Causes irritation, with redness and pain. Solutions are corrosive. Eye irritant! May cause irritation and serious eye damage. Effects may not appear immediately.
Sulfuric Acid	Corrosive Oxidizer Dehydrator Poison Carcinogen	1 Mg/M3-TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

5.4 Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Cut resistant gloves must be worn doing any other task that presents a strong possibility of getting cut. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.5. Exposure to chemicals must be maintained **as low as reasonably achievable**, therefore; unless they are known to be non-hazardous, all samples must be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation when possible. All samples with a pink stickers that read "Caution/Use Hood!" **must** be opened in the hood. Contact the EH&S co-ordinator if this is not possible. Solvent and waste containers will be kept closed unless transfers are being made.

5.6. The preparation of standards and reagents will be conducted in a fume hood with the sash closed as far as the operation will permit.

5.7. All work must be stopped in the event of a known or potential compromise to the health and safety of a STL associate. The situation must be reported **immediately** to the EH&S Coordinator and to a laboratory supervisor.

6. EQUIPMENT AND SUPPLIES

6.1. Balance -- Analytical, capable of accurately weighing to the nearest 0.0001 g.

6.2. Ion Chromatograph -- Analytical system complete with ion chromatograph and all required accessories including analytical columns, compressed gases and detectors.

6.2.1. Anion guard column: A protector of the separator column. If omitted from the system the retention times will be shorter. Usually packed with same substrate as the separator column. 4 x 50 mm, Dionex IonPac AG14 P/N 46134, or equivalent.

6.2.2. Anion separator column: The separation shown in Figure 1 was generated using a Dionex IonPac AS14 column (P/N 46134). Equivalent column may be used if comparable resolution is obtained, and the requirements of Sect. 9.2 can be met.

6.2.3. Anion suppresser device: Dionex anion micro membrane suppresser (P/N 37106) or ASRS-Ultra Self-Regenerating Suppressor (4mm) P/N 53946 or equivalent.

6.2.4. Detector -- Conductivity cell: approximately 1.25 uL internal volume, Dionex, or equivalent.

6.2.5. Dionex –PeakNet 5.1Data Chromatography Software or equivalent.

6.3. Assorted laboratory glassware (pipettes, volumetric flasks, etc.).

7. REAGENTS AND STANDARDS

7.1. Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. 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.

7.2. Reagent water: Distilled or deionized water, free of the anions of interest. Water should contain particles no larger than 0.20 microns.

7.3. Eluent solution: sodium bicarbonate (CASRN 144-55-8) 1.0 mM, sodium carbonate (CASRN 497-19-8) 3.5 mM. Dissolve 1.680 g sodium bicarbonate ($NaHCO_3$) and 7.417 g of sodium carbonate (Na_2CO_3) in reagent water (7.2) and dilute to 100 mL in a volumetric flask. Take 10 mL of this concentrated eluent solution and dilute to 2 L for use as the working eluent solution or dissolve the entire bicarbonate/carbonate amount in 20 L of reagent water.

7.4. Stock solutions (1,000 mg/L): All stocks are purchased from commercial sources. Primary and secondary sources are required for each target analyte.

7.4.1. Commercial stock solution A: F^- - 25 mg/L, Cl^- - 500 mg/L, Br^-- 100 mg/L, NO_3^- - N- 25 mg/L, PO_4 – P - 25 mg/L, SO_4^{-2}- 500 mg/L. The stock solution may also be at the folloing concentrations: F^- - 125 mg/L, Cl^- - 2500 mg/L, Br^-- 500 mg/L, NO_3^- - N- 125 mg/L, PO_4 – P - 125 mg/L, SO_4^{-2}- 2500 mg/L.

7.4.2. Commercial stock solution B: NO_2^- - N- 25 mg/L. The spike solution may also be at 125 mg/L.

7.4.3. Commercial IC Spike solution A: : F^- - 125 mg/L, Cl^- - 2500 mg/L, Br^-- 500 mg/L, NO_3^- - N- 125 mg/L, PO_4 – P - 125 mg/L, SO_4^{-2}- 2500 mg/L

7.4.4. Commercial IC Spike solution B: NO_2^- - N- 125 mg/L

7.5. Working standards: Prepare calibration standard #5 in a 10 mL volumetric flask and transfer to a vial. Adjust the amount of stock solution used to prepare the working standards if the stock concentration differs from 1000 mg/L as assumed Alternatively prepare Cal standard #5 by mixing 4.0 mL commercial stock A, 4.0 mL commercial stock B and 2.0 mL of eluent or, if the more concentrated solution is used, by mixing 0.8 mL A, 0.8 mL B, and 8.4 mL of eluent.

Calibration Standard #5

Analyte	mL of Stock	Final Conc.
Fluoride	0.10mL	10.0 mg/L
Chloride	2.0 mL	200. mg/L
Nitrite	0.10 mL	10.0 mg/L
Bromide	0.40 mL	40.0 mg/L
Nitrate	0.10 mL	10.0 mg/L
Ortho-Phosphate	0.10 mL	10.0 mg/L
Sulfate	2.0 mL	200. mg/L

7.5.1. In 5 mL PolyVials prepare the following calibration standards in reagent grade water. Final concentrations of working standards are shown below.

Calibration Standard #4: take 2.50 mL of calibration standard #5 and add 2.50 mL of eluent.

Calibration Standard #2: take 250 µL of calibration standard #5 and add 4.75 mL of eluent.

Calibration Standard #1: take 25.0 µL of calibration standard #5 and add 4.95 mL of eluent.

Calibration Standard #3: take 1.25 mL of calibration standard #5 and add 3.75 mL of eluent.

Calibration Standard #1

Analyte	25.0 µL of Cal Std #5	Final Conc
Fluoride		0.05 mg/L
Chloride		1.0 mg/L
Nitrite		0.05 mg/L
Bromide		0.20 mg/L
Nitrate		0.05 mg/L
Ortho-Phosphate		0.05 mg/L
Sulfate		1.0 mg/L

Calibration Standard #2

Analyte	250 µL of Cal Std #5	Final Conc.
Fluoride		0.5 mg/L
Chloride		10. mg/L
Nitrite		0.5 mg/L
Bromide		2.0 mg/L
Nitrate		0.5 mg/L
Ortho-Phosphate		0.5 mg/L
Sulfate		10. mg/L

Calibration Standard #3

Analyte	1.25 mL of Cal Std #5	Final Conc.
Fluoride		2.5 mg/L
Chloride		50. mg/L
Nitrite		2.5 mg/L
Bromide		10. mg/L
Nitrate		2.5 mg/L
Ortho-Phosphate		2.5 mg/L
Sulfate		50. mg/L

Calibration Standard #4

Analyte	2.5 mL of Cal Std #5	Final Conc.
Fluoride		5.0 mg/L
Chloride		100 mg/L
Nitrite		5.0 mg/L
Bromide		40. mg/L
Nitrate		5.0 mg/L
Ortho-Phosphate		5.0 mg/L
Sulfate		100 mg/L

7.5.2. Prepare or purchase a secondary stock standard(s) using a standards source other than that used for the primary standards as described in Section 7.5. Dilute these stock standards to as indicated in the table below to prepare the mixture to be used for the LCS and CCV solution. The CCV/LCS solution may be prepared by mixing 20 mL of A and 20 mL of B and diluting to 200 mL. A higher dilution solution may also be prepared by taking 5mL of A (5X) and 4 mL of B (5X) and diluting to 200 mL.

LCS & Continuing Calibration Verification Solution

Analyte	Final Conc. (V_f=5ml)
Fluoride	2.5 mg/L
Chloride	50. mg/L
Nitrite	2.5 mg/L
Bromide	10. mg/L
Nitrate	2.5 mg/L
Ortho Phosphate	2.5 mg/L
Sulfate	50. mg/L

7.5.3. Prepare or purchase a secondary stock standard(s) using a standards source other than that used for the primary standards as described in Section 7.5. Dilute these stock standards to prepare the mixture to be used for the Matrix Spike solution. Alternatively purchase these mixes (ready to use) from a commercial source. Add 100 uL of each IC Spike solution to 5 mL of sample when preparing the MS. Dilute as needed after spiking the sample.

Matrix Spike "True" Values

Analyte	Final Conc.
Fluoride	2.5 mg/L
Chloride	50. mg/L
Nitrite	2.5 mg/L
Bromide	10. mg/L
Nitrate	2.5 mg/L
Ortho Phosphate	2.5 mg/L
Sulfate	50. mg/L

NOTE: Stock standards, calibration standard #5 and LCS standard should be stored in the dark at 4° ± 2°C. Replace these standards when instrument response indicates target analyte degradation may have occurred or after the standard has expired (12 months commercial mix or

6 months in house mix), which ever occurs first. Nitrite and ortho-phosphate are particularly light and oxygen sensitive.

8 SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Samples should be collected in plastic or glass bottles. All bottles must be thoroughly cleaned and rinsed with reagent water. The volume collected should be sufficient to ensure a representative sample, allow for replicate analysis, if required, and minimize waste disposal.

8.2. Sample preservation and holding times for the anions that can be determined by this method for water samples are as follows:

QuanTIMs Method Code		Analyte	Preservation	Holding Time
EPA 300.0A	SW846 9056A	Fluoride	4° ± 2°C	28 days
C8	3C			
CX	3D	Chloride	4° ± 2°C	28 days
GO	3E	Nitrite	4° ± 2°C	48 hours
GM	3F	Bromide	4° ± 2°C	28 days
C9	3G	Nitrate	4° ± 2°C	48 hours
DO	3H	Ortho Phosphate	4° ± 2°C	48 hours
CY	3I	Sulfate	4° ± 2°C	28 days

Note: Soil leachates will follow the same preservation and holding times as the water samples; starting from the time of extraction.

9. QUALITY CONTROL

9.1. The STL QC Program document provides further details of the QC and corrective action guidelines presented in this SOP. Refer to this document if additional guidance is required.

9.2. Table I provides a summary of quality control requirements including type, frequency, acceptance criteria and corrective action.

9.3. Initial Demonstration of Capability

9.3.1. Prior to the analysis of any samples by Ion Chromatography, the following requirements must be meet:

9.3.1.1. Method Detection Limit (MDL): An MDL must be determined prior to analysis of any samples. The MDL is determined using seven replicates of eluent spiked with the anions of interest that has been carried through the entire analytical procedure. MDLs must be redetermined on an annual basis. The spike level must be greater than the calculated MDL but less than or equal to 10x the MDL. The result of the MDL determination must be below the STL reporting limit.

9.4. Batch definition: Preparation and QC batch definitions are provided in the STL QC Policy.

9.5. Method Blank (MB): One method blank must be processed with each preparation batch. The method blank consists of eluent that has been taken through the entire preparation and analytical process. The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. The method blank should not contain any analyte of interest above the reporting limit.

9.6. Laboratory Control Sample (LCS): One LCS must be processed with each preparation batch and must be carried through the entire analytical procedure. The LCS is used to monitor the accuracy of the analytical process. On-going monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines. If the result is outside established control limits the system is out of control and corrective action must occur. Until in-house limits are established, a control limit of 90 - 110% recovery must be applied. Corrective action will be repreparation and reanalysis of the batch unless the client agrees that other corrective action is acceptable. The LCS is prepared from a separate stock standard, or neat material, of a different manufacturer than the stock, or neat material, used to prepare the calibration standard.

9.7. Matrix Spike/Matrix Spike Duplicate (MS): One MS sample must be analyzed every 10 samples. A matrix spike (MS) is a field sample to which a known concentration of target analyte has been added. Some client specific DQO's may require the use of sample duplicates in place of or in addition to MS's. The MS result is used to determine the effect of a matrix on the precision and accuracy of the analytical process. Due to the potential variability of the matrix of each sample,

these results may have immediate bearing only on the specific sample spiked. Spiking levels will be the same as the LCS values.

- If the MS recovery or RPD falls outside the acceptance range, the recovery of the analyte must be in control for the LCS. Until in-house control limits are established, a control limit of 80-120% recovery and 20% RPD must be applied to the MS.
- If the native analyte concentration in the MS exceeds 4x the spike level for that analyte, the recovery data is reported as "amount" MSB. The Exception Code is changed to NC. The following two footnotes will appear on the report page "NC The recovery and/or RPD were not calculated." "MSB The recovery and RPD were not calculated because the sample amount was greater than four times the spike amount."
- If the LCS recovery is within limits, then the laboratory operation is in control and the results may be accepted.
- If the recovery of the LCS is outside the limits, corrective action must be taken. Corrective action will include repreparation and reanalysis of the batch.
- If an MS is not possible due to limited sample volume then a LCS duplicate must be analyzed. The RPD of the LCS and LCSD must be compared to the matrix spike limits.

9.8. Continuing Calibration Verification (CCV/CCB): Continuing calibration is verified by analyzing the calibration standard after every ten (10) samples . The CCV must fall within +/- 10% of the true value for each target analyte. A CCB is analyzed immediately following the CCV to monitor low level accuracy and system cleanliness. The CCB result must be below the reporting limit for that analyte. If either the CCV or CCB fail to meet criteria, the analysis must be terminated, the problem corrected and repreparation and analysis of all samples following the last CCV and CCB which were in control.

9.9. Reporting Limit Check – Drinking Water Samples. A reporting limit check must be analyzed every day drinking water samples are analyzed. The acceptance criteria is ± 30% for the check.

9.10. Control Limits

9.10.1. Control limits are specified in the method.

9.10.2. Control limits are listed in the Laboratory Quality Manual (LQM) and the latest version is easily accessible via the LIMs (QC Browser program).

9.11. Method Detection Limits (MDLs) and MDL Checks

9.11.1. MDLs and MDL Checks are established by the laboratory as described in SOPs S-Q-003 and NC-QA-0021.

9.11.2. MDLs are listed in the Laboratory Quality Manual (LQM) and the latest version is easily accessible via the LIMs (QC Browser program).

9.12. Nonconformance and Corrective Action

9.12.1. Any deviations from QC procedures must be documented as a nonconformance, with applicable cause and corrective action approved by the facility QA Manager.

10. CALIBRATION AND STANDARDIZATION

10.1. Establish ion chromatographic operating parameters equivalent to those indicated in table 2. Refer to Table 3 for typical standard run retention times. Other than the presence of the analytical column the instrument conditions are the same.

10.2. For each analyte of interest, prepare a **minimum** of 3 calibration standards and a blank by adding accurately measured volumes of one or more stock standards to a volumetric flask and dilution to volume with eluent. If a sample analyte concentration exceeds the calibration range the sample may be diluted to fall within the range. If this is not possible then three new calibration concentrations must be chosen, two of which must bracket the concentration of the sample analyte of interest. Each attenuation range of the instrument used to analyze a sample must be calibrated individually.

10.3. Using an injection volume of 25 uL of each calibration standard, tabulate peak height or area responses against the concentration. The results are used to prepare a calibration curve for each analyte. During this procedure, retention times must be recorded. All analytes will be calibrated using a quadratic regression forced through the origin. Correlation coefficients (R^2) must be 0.995 or better.

10.3.1. For Drinking Water samples, a linear curve, that is not forced through the origin, is used.

10.3. Initial Calibration Verification (ICV) – The Initial Calibration is verified at the start of each day following calibrating prior to sample analysis. The acceptance criteria is ± 10% of the true value. If this criteria is not met, the instrument must be re-calibrated.

11. PROCEDURE

11.1. One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance

Memo and is approved by a Technical Specialist and QA Manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file.

11.2. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

11.3. Table 2 summarizes the recommended operating conditions for the ion chromatograph. Included in this table are estimated retention times that can be achieved by this method. Other columns, chromatographic conditions, or detectors may be used if the requirements of Sect. 9.2 are met.

11.4. Check system calibration daily as outlined in Table 1 and, if required, recalibrate as described in Sect 10.

11.5. Load and inject a fixed amount (25 uL) of settled & filtered sample. If the sample is cloudy then it should be filtered prior to loading into the autosampler polyvial. Flush injection loop thoroughly, using each new sample. Use the same size loop for standards and samples. Record the resulting peak size in area or peak height units. An automated constant volume injection system may also be used.

11.6. The width of the retention time window used to make identifications should be based upon measurements of actual retention time variations of various concentration. Three times the standard deviation of a retention time can be used to calculate a suggested window size for each analyte. However, the experience of the analyst should weigh heavily in the interpretation of chromatograms since retention time is concentration dependent for most analytes..

11.7. If the response for the peak exceeds the working range of the system, dilute the sample with an appropriate amount of eluent and reanalyze.

11.8. If the resulting chromatogram fails to produce adequate resolution, or if identification of specific anions is questionable, fortify the sample with an appropriate amount of standard and reanalyze.

NOTE: Retention time is affected by concentration. Nitrate and sulfate exhibit the greatest amount of change, although all anions are affected to some degree. See Table 3. In some cases this peak migration may produce poor resolution or identification.

11.9. The following extraction should be used for solid materials: Add an amount of reagent water equal to ten times the weight of dry solid material taken as a sample. This slurry is mixed for one hour using a magnetic stirring device or tumbler. Filter the resulting slurry before injecting using a 0.45 um membrane type filter. This can be the type that attaches directly to the end of the syringe

11.10. Should more complete resolution be needed between peaks the eluent (7.3) can be diluted. This will spread out the run but will also cause the later eluting anions to be retained longer. The analyst must determine to what extent the eluent is diluted. This dilution should not be considered a deviation from the method.

11.11. Analytical Documentation

11.11.1. Record all analytical information in the analytical logbook/logsheet which may be in an electronic format, including the analytical data from standards, blanks, LCSs, MSs, and any corrective actions or modifications to the method.

11.11.2. All standards are logged into a department standard logbook. All standards are assigned an unique number for identification. Logbooks are reviewed by the supervisor or designee.

11.11.3. Documentation such as all associated instrument printouts (final runs, screens, reruns, QC samples, etc.) and daily calibration data corresponding to all final runs is available for each data file.

11.11.4. Sample results and associated QC are entered into the LIMs after final technical review.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Prepare a calibration curve for each analyte by plotting instrument response against standard concentration. Compute sample concentration by comparing sample response with the standard curve. Multiply answer by appropriate dilution factor.

12.2. Report only those values that fall between the lowest and the highest calibration standards. Samples exceeding the highest standard should be diluted and reanalyzed.

12.3. Report results in mg/L for aqueous samples and mg/Kg for 1 hour leachates and mg/L for 18 hour leachates of solid samples.

12.4. Report NO_2^- as N, NO_3^- as N, $HPO_4^{=}$ as P

13. METHOD PERFORMANCE

13.1. The reporting limits for the following analytes are based on a 25 uL injection volume:

Analyte	Water RL	Soil RL
Fluoride	1.0 mg/L	10 mg/kg
Chloride	1.0 mg/L	10 mg/kg
Nitrite	0.5 mg/L	5 mg/kg
Bromide	0.5 mg/L	5 mg/kg
Nitrate	0.05 mg/L	0.5 mg/kg
O-Phosphate	0.5 mg/L	5 mg/kg
Sulfate	1.0 mg/L	10 mg/kg

13.2. The group/team leader has the responsibility to ensure that this procedure is performed by an analyst who has been properly trained in its use and has the required experience. The analyst must be given two blind performance samples to analyze or process for analysis. Upon successful completion of the performance evaluation (PE) samples, these analyses will be documented as initial qualification,. Requalification must be performed annually thereafter for this procedure. The group/team leader must document the training and PE performance and submit the results to the QA Manager for inclusion in the associate's training files.

14. POLLUTION PREVENTION

14.1. This method does not contain any specific modifications that serve to minimize or prevent pollution.

15. WASTE MANAGEMENT

15.1. All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

15.2. Waste Streams Produced by the Method

15.2.1. The following waste streams are produced when this method is carried out.

15.2.1.1. Spent samples. Solid samples are disposed of as solid debris waste in the container labeled "Solid Waste."

15.2.1.2. Alkaline and/or acidic waste generated by the analysis. Aqueous waste can be poured down the drain if the pH is between 4 and 10. Any sample waste generated that is not in this pH range must be collected and disposed of in the designated acid waste drum located in the lab. This waste is collected in the laboratory in a designated container identified as "Acid Waste".

15.2.1.3. Contaminated plastic materials such as IC syringes, filters, caps and vials utilized for sample preparation. This waste is disposed of in containers labeled "Solid Waste."

16. REFERENCES

16.1. References

16.1.1. Method 300.0, "Determination of Inorganic Anions by Ion Chromatography", Environmental Monitoring Systems Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Cincinnati, Ohio, Revision 2.1, August 1993.

16.1.2. Method 9056A, "Determination of Inorganic Anions by Ion Chromatography", SW846, Test Methods for Evaluating Solid Waste, Third Edition, Draft Revision 1, September 1999.

16.1.3. STL North Canton Laboratory Quality Manual (LQM), current version.

16.1.4. Corporate Quality Management Plan (QMP), current version.

16.1.5. STL Corporate Safety Manual, M-E-0001 and STL North Canton Facility Addendum and Contingency Plan, current version.

16.2. Associated SOPs and Policies, latest version

16.2.1. QA Policy, QA-003

16.2.2. Glassware Washing, NC-QA-0014

16.2.3. Statistical Evaluation of Data and Development of Control Charts, NC-QA-0018

16.2.4. Method Detection Limits and Instrument Detection Limits, NC-QA-0021 and S-Q-003.

16.2.5. Navy/Army SOP, NC-QA-0016

17. MISCELLANEOUS (TABLES, APPENDICES, ETC...)

17.1. Reporting limits

17.1.1. If samples require dilution or smaller volumes than specified in this method, the RL will be elevated.

17.2. Attachment #1, method Flow Chart

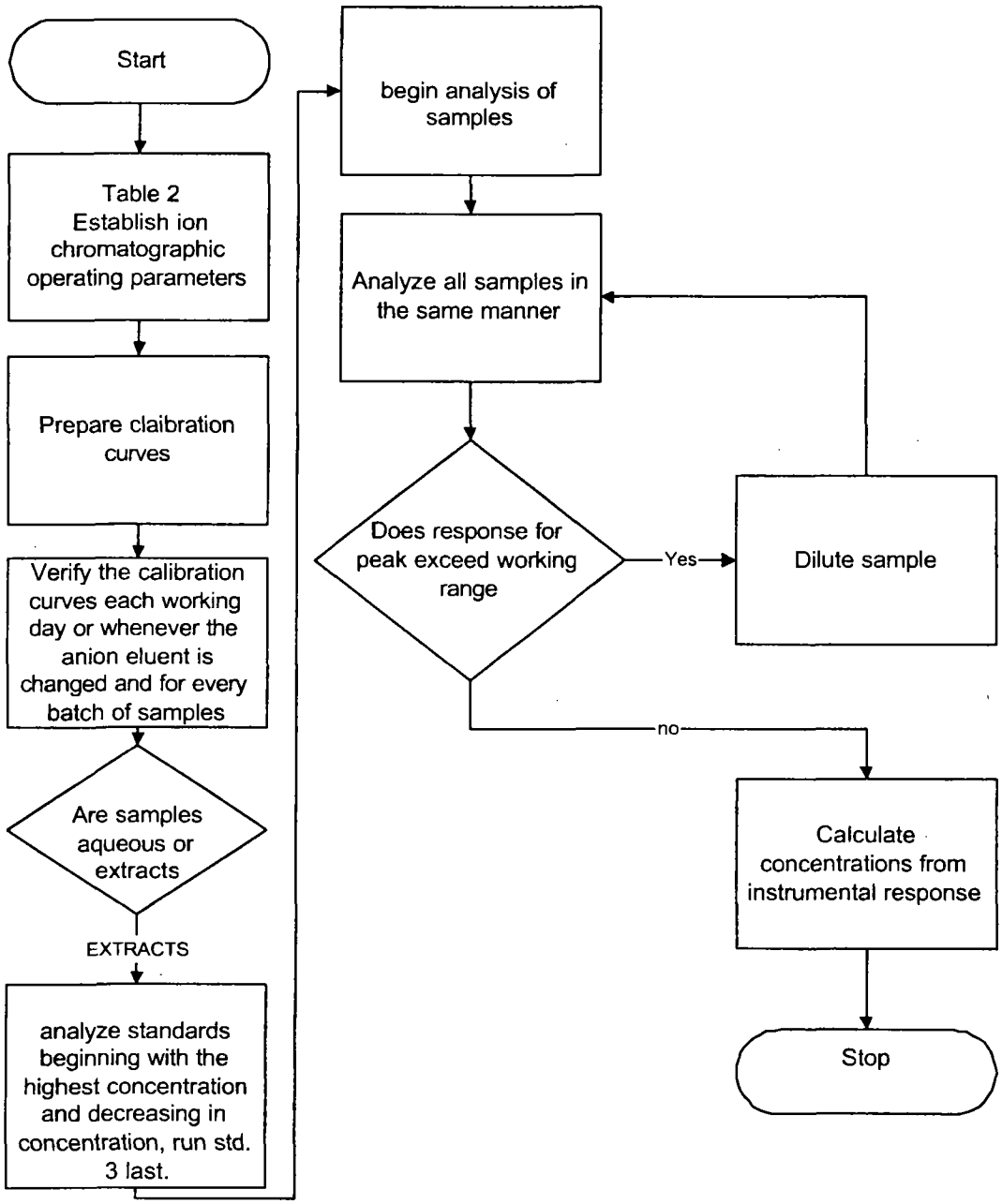
17.3. Table 1, Quality Control Samples

17.4. Table 2, Standard Instrument Operating Parameters

17.5. Table 3, Retention Time Matrix

17.6. Figure 1, Example Chromatogram

Determination Of Inorganic Anions By Ion Chromatography



ATTACHMENT #1

TABLE 1

QUALITY CONTROL SAMPLES

QC Samples	Frequency	Acceptance Criteria	Corrective Action
Initial Calibration Verification (ICV)	At the start of each day following calibrating prior to sample analysis	+/- 10% of true value	Recalibrate and reanalyze
Initial Calibration Blank (ICB)	After Initial Calibration Verification and prior to sample analysis	< the Reporting Limit	Reprepare and reanalyze
Laboratory Control Sample (LCS)	1 per batch of 20 samples	Meets laboratory historical limits	Reanalyze all samples associated with unacceptable LCS
Matrix Spike Sample (MS)	1 MS per every 10 samples	Meets laboratory historical limits	Supervisor's technical judgment
Continuing Calibration Verification (CCV)	Between each group of 10 injections and at the end of the analytical sequence	+/- 10% of true value	Recalibrate and reanalyze all samples since the last acceptable CCV
Continuing Calibration Blank (CCB)	Between each group of 10 injections and at the end of the analytical sequence	< the Reporting Limit	Recalibrate and reanalyze all samples since the last acceptable CCB

TABLE 2

Standard Instrument Operating Parameters

Standard Conditions:

Eluent Pump Rate:	1.20 mL/min (DX-120 and DX-320)
Sample Loop:	25 uL
Eluent:	1.0mM sodium bicarbonate, 3.5mM sodium carbonate
Detector output	Baseline conductivity should be 15 - 20 uS prior to sample analysis.

TABLE 3

Standard Run Retention Time Matrix (minutes)*

	Concentration (mg/L)													
Analyte	0.05	0.2	0.5	1	2	2.5	5	10	20	40	50	100	200	RT window
F^-	2.75		2.75			2.75	2.75	2.75						
Cl^-				3.97				3.98			4.03	4.08	4.17	
NO_2^-	4.80		4.80			4.78	4.78	4.80						
Br^-		6.15			6.13			6.10	6.08	6.07				
NO_3^-	7.33		7.27			7.17	7.13	7.07						
$o\text{-}PO_4^{2-}$	9.53		9.53			9.52	9.50	9.48						
SO_4^{2-}				11.50				11.48			11.43	11.38	11.27	

* Analyte retention time is concentration dependent for most anions. Retention time increases with increasing concentration for chloride. Retention time decreases with increasing concentration for bromide, nitrate, ortho-phosphate and sulfate.

EXAMPLE ION CHROMATOGRAM

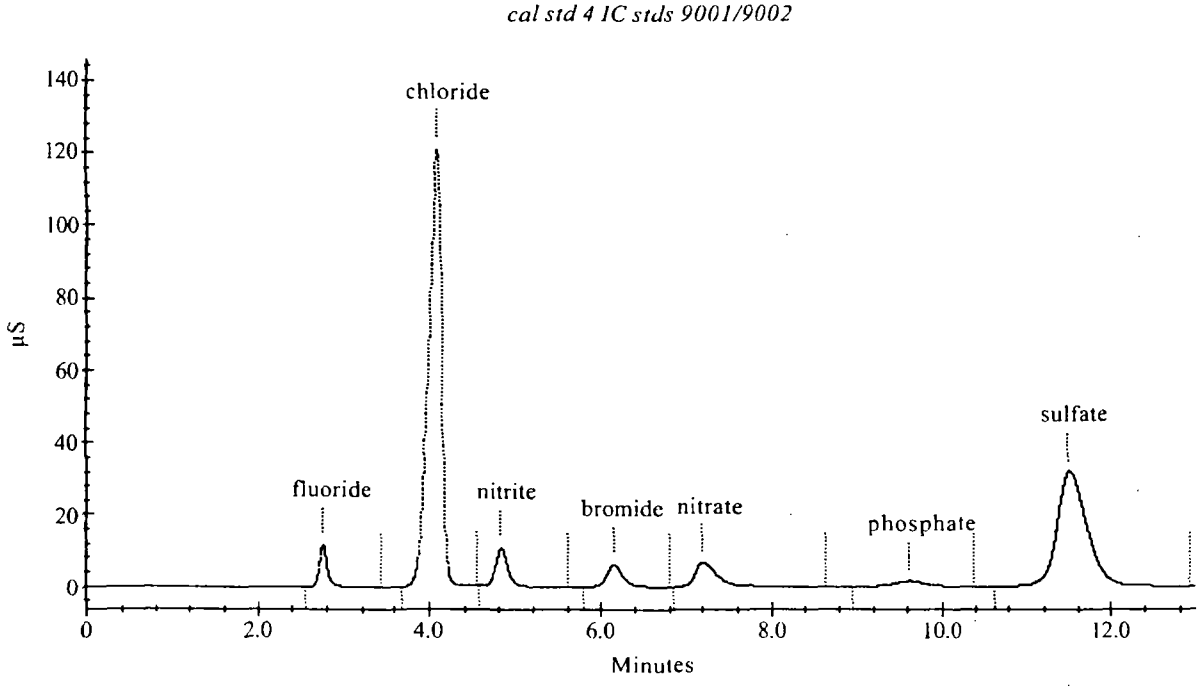


Figure #1

TESTAMERICA STANDARD OPERATING PROCEDURE

TITLE: TOTAL SOLIDS, PERCENT MOISTURE, TOTAL SETTLEABLE SOLIDS, ASH, AND TOTAL VOLATILE SOLIDS

(SUPERSEDES: REVISION 3.2, DATED 02/02/06)

Reviewed by:	Technology Specialist	9/27/07 Date
Approved by:	Quality Assurance Manager	10/4/07 Date
Approved by:	Environmental Health and Safety Coordinator	10-2-07 Date
Approved by:	Laboratory Director	10/3/07 Date

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1. SCOPE AND APPLICATION

1.1. This method is applicable to the determination of Total Solids, Total Volatile Solids, Percent Moisture, Settleable Solids, and Ash in waters, wastewaters, sludges, and solids. It is based on EPA 160.3, EPA 160.5, ASTM D2216-90, ASTM D1553-83. The approximate working range for Total Solids is 10 - 20,000 mg/L for waters and 0.5 to 100% for non-waters.

1.2. The applicable method codes are SM (160.3), AN (160.4) , NJ (D2216-90), AP (160.5), HB (D1553-83). The associated preparation code is 88.

1.3. This document accurately reflects current laboratory standard operating procedures (SOP) as of the date above. All facility SOPs are maintained and updated as necessary.

2. SUMMARY OF METHOD

2.1. A homogenous sample is dried at 104 °C ± 1°C and the difference in the weight loss of the sample (non-water) or the weight gain of the vessel (water) represents the Total Solids.

2.2. Total Volatile Solids and Ash: The residue obtained from the determination of total solids is ignited at 550 °C in a muffle furnace. The loss of weight on ignition is reported as mg/L volatile solids.

2.3. Settleable Solids: Settleable matter is measured volumetrically with an Imhoff cone.

3. DEFINITIONS

3.1. Refer to the glossary in the Laboratory Quality Manual (LQM), latest version.

4. INTERFERENCES

4.1. Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus that lead to discrete artifacts. All of these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. Specific selection of reagents may be required to avoid introduction of contaminants.

4.2. Samples high in concentrations of minerals must be dried longer, desiccated, and weighed quickly to prevent any excess weight added due to absorption of water from the atmosphere.

4.3. Non-homogeneous samples may give erratic results.

5. SAFETY

5.1. Employees must abide by the policies and procedures in the Corporate Safety Manual and this document.

5.2. Oily samples or those that contain volatile chemicals may ignite during this procedure. In the case of a fire, the muffle should be turned off and allowed to cool before the sample can be removed and put under a hood.

5.3. Extreme care should be used when using a muffle furnace, as temperatures are extremely high. Gloves designed for dealing with extreme temperatures must be used when handling any samples or glassware that has been in a muffle furnace.

5.4. There are no materials used in this method that have a significant or serious hazard rating. **NOTE: This list does not include all materials used in the method.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

5.5. Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately. Cut-resistant gloves must be worn doing any other task that presents a strong possibility of getting cut.

5.6. Exposure to chemicals must be maintained **as low as reasonably achievable**, therefore, unless they are known to be non-hazardous, all samples must be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. All samples with stickers that read "Caution/Use Hood!" **must** be opened in the hood. Contact the EH&S Coordinator if this is not possible. Solvent and waste containers will be kept closed unless transfers are being made.

5.7. The preparation of standards and reagents will be conducted in a fume hood with the sash closed as far as the operation will permit.

5.8. All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica associate. The situation must be reported **immediately** to the EH&S Coordinator and to a Laboratory Supervisor.

6. EQUIPMENT AND SUPPLIES

6.1. Drying Oven

6.2. Desiccators

6.3. Evaporating dishes: various

6.4. Tongue blades

6.5. Sample containers

6.6. Top loading balance: capable of accurately weighing ± 0.01 g

6.7. Analytical balance: capable of accurately weighing ±0.0001 g

6.8. Beakers: glass, various

6.9. Muffle furnace

6.10. Volumetric flasks: various

6.11. Imhoff cones

6.12. Labels

7. REAGENTS AND STANDARDS

7.1. Reagents

7.1.1. Reagent water

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Samples are not chemically preserved.

8.2. Samples are stored in plastic or glass containers at 4°C ± 2°C.

8.3. The holding time is 48 hours for settleable solids.

8.4. There is no recommended holding time for non-water samples.

9. QUALITY CONTROL

9.1. Batch Definition

9.1.1. A batch is a group of no greater than 20 samples excluding QC samples (LCS, Method Blank, sample duplicate) which are processed similarly, with respect to the procedure. All sample setups must be initiated within a 24 hour period from the initial preparation or extraction and without interruption of the process. All samples within the batch must be treated with the same lots of reagents and the same processes.

9.2. Method Blank

9.2.1. One method blank (MB) must be processed with each preparation batch. The method blank consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. The method blank should not contain any analyte of interest at or above the reporting limit.

9.2.2. Corrective Action for Blanks

9.2.2.1. If the analyte level in the method blank exceeds the reporting limit for the analytes of interest in the sample, all associated samples are reprepared and reanalyzed. If this is not possible due to limited sample quantity or other considerations, the corresponding sample data **must be addressed in the project narrative.**

9.2.2.2. If there is no analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. **Such action must be addressed in the project narrative.**

9.3. Duplicates

9.3.1. A sample duplicate (DU) is a second aliquot of an environmental sample, taken from the same sample container when possible, that is processed with the first aliquot of that sample. That is, sample duplicates are processed as independent samples within the same QC batch. The sample and DU results are compared to determine the effect of the sample matrix on the precision of the analytical process. As with the MS/MSD results, the sample/DU precision results are not necessarily representative of the precision for other samples in the batch.

9.3.2. Sample duplicates are performed at a frequency of 10% and must meet laboratory-specific limits for precision.

9.4. Control Limits

9.4.1. Control limits are established by the laboratory as described in SOP, NC-QA-0018.

9.4.2. Laboratory control limits are internally generated and updated periodically unless method specified. Control limits are easily accessible via the LIMs (QC Browser program).

9.5. Method Detection Limits (MDLs) and MDL Checks

9.5.1. MDLs and MDL Checks are established by the laboratory as described in SOPs S-Q-003 and NC-QA-0021.

9.5.2. MDLs are easily accessible via the LIMs (QC Browser program).

9.6. Nonconformance and Corrective Action

9.6.1. Any deviations from QC procedures must be documented as a nonconformance, with applicable cause and corrective action approved by the facility QA Manager.

10. CALIBRATION AND STANDARDIZATION

10.1. Not Applicable

11. PROCEDURE

11.1. One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and is approved by a Technical Specialist and QA Manager. The Nonconformance Memo shall be filed in the project file.

11.2. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

11.3. Non-water Samples

11.3.1. For liquid, sludge, TVS and ash samples, label and weigh an evaporating dish on a top loading balance. Record the weight on the analytical logsheet. For solid samples (TS), a universal tare weight is recorded on the bench sheet. For solid samples, sample receiving will divide the soil sample into a pre-tared container

with a label. Weigh and record the wet weight on the analytical logsheet or the computer spreadsheet. For liquids and sludges, transfer the sample to the tared evaporating dish then weigh and record the actual weight on the analytical logsheet.

11.3.2. Method Blank for solid samples (TS), use a new container with a label. Weigh and record the weight on the analytical logsheet or computer spreadsheet.

11.3.3. Sample Duplicate for solid samples (TS), sample receiving will supply the sample duplicate. If the sample duplicate is not supplied from receiving, split some sample off from another container into a new container with a label. Weigh and record the weight on the analytical logsheet.

11.3.4. Place dishes with sample in the drying oven (103° - 105°C) until dry (minimum of 12 hours). Document the time samples were placed in the oven on the logsheet or spreadsheet.

11.3.5. Remove the samples from the drying oven when they are dry. Document the time samples were removed from the oven on the logsheet or spreadsheet.

11.3.6. Place the dishes in the desiccator for at least one hour. Weigh the sample and dish on the top loading balance. Record the weight on the analytical logsheet.

Note: If the drying time was not overnight, it may be necessary to repeat the drying, desiccating, and weighing cycle until a constant weight is achieved as described in Section 11.5.2.

11.3.7. If a Total Volatile Solid or Ash is required, go to Section 11.7. All other samples may be properly disposed in the solid hazardous waste container.

11.4. Total Volatile Solids (TVS) and Ash Samples

11.4.1. Follow Section 11.6 for non-water samples

11.4.2. After the final dried weight has been taken, place the evaporating dish and dried sample in the muffle furnace. Muffle the sample for one hour at 550°C ± 50°C.

Note: Open the oven slowly and allow to cool for at least one hour before removing the samples.

11.4.3. Remove the dish with sample and place it in the desiccator for at least one hour, then weigh it on the top loading balance. Record the weight on the analytical logsheet or computer spreadsheet.

11.5. Percent Moisture

11.5.1. Follow Section 11.6

11.6. Settleable Solids

11.6.1. A method blank is prepared from one liter of reagent water. A blank must be analzyed with each batch of 20 or less samples to ensure Imhoff cones are clean and free of particulate contamination.

11.6.2. Shake one liter of sample vigorously for ten seconds.

11.6.3. Pour the sample into an Imhoff cone, filling the cone to the one-liter mark.

11.6.4. Allow the sample to settle for one hour.

11.6.5. Measure the volume of settleable solids by observing the location of the border between the settled matter and the supernatant liquid.

11.6.5.1. If pockets of liquid are trapped beneath large settled particles, estimate the volume of the pockets and subtract from the total measured volume.

11.7. Analytical Documentation

11.7.1. Record all analytical information in the analytical logbook/logsheet or computer spreadsheet, including the analytical data from standards, blanks, LCSs, MS/MSDs, and any corrective actions or modifications to the method.

11.7.2. All standards are logged into a department standard logbook. All standards are assigned an unique number for identification. Logbooks are reviewed by the supervisor or designee.

11.7.3. Documentation such as all associated instrument printouts (final runs, screens, reruns, QC samples, etc.) and daily calibration data corresponding to all final runs is available for each data file.

11.7.4. Sample results and associated QC are entered into the LIMs after final technical review.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Total Solids

$$\textit{Total Solids, \% (non-waters)} = \frac{(A - B)\ x\ 100}{(C - B)}$$

Where: A = *Final weight of dried sample and dish, g*
B = *Initial weight of dish, g*
C = *Initial weight of wet sample and dish, g*

12.2. Ash

$$\textit{Ash, \% (non - waters)} = \frac{(C - B)\ x\ 100}{A - B}$$

Where: A = *Weight of dried sample and dish (after Total Solid), g*
B = *Weight of dish only, g*
C = *Weight of muffled sample and dish, g*

12.3. Total Volatile Solids (TVS)

$$\textit{TVS, \% (non - waters)} = \frac{(A - C)\ x\ 100}{(A - B)}$$

Where: A = *Weight of dried sample and dish (after Total Solid), g*
B = *Weight of dish only, g*
C = *Weight of muffled sample and dish, g*

12.4. LCS % Recovery

$$\textit{LCS \% Recovery} = \frac{mg / L}{2{,}500\ (true)}\ x\ 100$$

12.5. Dry Weight

$$\textit{Dry Weight} = \frac{\textit{Sample Test Result x 100}}{\textit{(\%) Total Solid Results}} = \textit{Dry Weight}$$

12.6. Percent Moisture

$$\textit{\%Moisture} = 100 - \textit{\%TS (Section 12.1)}$$

13. METHOD PERFORMANCE

13.1. Each laboratory must have initial demonstration of performance data on file and corresponding method detection limit files.

13.2. Training Qualifications:

13.2.1. The group/team leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience.

13.2.2. Method validation information (where applicable) in the form of laboratory demonstrations of capabilities is maintained for this method in the laboratory QA files.

14. POLLUTION PREVENTION

14.1. This method does not contain any specific modifications that serve to minimize or prevent pollution.

15. WASTE MANAGEMENT

15.1. All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

15.2. Waste Streams Produced by the Method

15.2.1. The following waste streams are produced when this method is carried out.

15.2.1.1. Acidic sample waste generated by the analysis. This waste is collected in the laboratory in a designated container identified as "Acid Waste".

15.2.1.2. Contaminated filter and filter residue generated by the analysis. This waste is collected in the laboratory in a designated container identified as "Solid Waste".

15.2.1.3. Weighing containers and filter residue generated by solid sample analysis. This waste is collected in the laboratory in a designated container identified as "Solid Waste".

15.3. Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices of TestAmerica. They must have training on the hazardous waste disposal practices upon initial assignment to these tasks, followed by an annual refresher training.

16. REFERENCES

16.1. References

16.1.1. EPA 600, 1984, Total Residual Solids, Method 160.3

16.1.2. EPA Settleable Solids, Method 160.5

16.1.3. Annual Book of ASTM Standards, Volume 04.08, 1990

16.1.4. Corporate Quality Management Plan (QMP), current version.

16.1.5. TestAmerica Laboratory Quality Manual (LQM), current version.

16.1.6. TestAmerica Corporate Safety Manual, M-E-0001 and TestAmerica North Canton Facility Addendum and Contingency Plan, current version.

16.2. Associated SOPs and Policies, latest version

16.2.1. QA Policy, QA-003

16.2.2. Glassware Washing, NC-QA-0014

16.2.3. Statistical Evaluation of Data and Development of Control Charts, NC-QA-0018

16.2.4. Method Detection Limits and Instrument Detection Limits, S-Q-003 and NC-QA-0021

16.2.5. Supplemental Practices for DoD Project Work, NC-QA-0016

16.2.6. Standards and Reagents, NC-QA-0017

17. MISCELLANEOUS (TABLES, APPENDICES, ETC.)

17.1. Reporting limits

17.1.1. The lower reporting limit (RL) for Total Solids, TVS, and Ash is 10 mg/L for water and 0.5% for non-waters. The reporting limit for Method 160.3 is 10%. The reporting limit for Method 160.5 is 0.1 ml/L/hr.

17.1.2. If samples require dilution or smaller volumes than specified in this method, the RL will be elevated.

STL KNOXVILLE

STANDARD OPERATING PROCEDURE

TITLE: VOA CANISTER ANALYSIS

(SUPERSEDES: KNOX-MS-0001, Revision 8)

Prepared By: _____

Reviewed By: _____ 10/5/06
Technical Specialist

Approved By: _____ 10/05/06
Quality Assurance Manager

Approved By: _____ 10-5-06
Environmental, Health and Safety Coordinator

Approved By: _____ 10-6-06
Laboratory Director

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1. Scope and Application

1.1. The purpose of this standard operating procedure is to define the procedures and quality control necessary to analyze samples collected in "SUMMA™ passivated" stainless steel canisters.

1.2. This procedure is applicable to the analysis of ambient air, indoor air, landfill gases, soil gases, vapor intrusion, and other gaseous samples. It is based on EPA Methods TO-14, TO14A and TO-15.

1.3. Responsibilities to perform this procedure in the lab are as follows:

Position	Responsibilities
Analyst	- Prepares and analyzes samples - Summarizes/assembles data package - Reviews the data package
Team/Group Leader	- Schedules/assigns analyses - Reviews data package

2. Summary of Method

2.1. Microscale Purge and Trap (MSPT): A precisely measured aliquot is removed from the canister or Tedlar bag and concentrated on a cryogenic trap. The cryogenic trap is desorbed. Polar and nonpolar compounds are quantitatively transferred to a subambient Tenax™ trap. Most of the water remains on the Cryotrap and CO2 passes through the Tenax trap and is vented. The Tenax™ trap is thermally desorbed to the on-column cryofocuser. Sample components are separated by temperature programmed gas chromatography and detected with a quadrupole mass spectrometer.

2.2. The compounds analyzed by this method are listed in Tables 1, 2 and 3.

3. Definitions

3.1. Canister - a stainless steel container, typically 6-liter volume, equipped with a stainless steel shut-off valve, suitable for use from vacuum to 40 psig. 1-L cans are available for reduced volume analysis.

3.2. SUMMA™ Passivation - a proprietary treatment process used to deactivate stainless steel surfaces. It produces a pure chrome/nickel oxide surface that features a high level of inertness.

3.3. Absolute pressure - pressure measured with reference to absolute zero pressure, expressed as kpa, mmHg, or psia.

3.4. Gauge pressure - pressure above atmospheric pressure as measured by a standard gauge. Zero gauge pressure is equal to ambient atmospheric pressure, expressed as mmHg, inches Hg, or psig.

3.5. Polar compound - Oxygen-containing compound capable of forming hydrogen bonds in water; compound having significant solubility in water.

3.6. Batch – A batch is a set of up to 20 samples of the same matrix processed using the same procedures and reagents within the same 24 hour time period. The Quality Control batch must contain a blank and a Laboratory Control Sample (LCS). Refer to the QC Program document (QA-003, current revision) for further details of the batch definition.

3.7. Additional definitions can be found in the STL Knoxville LQM glossary and in the STL Quality Management Plan.

3.8. Tedlar bag - Tedlar bags are manufactured from PVF (Tedlar) film with a polypropylene valve and septum. Various volume capacities available.

4. Interferences

4.1. Only compounds having both a similar mass spectrum and GC retention time would be expected to interfere in the method. The most common occurrence of this would be with structural isomers.

4.2. Large concentrations of water, methane, or carbon dioxide may limit the size of the aliquot that can be effectively cryotrapped. This may elevate the quantitation limits obtainable for samples of this type.

4.3. Matrix interferences may be caused by non-target contaminants that are present in the sample. The extent of matrix interferences will vary considerably from source to source depending upon the nature and diversity of the site being sampled.

4.4. Cross-contamination can occur whenever high-level and low-level samples are analyzed sequentially or in the same purge position on an autosampler. Whenever an unusually concentrated sample is analyzed, it should be followed by one or more blanks to check for cross-contamination, or evaluate the next sample for blank acceptance criteria. The autosampler and concentrator may require extensive bake-out and cleaning after a high-level sample.

5. Safety

5.1. Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document.

5.2. Procedures shall be carried out in a manner that protects the health and safety of all associates. Exposure to chemicals and samples will be maintained as low as reasonably achievable, therefore, unless they are known to be non-hazardous, all samples must be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made. The preparation of all standards, reagents and glassware cleaning procedures that involve solvents will be conducted in a fume hood with the sash closed as far as the operations will permit.

5.3. All work must be stopped in the event of a known or potential compromise to the health and safety of any associate. The situation must be reported **immediately** to a laboratory supervisor.

5.4. Specific Safety Concerns or Requirements

5.4.1. The effluents of sample splitters for the gas chromatograph and roughing pumps on the mass spectrometer must be vented to the laboratory hood exhaust system or must pass through an activated charcoal filter.

5.4.2. The gas chromatograph and mass spectrometer contain zones that have elevated temperatures. The analyst needs to be aware of the locations of those zones, and must cool them to room temperature prior to working on them.

5.4.3. The mass spectrometer is under deep vacuum. The mass spectrometer must be brought to atmospheric pressure prior to working on the source.

5.4.4. There are areas of high voltage in both the gas chromatograph and the mass spectrometer. Depending on the type of work involved, either turn the power to the instrument off, or disconnect it from its source of power

5.5. Primary Materials Used: The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material	Hazards	Exposure Limit (1)	Signs and symptoms of exposure
Methanol	Flammable Poison Irritant	200 ppm-TWA	A slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness and dizziness. Methyl alcohol is a defatting agent and may cause skin to become dry and cracked. Skin absorption can occur; symptoms may parallel inhalation exposure. Irritant to the eyes.
Methylene Chloride	Carcinogen Irritant	25 ppm-TWA 125 ppm-STEL	Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. May be absorbed through skin.
Acetonitrile	Flammable Poison	40 ppm-TWA	Early symptoms may include nose and throat irritation, flushing of the face, and chest tightness. Prolonged exposure to high levels of vapors may cause formation of cyanide anions in the body.
Hexane	Flammable Irritant	500 ppm-TWA	Inhalation of vapors irritates the respiratory tract. Overexposure may cause lightheadedness, nausea, headache, and blurred vision. Vapors may cause irritation to the skin and eyes.
Acetone	Flammable	1000 ppm (TWA)	Inhalation may cause coughing, dizziness, dullness, and headache. Contact causes redness, pain, drying and cracking of the skin. Vapors cause eye irritation. Eye splashes may cause severe irritation, with stinging, tearing, redness and pain.
Benzene	Carcinogen Flammable Poison	1 ppm-TWA 5 ppm-STEL	Toxic by ingestion, inhalation and absorption. Causes headache, nausea, dizziness, weakness and breathing difficulties. This material is irritating on contact with the skin and eyes and may cause permanent eye damage.
Carbon Tetrachloride	Carcinogen Poison	10 ppm-TWA 200 ppm-STEL	Toxic by ingestion, inhalation and absorption. Causes headache, nausea, dizziness and narcosis. Contact with skin or eyes may cause irritation. Consumption of alcohol may increase toxic effects
Chloroform	Carcinogen Irritant	50 ppm Ceiling	Acts as a relatively potent anesthetic. Irritates respiratory tract and causes central nervous system effects, including headache, drowsiness, dizziness. Causes skin irritation resulting in redness and pain. Removes natural oils. May be absorbed through skin. Vapors cause pain and irritation to eyes. Splashes may cause severe irritation and possible eye damage.
1,4-Dichlorobenzene	Irritant	75 ppm-TWA	Can cause irritation by ingestion and inhalation. Causes nausea, vomiting and diarrhea. Contact with material or vapors can cause irritation to skin and eyes.
Vinyl Chloride	Carcinogen Flammable Poison	1 ppm TWA	Toxic by inhalation, ingestion and absorption. Can cause respiratory irritation, dizziness, weakness, fatigue, nausea and headache. Contact with the material can cause eye and skin irritation.
1 – Exposure limit refers to the OSHA regulatory exposure limit.			

6. Equipment and Supplies

6.1. Canisters, 1, 6-, 15-, and 30-liter sizes, preferably equipped with two valves and integral vacuum/pressure gauge, Scientific Instrumentation Specialists or equivalent.

6.2. Static gas dilution bottles (SGDB), nominally 2000 ml, with mininert valves, Tekmar Co., or equivalent.

6.3. Syringes, gas-tight, 10 uL, 50 uL, 500 uL, 1000 uL, 2.5 mL, 50 mL, 500 mL, all side port needle, Hamilton, Inc., or equivalent.

6.4. Gas Chromatograph/Mass Spectrometer System, Agilent HP 6890 GC and 5973 MSD or equivalent.

6.5. Fused silica capillary column, 60 m x 0.32 x 1um film DB-5, J&W Scientific, or equivalent.

6.6. Vacuum pump, Model 726.3 TTP, KNF Newberger, or equivalent.

6.7. Canister concentrator system, Model 7100 or 7100A, Entech Co., with a Model 7016CA, 16-position auto sampler.

6.8. Gauges: The following gauges are certified annually

6.8.1. Test gauge, 0 to 30 in. Hg vacuum, Ashcroft Co., or equivalent

6.8.2. Test gauge, 0-60 psi, Ashcroft Co., or equivalent

6.8.3. Test gauge, 0 to 100 in. Hg pressure, Ashcroft Co., or equivalent

6.8.4. Digital gauge 0 to 30" Hg vacuum, Dwyer or equivalent

6.8.5. Digital gauge 0 to -29.9" Hg vacuum, 0 to 99.9 psi, Dwyer or equivalent

6.9. Tedlar Bags: Variety of sizes. SKC or equivalent.

7. Reagents and Standards

7.1. Helium, ultra high purity, 99.999+%, Air Products, or equivalent.

7.2. Liquid nitrogen, Air Products, or equivalent.

7.3. Nitrogen, ultra high purity, Air Products or equivalent

7.4. Internal/Surrogate Standard (all at 100 ppb) in nitrogen, 2000 psig, Scott Specialty Gases, or equivalent:

CAS NUMBER	Internal Standards	MOLECULAR WEIGHT (ng/n mole)
74-97-5	bromochloromethane	129.4
540-36-3	1,4-difluorobenzene	114.1
3114-55-4	chlorobenzene-d5	117.6
	Surrogates	
17060-07-0	1,2-dichloroethane-d4	103.0
2037-26-5	toluene-d8	100.2
460-00-4	4-bromofluorobenzene	175.0

7.4.1. A sufficient volume from the internal/surrogate standard cylinder is transferred to the 15-liter summa canister to produce a positive pressure.

7.4.2. The working internal/surrogate standard may be used as long as the pressure in the canister remains above ambient pressure and is not past its expiration date.

7.4.3. The Entech is programmed to add 20 mL of the internal standard/surrogate can. This results in a concentration of 4 ppb/v of internal standard/surrogate (based on 500 mL volume).

7.5. Primary Target and Laboratory Control Sample Gaseous Standards: target compounds, 1000 ppb v/v, vendor-certified high-pressure aluminum cylinder.

7.5.1. An expiration date of one year from the date of vendor certification is assigned to the standard cylinder. This expiration date may be extended through comparison against an unexpired standard that meets the second source standard criteria in Section 10.4.

7.6. Initial Calibration Verification Standard (2nd source) stock cylinders (ICV): Target compounds, 300 ppb v/v, vendor-certified high-pressure aluminum cylinders.

7.6.1. These cylinders have been used for over 10 years and no significant degradation in response has been observed. Due to this stability, the calibration verification (second source) standard stock cylinders may be used for 20 years from date of certification or until the vendor supplied expiration date, whichever is earlier. It is also subject to ongoing monitoring of target analytes against the primary calibration standard.

7.7. Standard grade neat compounds of hexachlorobutadiene (HCBD) and naphthalene, 99+% or of known purity, Chem Service, or equivalent.

7.7.1. Naphthalene/Hexachlorobutadiene (HCBD) Stock Standard: Approximately 3.6 mg of naphthalene is weighed into a glass container small enough to be dropped into a SGDB. The glass container is introduced into the SGDB and the bottle is capped with a mininert valve. Approximately 4.4 uL of HCBD is added to the SGDB using a 10 uL syringe. The SGDB is placed in an oven at approximately 60°C. The exact weight/volume to be added is calculated from the volume of the SGDB such that adding 2.5 milliliters from the SGDB to a 15-L can (or 1

mL in a 6-L can) pressurized to 30 psig yields a concentration of 25 ppb (v/v) of HCBD and Naphthalene in the working standard. See section 12.7 and 12.8 for calculations.

7.8. Prepared Standard, polar compounds, vendor certified mix containing methanol, ethyl ether, acetone, acrylonitrile, vinyl acetate, 2-butanone, 1-butanol, 4-methyl-2-pentanone, 2-hexanone, methyl-tert-butyl ether, acrolein, acetonitrile, 99+% or of known purity, Ultra Scientific or equivalent.

7.9. Polar stock standard and 1,2,3-trichloropropane, 99+% or of known purity, Chem Service or equivalent.

7.9.1. SGDB stock method: Approximately 27 µL of the polar standard mix (section 7.8) and approximately 1.3 uL of 1,2,3-trichloropropane is injected into a SGDB. The exact volume to be added is calculated from the volume of the SGDB such that adding 5 mL from the SGDB to the working standard yields a concentration of 100 ppb (v/v) for methanol and 50 ppb (v/v) for the other polar compounds and 25 ppb (v/v) of 1,2,3-trichloropropane in the working standard.

7.9.2. Water stock method: 67.5 uL of the polar standard mix and 3.25 uL of 1,2,3-trichloropropane are dissolved in water to a final volume of 10 mL.

7.10. Additional Standards: Neat materials, not contained in the certified cylinders, can be added to a SGDB either individually or as a mix.

7.10.1. If the desired compound is a gas at room temperature, a measured volume is injected into an evacuated summa canister and pressurized. See section 12.9 and 12.10 for calculation. If the desired compound is a liquid or solid at room temperature, the volume of each compound to be added to the SGDB should be back calculated to the desired final concentration in the canister. See section 12.7 and 12.8 for calculation.

7.11. 50ppb v/v Canister Working Standard (for a 15-L can. For a 6-L can, reduce the volume of standards appropriately).

7.11.1. 100ul of reagent water is injected through a septum (inserted into a ¼ in. nut) into a clean evacuated 15-L canister.

7.11.2. The canister is then brought up to 0" gauge pressure with UHP nitrogen

7.11.3. 3 in (Hg) of the 1000 ppb v/v high pressure gas standard from Section 7.5 is added to the 15-liter canister. The can is pressurized to 30 in (Hg) with

UHP nitrogen for a final volume of 30 L and final concentration of 50ppb v/v.

7.11.4. Alternate concentrations of the working standards may be made as long as the calculations, concentrations and volumes are adjusted appropriately and preparation is clearly documented in the standard preparation logbook.

7.12. Low Standard Preparation: Typically 1 ppb v/v or 2 ppb v/v calibration point

7.12.1. 40 µL of reagent water is injected through a septum (inserted into a 1/4 inch nut) into a clean evacuated 6-liter canister. The canister is allowed to stand for at least 20 minutes to allow all the water to evaporate from the valve area.

7.12.2. 240 mL (2.4" Hg) (for a 1 ppb v/v standard) or 480 mL (4.8" Hg) (for a 2 ppb v/v standard) of the 50 ppb (v/v) standard is transferred to a 6-liter canister.

7.12.3. The canister is pressurized to 30 in. Hg with UHP nitrogen.

7.13. 50 ppb v/v Canister Second Source Standard (for a 15-L can. For a 6-L can, reduce the volume of the standards appropriately).

7.13.1. 100 uL of reagent water is injected through a septum (inserted into a 1/4-in. nut) into a clean evacuated 15-liter canister. . The canister is allowed to stand for at least 20 minutes to allow all the water to evaporate from the valve area .

7.13.2. 10 uL from the water standard in 7.9.2 (or 5 mL of the polar stock from the SGDB in 7.9.1) and 2.5 mL of the naphthalene/HCBD stock in 7.7.1 are injected through the septum. . This step should be done quickly and the syringe for the naphthalene/HCBD stock should be heated in the oven along with the SGDB. The canister is then brought up to exactly zero inches gauge pressure with UHP nitrogen

7.13.3. 5 in. (Hg) of each 300 ppb v/v high-pressure gas standard from section 7.5 is added to the 15-liter canister. The can is pressurized to 30 in (Hg) with UHP nitrogen for a final volume of 30L and final concentration of 25 ppb v/v

7.13.4. Alternate concentrations of the working standards may be made as long as the calculations, concentrations and volumes are adjusted appropriately and preparation is clearly documented in the standard preparation logbook

7.14. Approved SGDB and canister stock standards (section 7.7, 7.8, 7.9 and 7.10) may be used for 6 months from the date of preparation or the earliest expiration of parent standard, whichever comes first. Working canister standards (7.11 and 7.12 and 7.13) may be used for two months from the date of preparation or the earliest expiration of parent standard, whichever comes first.

7.15. The HCBD/naphthalene SGDB is stored at approximately 60°C. Other SGDB and canister standards are stored at room temperature. If the analytes prove to be plating/condensing in the SGDB at room temperature, then the SGDB should be stored at approximately 60°C. Mixes and neat compounds (that are not in SGDB, cans, or cylinders) are stored at the manufacturer's recommended storage conditions.

7.16. Approval of Stock and Working Standards

7.16.1. When a new stock is prepared, it can either be verified at the SGDB stage or at the working level stage.

7.16.1.1. To compare the SGDB standards, humidify two 6 liter canisters with 40 µL of water each, and spike with equal known volumes (typically 5 - 10 mL) from the SGDB, and bring to an equal final pressure of nominally 15 psig.

7.16.1.2. The two standards must agree to within 20 percent difference after taking into account nominal volume differences between the two bottles.

7.16.2. Working canister standards are approved for use by passing the daily standard acceptance criteria given in Section 10.5 or the initial calibration verification in section 10.4. The working LCS canister is approved for use by passing the LCS acceptance criteria in section 9.3.

8. Sample Collection, Preservation and Storage

8.1. Sampling is not performed for this method by STL Knoxville. For information regarding sample shipping, refer to SOP KNOX-SC-0003, Receipt and Log In of Commercial Samples, current revision.

Container Type	Preservative	Holding Time
SUMMA canister	None	30 days
Tedlar bag	None	72 hours from collection to analysis or transfer to a can. After transfer to a can, the holding time is 30 day from sample collection.

9. Quality Control

9.1. Internal/Surrogate Standards

9.1.1. Internal standards and surrogates are added to each analytical standard, blank and sample. The acceptance criteria for each internal standard's area for every analysis must be ± 40% recovery of the internal standard area from the continuing calibration standard. The acceptance criteria for each internal standard's retention time in every analysis must be within ± 20 seconds (0.33 minutes) of the internal standard retention time from the continuing calibration standard.

9.1.2. Surrogate recoveries must fall within 70% to 130%, or within laboratory historical control limits if available.

9.1.3. If the internal standard areas or surrogate recoveries for a sample are outside their limits, the cause is determined. If it is a result of a system problem, then the problem must be corrected and the sample reanalyzed with acceptable results. If it is the result of a matrix effect, the sample must be reanalyzed to confirm this, unless the effect is caused by high levels of target or non-target compounds co-eluting with or interfering with the surrogates or internal standards.

9.1.4. If the sample surrogate recoveries are biased high outside acceptance limits and no target analytes are detected above the reporting limit, the sample data may be reported with qualification in the project narrative.

9.2. System Blanks

9.2.1. For each 24-hour tune in which samples are analyzed or every 20 samples, whichever is more frequent, an acceptable system blank must be analyzed before samples analysis may begin.

9.2.1.1. A system blank is defined as a cleaned canister, humidified with reagent water and filled with UHP nitrogen.

9.2.1.2. Typically, a 30L canister, humidified with 200 uL of reagent water and pressurized to 25-30 psi with nitrogen is used for the blank. A lot check from the can cleaning system can be used as a system blank (See section 9.5).

9.2.1.3. An acceptable system blank is one with all target analytes less than 0.2 ppbv. The data may still be reported if the concentration of the analyte is less than the laboratory

reporting limit (see Tables 1, 2 and 3), and meets internal standard and surrogate requirements in section 9.1. Any samples associated with a method blank with results above 0.2 ppbv are flagged in the data report. If a blank has a reportable result between the RL and the MDL, the associated samples are also flagged.

9.2.2. If a system blank does not meet the above criteria, then the blank must be reanalyzed or a new blank prepared and analyzed with acceptable results.

9.3. Laboratory Control Standard (LCS)

9.3.1. The LCS is defined as a working standard made by the same method as analytical standards, using the same source materials. It is used to assess analytical control of this procedure. The LCS is analyzed every 24 hour tune or every 20 samples, whichever is more frequent.

9.3.1.1. The daily calibration verification may also serve as the LCS as long as it meets the criteria of both the LCS and the daily calibration verification.

9.3.2. All non-polar analytes in the LCS must be within 70-130% recovery with the allowance of up to two non-polar analytes having 60-140% recovery. All polar analytes in the LCS must be within 60-140% recovery with the allowance of up to two polar analytes having 45-155% recovery.

9.3.3. The internal standards and surrogates must pass criteria specified in section 9.1.

9.3.4. If the above criteria cannot be met, corrective action must take place. Corrective action may include: a reanalysis of the LCS, performing instrument maintenance, preparation of a new working standard, or recalibration of the instrument. Corrective action is followed by reanalysis of any samples associated with the LCS that failed acceptance criteria.

9.3.5. Note: If the LCS recovery for a target analyte is biased high outside acceptance limits and that target analyte is not detected in any of the associated samples above the reporting limit, the sample data may be reported with qualification in the project narrative.

9.4. Duplicate Analysis

9.4.1. A duplicate is analyzed with every 20 samples. It is not reported unless specifically requested.

9.4.2. The acceptance criteria for the duplicate analysis are $\leq$ 25% RPD for target compounds that are greater than 5 times the RL. No criteria for methanol and n-butanol. The calculations are given in section 12,16.

9.4.3. If the RPD is outside acceptance criteria for the duplicate, the sample is rerun once. If upon reanalysis, the duplicate does not meet acceptance criteria, the original sample data is qualified in the project narrative.

9.4.4. Due to limited sample volume, duplicates are not performed for Tedlar bags unless otherwise specified in the project requirements.

9.5. Canister Blank Checking

9.5.1. From each cleaned lot of canisters, a canister is selected, humidified with 40 µL reagent water, and pressurized with UHP nitrogen. (See SOP KNOX-SC-0001, current revision, "Canister Cleaning and Preparation").

9.5.2. A blank check is analyzed within 24 hours of a valid tune check and calibration.

9.5.3. A blank check passes if there are no target analytes above the reporting limit, and the internal standards and surrogates pass criteria in section 9.1. Cans are considered certified "clean" if the result for all analytes are below 0.2 ppbv. However the can may still be used to collect samples if the concentration of the target analyte is less than the reporting limit. If analytes are detected in the can being certified as clean above 0.2 ppbv and below the reporting limit, this will be noted on the blank check quantitation report.

9.5.4. If a blank check canister does not pass, the can may be re-analyzed. If the acceptance criteria are still not met, the entire lot of canisters must be re-cleaned, and a blank check from the re-cleaned lot must pass.

9.6. Nitrogen check

9.6.1. Before a new nitrogen cylinder is used for pressurization of samples or standards, it must be analyzed as a blank and pass all the criteria in section 9.2.1.3.

9.7. Annual gauge calibration: The gauges that are used in calculations to measure cylinder and canister pressure or vacuum must be certified annually.

10. Calibration and Standardization

10.1. Instrument Conditions: The following steps are part of the software's automatic tuning procedure and are performed as needed.

10.1.1. Mass assignments of the mass spectrometer are checked and adjusted using perfluorotributylamine (PFTBA FC43).

10.1.2. The mass spectrometer is tuned to meet the criteria for BFB (see Figure 1).

10.1.3. The mass spectrometer is adjusted to minimize noise (see instrument manufacturer instruction manuals).

10.1.4. See Appendix III for examples of GC/MS and GC instrument parameters.

10.2. Daily Tune Check

10.2.1. 50 ng or less of BFB is analyzed for each 24-hour time tune period; the 24-hour time period begins at the moment of injection of BFB. All abundance criteria for BFB in Figure 1 must be met before the analysis of standards, QC samples or client samples.

10.2.2. The BFB must be acquired in the following manner: Three scans (the apex scan, and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction is conducted using a single scan prior to the elution of BFB.

10.2.3. Once the BFB passes criteria, the same mass spectral conditions used for the BFB must be used to acquire the data in that 24-hour tune period, until the next BFB event.

10.3. Initial Calibration

10.3.1. The GC/MS system must be calibrated with at least 5 concentrations that span the monitoring range of interest. The dynamic range of the curve is generally 0.2 ppb v/v to 30 ppb v/v based on 200 mL sample analysis for normal level reporting limits for most analytes, and 0.01 ppb v/v to 1 ppb v/v based on 500 mL sample analysis for low level reporting limits, for a limited set of analytes. The concentration of the low standard of the calibration must be at or below the reporting limit. If quadratic fit is required, there must be at least 6 points. See Appendix IV for the recommended calibration amounts.

10.3.2. See chart below to obtain the typical desired levels of quantitation. This is a typical schematic of the calibration; however the standard can

concentration, calibration levels and calculated concentrations may be different, as long as the calibration rules in 10.3.1 and 10.3.11 are followed. See Appendix IV and V for the table of analytes. If the actual standard amount trapped is greater than 5% from the programmed volume, the actual volume trapped is documented and used in calculations.

Normal Level Reporting Limit (calculation based on 200ml sample analysis) Volumes (mls) taken from the working stock canisters to prepare the calibration series concentrations listed (ppbv/v)

50 ppb v/v can	240	160	80	40	20	-	-	-	-
1 ppb v/v can	-	-	-	-	-	160	80	40	20
Calculated concentration ppb v/v	60	40	20	10	5	0.8	0.4	0.2	0.1

Low Level Reporting Limit (calculation based on 500ml sample analysis) Volumes (mls) taken from stock canisters to prepare the calibration series concentrations listed (ppbv/v)

2 ppb v/v can	250	125	50	-	-	-	-
0.1 ppb v/v can	-	-	-	500	200	100	50
Calculated concentration ppb v/v	1.0	0.5	0.2	0.1	0.04	0.02	0.01

10.3.3. See Tables 1, 2 and 3 for suggested quantitation ions.

10.3.4. A calibration curve is valid for all target analytes if the relative standard deviation (RSD) of the relative response factors is $\leq$30% for each target analyte, with the following allowance: up to two target analytes may have an RSD $\leq$ 40%.

10.3.5. The internal standard area response at each calibration level must be within 40% of the mean area response over the initial calibration range for each internal standard.

10.3.6. The retention time (RT) shift for each of the internal standards at each calibration level must be within 20 seconds of the retention time of the mean calibration for each internal standard.

10.3.7. Each analyte at each level must be within 0.06 RRT units of the mean RRT.

10.3.8. If the curve is acceptable and there is time remaining in the 24-hour tune, blanks, LCSs and samples may be analyzed.

10.3.9. The concentrations in the samples, LCSs and blanks are calculated using the response factors from the initial calibration curve.

10.3.10. Linear or quadratic curve fits may be used. Use of 1/Concentration^2 weighting may be used to improve the accuracy of quantitation at the low end of the curve. The analyst should consider instrument maintenance to improve the linearity of response. The correlation coefficient (coefficient of determination for non-linear curves, r^2) must be $\geq$ 0.990.

10.3.11. Analyst may elect to drop points from the calibration to improve subsequent quantitation. The rules for dropping points are:

- May drop points below the RL as long as there is a point remaining at or below the RL.
- May drop high points, decreasing linear range.
- May NOT drop a point between points.

For more guidance see "Selection of Calibration Points" Policy P-T-001, current revision.

Rules for curve use/acceptability:

- The Y intercept must be below the RL.
- The r^2 value obtained from Target must be $\geq$0.990.
- At least 5 points must be used for average or linear curve.
- At least 6 points must be used for a quadratic curve.
- Do not include the origin or force the curve through the origin.
- For quadratic curves, the tangent line to the slope of the curve must be continuous and positive (i.e. no parabola's or breaks in the curve).

10.4. Initial Calibration Verification (ICV)

10.4.1. The ICV is a second source standard containing the TO-14 list compounds at 10 ppb (Table 1) and is analyzed after the initial calibration and before any samples are analyzed. For each analyte, a percent recovery (%R) is calculated using the response factor from the initial calibration.

10.4.2. A working standard from an independently prepared stock containing all analytes is also analyzed as the ICV for analytes not included in the TO-14 list.

10.4.3. The ICV is valid for all analytes if the %R is between 65% and 135% for each TO-14 list analyte in the ICV. Benzyl chloride ICV acceptance criteria is 20-180%.

10.5. Daily Calibration Verification

10.5.1. A mid-level standard is analyzed following the daily tune check (section 10.2) as the calibration verification standard. Typically, this is 80 mL of

the 25-ppb (v/v) can. For all target analytes, a percent difference (%D) or percent drift is calculated using the response from the calibration verification standard and compared to the current initial calibration curve.

10.5.2. A calibration verification standard is acceptable if the %D or % drift is ≤30% for all target analytes. However, data may be reported from a calibration verification standard with up to four target analytes with % drift up to ≤40%. These analytes must be clearly noted in the data report.

10.5.2.1. For samples from New Jersey, the target analytes with drift >30% must be noted in the narrative.

10.5.3. The daily calibration verification may also serve as the LCS as long as it meets the criteria of both the LCS and the daily calibration verification (section 9).

10.5.4. If the calibration verification standard does not meet the above criteria, corrective action must be taken and/or a new initial calibration performed unless project specific analytes or client specified QC criteria are met. Corrective action may include a reanalysis of the calibration verification standard. If reanalysis of the standard does not meet acceptance criteria, further corrective action may include performing instrument maintenance, or preparation of a new working calibration verification standard. Either of these corrective actions must be followed by successful analysis of the calibration verification standard and reanalysis of any affected samples. If these corrective actions do not result in an acceptable calibration verification, a new initial calibration must be performed.

11. Procedure

11.1. Canister Preparation

11.1.1. Use the following guidelines when checking a sample upon receipt:

- Tedlar bags are inspected to ensure that the valve is closed and the bags are not leaking. Bags must be analyzed or transferred to a can within 72 hours of collection. Tedlar bags are analyzed directly from the bag or transferred to an evacuated SUMMA can within 72 hours of sampling. If the entire bag is transferred to a can, the bag is attached to a short line and the entire contents transferred to a 1-L or a 6-L evacuated can. If only a portion of the bag is to be transferred, a measured aliquot of the bag is transferred via syringe through a septa attached to the top of a 1-L or a 6-L humidified can. After transfer, the can is then pressurized to a positive pressure and the pressure is recorded. The lab default is to analyze tedlar bags at a 20x dilution. Based on a default dilution factor

at the bench, the RLs and MDLs will be 20 times higher for tedlar bag analysis. (If a client wants lower RLs than 20x the standard this will need to be communicated to the lab via special instructions.) If a client wants RLs lower than 20x and the client is supplying the tedlar bags, the PM should request that the client send an unused bag to be logged in and run along with their samples as a media blank check. If a client wants RLs lower than 20x and STL Knoxville is supplying the tedlar bags, the PM should have sample receiving set aside and log in a tedlar bag from the same lot as a media check.

- 1-L cans received between -10" Hg vacuum and a positive pressure are ready for a 20 mL analysis. If more volume is expected to be analyzed, the can will have to be pressurized in order to obtain more volume from the can.
- 6-liter cans received between -10" Hg vacuum and a positive pressure are ready for 200 mL analysis
- If any can is near zero psi (approximately -1" Hg to 1 psi), non-conformance the can as "suspect improper sampling event" and proceed with analysis. The project manager will discuss this with the client.
- Cans received –10" Hg or more vacuum should be pressurized to no more than approximately 5 psi.
- Cans below -20" Hg: non-conformance the can as "suspect improper volume sampled" and proceed with pressurizing the can to no more than approximately 5 psi for analysis. The project manager will discuss with the client that there may have not been enough sample collected for analysis and inform the analyst if sample analysis is to proceed or if the test is to be cancelled.
- Cans received at high vacuum (near -28" Hg or lower) should be inspected to determine if it is a trip blank. If the can is a trip blank, pressurize the can and use a dilution factor of one in analysis. If the sample cannot be determined to be a trip blank, non-conformance the can as "suspect improper sampling event" and proceed with pressurizing the can for analysis. The project manager will discuss with the client that there was not enough sample collected for analysis, and inform the analyst if sample analysis is to proceed or if the test is to be cancelled.

11.1.2. Measure the initial and final pressure/vacuum of the canister using an NIST traceable, certified vacuum or pressure gauge.

11.1.3. The barometric pressure, initial pressure/vacuum and final pressure/vacuum are recorded in a laboratory notebook, and used to calculate the dilution factor caused by pressurizing the can to working conditions

11.1.4. The canister is allowed to equilibrate for approximately one hour. If the canister was pressurized to greater than 15 psig, pressure should be released from the canister to bring the pressure below 15 psig. For autosampler volumes scheduled to be below 50 mL, the can pressure must be reduced to below 7 psig to more accurately measure the volume injected.

11.1.5. This canister may be further diluted, if necessary, by the dilution methods discussed in sections 11.3, 11.5 and 11.6.

11.2. Following a successful initial or calibration verification and prior to analysis of actual samples, an acceptable system blank and LCS must be analyzed (see sections 9.2 and 9.3). Following successful system blank and LCS analysis, actual sample analysis may begin. The LCS and blank are analyzed every 24 hour tune or every 20 samples, whichever is more frequent.

11.2.1. The desired sample size of each sample to be analyzed is determined by screening the cans according to SOP KNOX-MS-0010, current revision, Volatile Analyte Screening By Purge and Trap. The standard aliquot size is 200 mL for standard reporting limit work or 500 mL for low-level work. Sample volume injected can range from 10 mL to 1000 mL. For sample volumes below 50 mL, the can pressure must be reduced to below 7 psig to more accurately measure the volume injected. Volumes larger than 1000 mL can cause trap freeze-up when high humidity samples are trapped. If samples have been adequately pressurized with nitrogen, have been diluted, or only a small amount of sample collected in the can, then volumes larger than 1000 mL may be trapped, and the internal standards and surrogates monitored closely for breakthrough or freeze-up problems.

11.2.2. The pressure of each sample canister is checked. If the pressure is above 15 psig, the excess pressure is vented.

11.2.3. Each sample name, volume (aliquot), method, and autosampler position are typed into the Entech sequence table.

11.2.4. If necessary, the automated flush function is used to sweep each autosampler line in the name list with helium.

11.2.5. The cans are then securely tightened onto the autosampler with the canister valves closed.

11.2.6. An automated leak check is run on each position. A hard copy of the leak check results is included with the daily calibration package. This is only a

check to ensure that the valves are in proper working order and that the cans are attached securely to the autosampler.

11.2.7. If all positions pass the leak check, the canister valves are opened.

11.2.8. A name list similar to the Entech name list (section 11.2.3) is typed into the GC/MS sequence table. The sample volume programmed, the can number and a notation for in-can or serial dilution are noted in the analytical run log.

11.2.8.1. If the actual sample amount trapped is greater than 5% from the programmed volume, the actual volume trapped is documented and used in calculating the results.

11.2.9. The Entech autosampler is started and the GC/MS acquisition program is started. (Note: The scan and GC parameters are controlled by the GC/MS method.)

11.2.10. 20 ml of the surrogate/internal standard is trapped on the Entech concentrator prior to sample introduction.

11.2.11. The analysis proceeds automatically for each name in the Entech autosampler program.

11.2.12. The internal standards and surrogates must pass all the criteria specified in section 9.1.

11.3. Autosampler Dilutions

11.3.1. Volumes of 10 to 1000 mL may be analyzed by the autosampler (see section 11.2.1). The standard aliquot is 200 mL for standard reporting limit work and 500 mL for low-level work.

11.3.2. If an analyte found in the sample is over the curve by less than a factor of twenty (based on 200 ml nominal volume) or fifty (based on 500 ml nominal volume), then the aliquot size of the sample may be reduced to a volume as low as 10 mL. This dilution factor is multiplied with all other dilution factors for this sample to obtain the final dilution factor.

11.3.3. If a dilution is performed to bring one or more analytes within the calibration range, the analyte having the highest concentration should not be diluted to less than 20% of the calibration range unless there are significant amounts of non-target compounds present.

11.3.4. If the sample is initially run at a dilution and the baseline rise is less than the height of the internal standards, or if individual non target peaks are less than five times the height of the internal standards, then the sample should be reanalyzed at a more concentrated dilution (up to the nominal volume). This requirement is approximate and subject to analyst judgment.

11.3.5. Only the most concentrated dilution with no target compounds above the calibration range will be reported. Other dilutions will only be reported at client request.

11.3.6. The internal standards and surrogates must pass all the criteria specified in section 9.1.

11.4. Water addition

11.4.1. The analyst should be aware that humidity plays an important role in the recovery of certain target compounds, particularly polar compounds, and should be prepared to add humidity to canisters where appropriate. The addition of water helps to stabilize the behavior of these compounds, which might otherwise interact with the interior surface of the summa canister or with the stainless-steel lines of the sample manifold.

11.4.2. Since it is not practical to know the relative humidity of all canisters received at the laboratory, the analyst should assume that canisters are received at approximately 80 percent relative humidity. When making canister dilutions (see Sections 11.5, and 11.6), the analyst should attempt to preserve the relative humidity of canisters at a level that will minimize recovery loss due to low canister relative humidity.

11.4.3. Under normal laboratory conditions, a 6 liter summa canister at ambient pressure will have a relative humidity of 100 percent if approximately 100 uL of water is in the canister.

11.4.3.1. The minimum relative humidity at which canisters containing polar analytes can be analyzed before polar target recovery is negatively affected is approximately 20 - 30 percent.

11.4.3.2. The minimum relative humidity at which canisters containing nonpolar analytes can be analyzed before nonpolar target recovery is negatively affected is approximately 10 percent.

11.5. Serial Dilution

11.5.1. High-level samples, for example, are those containing ppm levels of volatile organic compounds.

11.5.2. The original sample canister must have a positive pressure. If the pressure is less than 0 psig, then proceed to Section 11.1.

11.5.3. A septum cap is attached to the sample canister and a gas-tight syringe is purged with UHP nitrogen. A septum cap is attached to a clean evacuated 6-liter canister (the dilution canister).

11.5.4. 40 uL of deionized water is added to the canister through the septum of the evacuated can (See Section 11.4 for guidance on addition of water).

11.5.5. The syringe is inserted into the septum cap of the canister containing the sample and the canister valve is opened. The syringe is purged twice with sample and vented. The desired volume is then withdrawn and transferred into the dilution canister. The dilution canister is then pressurized using UHP nitrogen.

11.5.6. The final pressure is measured in the serial dilution canister using a NIST traceable, certified gauge.

11.5.7. If the canister was pressurized to greater than 15 psig, pressure should be released from the canister to bring the pressure below 15 psig.

11.5.8. The barometric pressure, the aliquot volume, final canister pressure and canister serial number are recorded in a laboratory notebook. The serial dilution factor is calculated.

11.5.9. If a high level dilution is performed to bring one or more analytes within the curve, the analyte having the highest concentration should not be diluted to less than 20% of the upper calibration range, unless there are significant amounts of non-target compounds present. It is imperative that high levels of target and non-target analytes not contaminate the analytical system.

11.5.10. This serial dilution canister may be further diluted, if necessary, by another serial dilution or in-can dilution (see section 11.6) or on the autosampler (see section 11.3). The final dilution factor is the product of all the dilution factors for the sample.

11.6. In-canister Dilutions

11.6.1. If an analyte found or suspected to be in the sample is over the calibration range, to a level that an autosampler dilution would be insufficient, an in-canister dilution may be performed.

11.6.2. The canister vacuum/pressure is checked. If the can is under vacuum, then record the vacuum reading and proceed to section 11.6.3. If the canister is under pressure, then the can is bled to ambient pressure, then proceed to section 11.6.3.

11.6.3. The canister is pressurized to the desired pressure. The pressure should be no more than 40 psig.

11.6.4. The final pressure is measured using an NIST traceable, certified gauge.

11.6.5. If the canister was pressurized to greater than 15 psig, pressure should be released from the canister to bring the pressure below 15 psig.

11.6.6. The barometric pressure and the final pressures are recorded in a laboratory notebook and the in-can dilution factor is calculated.

11.6.7. If an in-canister dilution is performed to bring one or more analytes within the curve, the analyte having the highest concentration should not be diluted to less than 20% of the upper calibration range, unless there are significant amounts of non-target compounds present. Care should be taken to avoid over-dilution for in-canister dilutions since the original sample is affected.

11.6.8. This in-can dilution canister may be further diluted, if necessary, by another in-can dilution or a serial dilution (see section 11.6) or on the autosampler (see section 11.3). This dilution factor is multiplied with all other dilution factors for this sample to obtain the final dilution factor.

11.7. Major Maintenance

11.7.1. A new initial calibration is necessary following major maintenance. Major maintenance includes changing the column, cleaning or repairing the source, replacing filaments, changing electronics, replacing the multiplier or changing moisture or Tenax traps.

11.8. Minor Maintenance

11.8.1. Minor maintenance includes cleaning the injector port, replacing filters, changing the pump oil, autotuning, switching filaments (instrument contains two filaments under vacuum), replacing valves or rotors,

change/refill the calibration vial, changing seals and o-rings, ballasting pump, replacing fuses, replacing roughing pumps or transfer lines.

11.9. One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure, except those specified by project specific instructions, shall be completely documented using a Nonconformance Memo and approved by a Technical Specialist, Project Manager and QA Manager. If contractually required, the client shall be notified.

11.10. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

12. Data Analysis and Calculations

12.1. Refer to Figure 2 for an example data review checklists used to perform and document the review of the data. Using the data review checklist, the analyst also creates a narrative which includes any qualifications of the sample data.

12.2. Tentatively Identified Compounds (TICs): Library searches of peaks present in the chromatogram that are not target compounds (Tentatively Identified Compounds, TIC) may be performed if required by the client. They are evaluated using the STL Knoxville SOP KNOX-MS-0014, current revision, "Determination of Tentatively Identified Compounds (TICs)"

12.3. Calculation legend:

A	=	amount of neat compound, uL
CB	=	concentration in SGDB, ug/mL
CC	=	concentration in canister, ppb v/v
CS	=	concentration in mix, ug/uL
Cx	=	the value determined by vendor certification analyses is used in the following calculations, ppb v/v (300 ppb nominal)
d	=	density of neat compound, g/mL
DF	=	dilution factor, unitless
FV	=	final volume in a pressurized canister, liters
GC	=	gas constant at 25°C and standard pressure, 24.45 nL/n mole
MW	=	molecular weight, ng/n mole
PB	=	barometric pressure
PF	=	final pressure, units specified
PI	=	initial pressure, units specified
PT	=	transfer pressure, units specified
Px	=	pressure in X = inches, psia or mmHg
TK	=	temperature in Kelvin

TV = transfer volume, liters or uL
Vbottle= volume of static gas dilution bottle, mL
Vmix = volume of mix, µL

12.4. Calculations:

12.4.1. Final Canister Volume

$$FV = \frac{Canister\ size(L)\ x\ P_F(mm\ Hg\ Abs)}{P_B(mm\ Hg\ Abs)}$$

Pmm Hg = P inches x 25.4
P inches = Ppsi * 2.036
Pmm Hg = P_{psi} x 51.7149

12.5. Polar stock:

12.5.1. $$CS\ \mu g / uL = \frac{A * d * 1000}{V_{mix}}$$

12.5.2. $$CB\ \mu g / mL = \frac{CS * TV,\ \mu L}{V_{bottle}}$$

12.6. Polar concentration in target dilution standard

$$CC,\ ppb\ v/v = \frac{TV,\ \mu L\ *\ CB\ x\ GC}{MW\ *\ FV}$$

12.7. Stock standards in SGDB

$$CB_{LIQUID},\ \mu g/mL = \frac{\#\ \mu L * d * 1000 * 0.8829}{V_{bottle}}$$

where 0.8829 is a temperature correction factor (from 21 °C to 60°C)—only used if the SGDB standard is in the oven at 60 C; = 294 °K / 333 °K.

12.7.1. Liquid formula

12.7.2. Solid formula

$$CB_{SOLID}, \mu g/mL = \frac{\#\, mg * 1000 * 0.8829}{V_{bottle}}$$

where 0.8829 is a temperature correction factor (from 21 °C to 60°C)—only used if the SGDB standard is in the oven at 60 C; = 294 °K / 333 °K.

12.8. Concentration of standards in primary target standard made from SGDB

$$CC, ppb\ v/v = \frac{TV, mL * CB\ x\ 1000 * GC}{FV * MW}$$

12.9. Concentration of Cylinder Standards: Concentration of Analytes in Primary Target Standard

$$CC, ppb\ v/v = \frac{(P_T - P_I, psi)(Cx)}{(P_F, psi + PB, psi)}$$

12.10. Target Dilution Standard (CC is the concentration of the Primary Target Standard).

$$CC, ppb\ v/v = \frac{(P_T - P_I)(CC)}{(P_F + PB, psi)}$$

12.11. Dilution Factors of original sample canisters

12.11.1. In Can Dilution Factor

$$DF = \frac{P_{f(mm\,Abs)}}{P_{i(mm\,Abs)}}$$

12.11.2.Serial Dilution Factor

DF = FV/TV

12.11.3. Instrument Dilution Factor

$$DF = \frac{\text{Nominal Sample Volume}}{\text{Sample Volume Injected}}$$

12.12. Response Factor (RF)

$$RF = \frac{Ax * Cis}{Ais * Cx}$$

where:

x	=	area of the characteristic ion for the target compound.
Ais	=	area of the characteristic ion for the internal standard.
Cx	=	amount of the target compound.
Cis	=	amount of the internal standard.

12.13. Average Response Factor (ARF)

$$ARF = \frac{RF_1 + RF_2 + \ldots + RF_n}{n}$$

where:

n	=	the number of calibration points

12.14. Standard deviation of the ARF:

$$S = \sqrt{\frac{\sum_i^n (ARF - RF_n)^2}{n-1}}$$

12.15. Relative standard deviation (RSD) of the ARF:

$$RSD = \frac{S}{ARF} * 100\%$$

12.16. Calibration Verification : Percent deviation (% D) of the daily RF values as compared with the initial ARF values:

$$\%D = \frac{|RF - ARF|}{ARF} * 100\%$$

12.17. Laboratory Control Sample percent recovery (%R):

$$\%R = \frac{FoundAmount, ppb}{SpikeAmount, ppb} * 100\%$$

12.18. Duplicate relative percent difference (RPD):

$$RPD = \frac{|A_1 - A_2|}{\bar{A}} \times 100\%$$

where:

A_1	=	amount determined in first analysis
A_2	=	amount determined in second analysis
A	=	average determination, $(A_1 + A_2)/2$

12.19. Calibration verification percent drift and difference from the initial calibration:

$$\%\ \text{Drift} = \frac{C_{expected} - C_{found}}{C_{expected}} \times 100$$

Where

$C_{expected}$ = Known concentration in standard

C_{found} = Measured concentration using selected quantitation method

$$\%Difference = \frac{\overline{RF} - RF}{\overline{RF}} \times 100$$

$\overline{RF}$ = Average Analyte Response Factor from Initial Calibration

RF = Measured Analyte Response Factor from Calibration Verification

12.19.1. Target analyte concentrations in samples are typically calculated using the average response factor from the initial calibration. Quantitation may also be determined using linear or second order curves at the analyst's discretion to improve the quantitation of target analytes.

12.19.1.1. Calculation of concentration using Average Response Factors

$$C_{pv} = \frac{R_x C_{is}}{R_{is}\overline{RF}}$$

12.19.1.2.Calculation of concentration using Linear fit

$$C_{pv} = A + B\frac{(R_x C_{is})}{R_{is}}$$

C_{pv} = Concentration, ppb (v/v)
R_x = Response for analyte (area of quantitation ion)
R_{is} = Response for internal standard (area of quantitation ion)
C_{is} = Concentration of internal standard
A = Intercept
B = Slope

The corresponding Target software calculation is as follows:

$$Cpv = Cis(b + \frac{1}{ml} \times \frac{Rx}{Ris})$$

b = Concentration Ratio Intercept
ml = Inverse of Slope

12.19.1.3.Calculation of concentration using Quadratic fit

$$Cpv = A + B\left(\frac{RxCis}{Ris}\right) + C\left(\frac{RxCis}{Ris}\right)^2$$

C = Curvature

The corresponding Target software calculation is as follows:

$$Cpv = Cis\left(b + ml \times \frac{Rx}{Ris} + m2 \times \left(\frac{Rx}{Ris}\right)^2\right)$$

ml = First order coefficient
m2 = Curvature (Second order coefficient)

12.20. Sample Quantitation: The amount of target compound detected is determined using the average RF or calibration curve values from the initial calibration (not the continuing calibration):

$$Amount = Cpv * DF$$

12.21. Unit conversions

12.21.1.

$$\text{Amount}, \mu g/m^3 = \frac{\text{Amount}, ppb\,(v/v) * MW}{GC}$$

12.21.2.

$$\text{Amount, ppm v/v} = \text{amount}, \frac{ppb\,(v/v)}{1000}$$

12.22. Quantitation of Unknowns

12.22.1. If required, nontarget peaks are reported with probable identifications as Tentatively Identified Compounds (TICs). These are quantitated using the nearest internal standard and assuming a response factor of 1; correction for dilution factor is also made. Search criteria are those in the STL Knoxville SOP KNOX-MS-0014, current revision, Tentatively Identified Compounds (TICs).

13. Method Performance

13.1. Method Detection Limit (MDL) - An MDL must be determined for each analyte in each routine matrix prior to the analysis of any samples. The procedure for determination of the method detection limit is given in the SOP S-Q-003 current revision based on 40 CFR Part 136 Appendix B. The result of the MDL determination must support the reporting limit. MDL summaries are stored on the local area network.

13.2. Initial Demonstration of Capability – Each analyst must perform an initial demonstration of capability (IDOC) for each target analyte prior to performing the analysis independently. The IDOC is determined by analyzing four replicate spikes (e.g., LCSs) as detailed in STL Knoxville SOP KNOX-QA-0009. Recovery limits must be 70-130% and RSD must be less than or equal to 25%. Recovery limits for Methanol are 60-140% and RSD must be less than or equal to 30%.

13.3. Training Qualification: The group/team leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience. Refer to SOP KNOX-QA-0009 current revision for further requirements for performing and documenting initial and on-going demonstrations of capability.

14. Pollution Prevention

14.1. All attempts will be made by laboratory personnel to minimize the use of solvents when performing this procedure.

15. Waste Management

15.1. All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

15.2. The following waste streams are produced when this method is carried out.

- Expired solid and liquid standards are stored in metal closed-top containers.

16. References

16.1. Compendium Method TO-14, "The Determination of Volatile Organic Compounds (VOCs) in Ambient Air Using SUMMATM Passivated Canister Sampler and Gas Chromatographic Analysis," U.S. EPA 600/4-89/017, June 1988.

16.2. Compendium Method TO-14A, "Determination of Volatile Organic Compounds (VOCs) in Ambient Air Using Specially Prepared Canisters With Subsequent Analysis by Gas Chromatography," U.S. EPA 625/R-96/010b, January 1999.

16.3. Compendium Method TO-15, "Determination of Volatile Organic Compounds (VOCs) in Air Collected in Specially-Prepared Canisters and Analyzed by Gas Chromatography/Mass Spectrometry (GCMS)", U.S. EPA 625/R-96/010b, January 1999.

16.4. STL Quality Management Plan (QMP), current revision.

16.5. STL Knoxville Laboratory Quality Manual (LQM), current revision.

16.6. Entech Instruments Inc. 7100 Operators Manual. Version 2.0 for the 7100 Preconcentrator and Accessories.

17. Miscellaneous

17.1. Other SOPs cross-referenced in this SOP: KNOX-SC-0001, "Canister Cleaning and Preparation", latest revision.

17.2. Modification from the referenced methods

17.2.1. The TO-15 tune criteria were not used in this procedure. The tune criteria listed in TO-14 is tighter and thus was used in this procedure. This SOP also allows for 50 ng or less of BFB to verify tuning of the instrument.

17.2.2. The continuing calibration listed in this procedure allows up to 4 target analytes with a %D of $\leq$ 40%, with a narrative note (or data review checklist note for non-NJ DEP analysis) of those target analytes that are over 30% D, but $\leq$ 40% D.

17.2.3. This procedure uses purified nitrogen in place of zero humid air specified in the reference methods.

17.2.4. TO-14 requires that the RT shift for the internal standards at each calibration level must be within 20 seconds of the RT of the mid-level calibration for each internal standard. TO-15 specifies that the comparison is made to the mean RT over the initial calibration range for each internal standard. This SOP uses the TO-15 criteria.

17.2.5. Section 7.13 Method TO-15 states that the working standard may be stored for 30 days. This laboratory experience has allowed the standard expiration date to be 2 months with no significant degradation of the standards.

17.2.6. Surrogates are not required by the methods. This SOP adds surrogates to every sample to help monitor for matrix effects and method performance.

17.2.7. The TO-15 method states that the scan time must give 10 scans per peak, not to exceed 1 second per scan. The GC/MS software is set for a sampling rate of 3, which corresponds to approximately 2 to 3 scans per second, depending on the instrument. See the GC/MS operator's manual or "help" on the software for more information about the sampling rate.

17.2.8. EPA Method TO-14A specifies that the relative accuracy of the field sampler or sample delivery system must meet 90-110% for a standard at 8 ppb v/v. The laboratory Control Sample (LCS) summary data is evaluated against alternate acceptance criteria based on this laboratory procedure for method TO-14A. When TO-14A work is performed, this must be noted in the case narrative.

17.3. List of Appendices

17.3.1. Appendix I: Target Analyte Tables

17.3.1.1.Table 1: Target Analytes - TO-14 and TO-15 Compounds

17.3.1.2.Table 2: Target Analytes - Other Nonpolar Compounds

17.3.1.3.Table 3: Target Analytes - Other Polar Compounds

17.3.2. Appendix II: Figures

17.3.2.1.Figure 1: BFB Tuning Criteria

17.3.2.2.Figure 2: Example of a Data Review Checklist

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17.3.3. Appendix III: Example Instrument Parameters

17.3.4. Appendix IV: Recommended Calibration Levels (normal reporting limits)

17.3.5. Appendix IV: Recommended Calibration Levels (low level reporting limits).

Appendix I: Target Analyte Tables

Table 1: Target Analytes – Method TO-14A Target Compounds

CAS NUMBER	METHOD TO-14 COMPOUND	REPORTING LIMIT (ppb, v/v) (i)	REPORTING LIMIT (ug/m^3) (i)	Low Level Reporting Limit (ppb, v/v) (j)	MOLECULAR WEIGHT (ng/n mole)	SUGGESTED ION
75-71-8	Dichlorodifluoromethane (b)	0.2	0.99	0.020	120.9	85
76-14-2	1,2-Dichlorotetrafluoroethane (c)	0.2	1.40	0.020	170.9	135
74-87-3	Chloromethane	0.5	1.03	n/a	50.49	52
75-01-4	Vinyl Chloride	0.2	0.51	0.020	62.50	62
74-83-9	Bromomethane	0.2	0.78	0.060	94.94	94
75-00-3	Chloroethane	0.2	0.53	0.030	64.51	64
75-69-4	Trichlorofluoromethane (d)	0.2	1.12	0.030	137.4	101
75-35-4	1,1-Dichloroethene	0.2	0.79	0.090	96.94	96
76-13-1	1,1,2-Trichlorotrifluoroethane (e,f)	0.2	1.53	n/a	187.4	101
75-09-2	Methylene Chloride (f)	0.5	1.74	n/a	84.93	84
75-34-3	1,1-Dichloroethane	0.2	0.81	0.020	98.96	63
156-59-2	cis-1,2-Dichloroethene	0.2	0.79	0.050	96.94	96
67-66-3	Chloroform	0.2	0.98	0.020	119.4	83
71-55-6	1,1,1-Trichloroethane	0.2	1.09	0.020	133.4	97
56-23-5	Carbon Tetrachloride	0.2	1.26	0.020	153.8	117
71-43-2	Benzene	0.2	0.64	0.030	78.11	78
107-06-2	1,2-Dichloroethane	0.2	0.81	0.020	98.96	62
79-01-6	Trichloroethene	0.2	1.07	0.020	131.4	130
78-87-5	1,2-Dichloropropane	0.2	0.92	0.030	113.0	63
10061-01-5	cis-1,3-Dichloropropene	0.2	0.91	0.030	111.0	75
108-88-3	Toluene	0.2	0.75	0.10	92.14	91
10061-02-6	trans-1,3-Dichloropropene	0.2	0.91	0.050	111.0	75
79-00-5	1,1,2-Trichloroethane	0.2	1.09	0.040	133.4	97
127-18-4	Tetrachloroethene	0.2	1.36	0.020	165.8	129
106-93-4	1,2-Dibromoethane (EDB)	0.2	1.54	0.020	187.9	107
108-90-7	Chlorobenzene	0.2	0.92	0.020	112.6	112
100-41-4	Ethylbenzene	0.2	0.87	0.020	106.2	91
1T5-30-5	m/p-Xylene (g, h)	0.2	0.87	0.10	106.2	91
95-47-6	o-Xylene (h)	0.2	0.87	0.030	106.2	91
100-42-5	Styrene	0.2	0.85	0.020	104.2	104
79-34-5	1,1,2,2-Tetrachloroethane	0.2	1.37	0.020	167.8	83
108-67-8	1,3,5-Trimethylbenzene	0.2	0.98	0.020	120.2	120
95-63-6	1,2,4-Trimethylbenzene	0.2	0.98	n/a	120.2	105
541-73-1	1,3-Dichlorobenzene	0.2	1.2	n/a	147.0	146
106-46-7	1,4-Dichlorobenzene	0.2	1.2	n/a	147.0	146
100-44-7	Benzyl Chloride	0.4	2.07	n/a	126.6	91
95-50-1	1,2-Dichlorobenzene	0.2	1.2	n/a	147.0	146
120-82-1	1,2,4-Trichlorobenzene	1.0	7.42	n/a	181.4	180
87-68-3	Hexachlorobutadiene	1.0	10.67	n/a	260.8	225

b) Freon 12
c) Freon 114
d) Freon 11
e) Freon 113
f) This is a common laboratory solvent
g) m-xylene and p-xylene coelute
h) Total xylenes (CAS # 1330-20-7) is the sum of m/p-xylenes and o-xylene.
i) Normal reporting limits (RLs) based on 200 mL sample volume. The ug/m3 values are example RLs using the value listed in the table.
j) Low level reporting limits based on 500 mL sample volume

Table 2: Target Analytes - Other Nonpolar Compounds

CAS NUMBER	OTHER NON-POLAR COMPOUNDS	REPORTING LIMITS (ppb, v/v) (i)	REPORTING LIMIT (ug/m^3) (i)	Low Level Reporting Limit (ppb, v/v) (j)	MOLECULAR WEIGHT (ng/n mole)	SUGGESTED ION
75-45-6	Chlorodifluoromethane (b)	0.2	0.71	n/a	86.47	51
106-97-8	n-Butane	0.4	0.95	n/a	58.12	43
106-99-0	1,3-Butadiene	0.4	0.88	0.030	54.09	54
109-66-0	Pentane	1.0	2.95	n/a	72.15	57
75-15-0	Carbon Disulfide	0.5	1.56	n/a	76.14	76
107-05-1	3-Chloropropene	0.2	0.63	0.060	76.52	39
156-60-5	trans-1,2-Dichloroethene	0.2	0.79	0.10	96.94	96
110-54-3	n-Hexane	0.5	1.76	0.10	86.18	56
110-82-7	Cyclohexane	0.5	1.72	0.040	84.16	69
540-84-1	2,2,4-Trimethylpentane	0.5	2.34	0.020	114.2	57
142-82-5	n-Heptane	0.5	2.05	0.020	100.2	43
74-95-3	Dibromomethane	0.4	2.84	n/a	173.8	93
75-27-4	Bromodichloromethane	0.2	1.34	0.020	163.8	83
111-65-9	n-Octane	0.4	1.87	n/a	114.2	85
124-48-1	Dibromochloromethane	0.2	1.7	0.020	208.3	129
111-84-2	Nonane	0.5	2.62	n/a	128.3	57
75-25-2	Bromoform	0.2	2.07	0.020	252.7	173
98-82-8	Cumene	0.4	1.97	n/a	120.2	105
103-65-1	n-Propylbenzene	0.4	1.97	n/a	120.2	120
95-49-8	2-chlorotoluene	0.4	2.07	n/a	126.6	126
622-96-8	4-ethyltoluene	0.4	1.97	0.020	120.2	105
124-18-5	Decane	1.0	5.82	n/a	142.3	57
98-83-9	alpha-Methylstyrene	0.4	1.93	n/a	118.2	118
135-98-8	sec-butylbenzene	0.4	2.20	n/a	134.2	105
104-51-8	n-Butylbenzene	0.4	2.20	n/a	134.2	91
1120-21-4	n-Undecane	1.0	6.39	n/a	156.3	57
112-40-3	n-Dodecane	1.0	6.97	n/a	170.3	57
91-20-3	Naphthalene	0.5	2.62	n/a	128.2	128

b) Freon 22

i) Normal reporting limits (RLs) based on 200 mL sample volume. The ug/m3 values are example RLs using the value listed in the table.

j) Low level reporting limits based on 500 mL sample volume.

Table 3: Target Analytes – Other Polar Compounds

CAS NUMBER	OTHER POLAR COMPOUNDS	REPORTING LIMITS (ppb, v/v) (i)	REPORTING LIMIT (ug/m^3) (i)	Low Level Reporting Limit (ppb, v/v) (j)	MOLECULAR WEIGHT (ng/n mole)	SUGGESTED ION
67-56-1	Methanol	10	13.1	n/a	32.04	31
593-60-2	Vinyl Bromide	0.2	0.88	0.050	107.0	106
60-29-7	Ethyl Ether	2.0	6.06	n/a	74.12	31
67-64-1	Acetone	5.0	11.88	n/a	58.08	58
75-65-0	Tert-Butanol	2.0	6.06	n/a	74.12	59
107-13-1	Acrylonitrile	2.0	4.34	n/a	53.06	53
108-05-4	Vinyl Acetate	1.0	3.52	n/a	86.09	43
78-93-3	2-Butanone	1.0	2.95	n/a	72.11	72
71-36-3	1-Butanol	2.0	6.06	n/a	74.12	31
108-10-1	4-Methyl-2-Pentanone	0.5	2.05	n/a	100.2	43
591-78-6	2-Hexanone	0.5	2.05	n/a	100.2	58
1634-04-4	Methyl-t-Butyl ether	1.0	3.61	0.050	88.15	73
107-02-8	Acrolein	0.8	1.83	n/a	56.06	56
75-05-8	Acetonitrile	1.0	1.68	n/a	41.05	40
96-18-4	1,2,3-Trichloropropane	0.5	3.01	n/a	147.4	110

i) Normal reporting limits (RLs) based on 200 mL sample volume. The ug/m3 values are example RLs using the value listed in the table.

j) Low level reporting limits based on 500 mL sample volume

Appendix II: Figures

Figure 1: BFB Tuning Criteria

Mass	Abundance Criteria
50	15 to 40% of mass 95
75	30 to 60% of mass 95
95	Base peak, 100% relative abundance
96	5 to 9% of mass 95
173	Less than 2% of mass 174
174	Greater than 50% of mass 95
175	5 to 9% of mass 174
176	95% to 101% of mass 174
177	5 to 9 % of mass 176

Note: All ion abundances must be normalized to m/z 95, the nominal base peak, even though m/z 174 may be over 100 % of m/z 95.

Figure 2: Example Data Review Checklist

STL Knoxville GC/MS Air Initial Calibration Data Review / Narrative Checklist
Method: TO-14 and TO-15 - KNOX-MS-0001, Rev 9

Analysis Date:		Instrument::		ICAL Batch/Scan Name:		Scanned ?

Review Items	N/A	Yes	No	If No, why is data reportable?	2d ✓
1. Did BFB meet tune criteria?					
2. Were all standards injected within 24 hr of BFB?					
3. Was date/time of analysis verified between analysis header and logbook as correct?					
4. Is low level std at or <RL and are the remaining points consecutive?					
5. Were at least 5 levels of each compound analyzed?					
6. Is %RSD for all target analytes ≤ 30%? (with up to 2 compounds with RSD ≤ 40%)					
7. Have all peaks been auto identified? If not, list:					
8. If curves were used, is correlation coefficient ≥0.990?					
9. At least 6 consecutive points used for quadratic curves, and at least 5 consecutive points for linear curves?					
10. For linear or quadratic: is a tangent's slope to the curve entirely positive or negative and continuous.					
11. For linear or quadratic: origin NOT included or forced?					
12. Is the "Y" intercept less than the RL for each curve?					
13. RT for each IS ±20 sec avg. RT?					
14. Area for each IS ± 40% avg. area?					
15. Each analyte ± 0.06 RRT of avg. RRT?					
16 If manual integrations were performed, are they clearly identified, initialed, dated and reason given?				Reasons: 1)Corrected split peak; 2)Unresolved peak; 3)tailing; 4)RT shift; 5)wrong peak selected; 6)other	
17. Have alternate hits/manual integrations been verified as correct and are correct RFs listed in ICAL summary?					
18. Was ICAL summary form processed using correct methods and files?					
19 Are the ICAL start and end dates/times correct on ICAL summary?					
20. Elution order checked on isomeric pairs? • dichlorodifluoromethane / 1,2-dichlorotetrafluoroethane • trichlorofluoromethane / 1,1,2-trichlorotrifluoroethane • vinyl acetate / hexane • cis- and trans- isomers • ethyl benzene / m/p -xylene / o-xylene • 4-ethyl toluene/1,3,5-trimethylbenzene/1,2,4-trimethylbenzene • 1,3-, 1,4-, and 1,2-dichlorobenzene					
21. Is the second source analysis of a reference standard within limits? (65-135% R; 20-180% for benzyl chloride)					
22 If criteria were not met, was a NCM generated, approved by supervisor, and copy included in folder?					
23. Does the ICAL folder contain complete data in the following order: Data review checklist, a complete runlog, Entech report, BFB info, ICAL summary, curves, followed by [Quan reports, chromatograms, manual integrations] in increasing amount order					

Analyst:	Date:	2nd Level Reviewer:	Date:
Comments:		Comments:	

Figure 2: Example Data Review Checklist (continued)

STL Knoxville GC/MS Air Continuing Calibration Review / Narrative Checklist
Method: TO-14 and TO-15 - KNOX-MS-0001, Rev 9

Analysis Date:		CCAL Batch/ Scan Name:		Instrument:		ICAL Batch/ Scan Name:		Scanned ?

Review Items	N/A	Yes	No	If No, why is data reportable?	2nd ✓
1. Did BFB meet tune criteria?					
2. Were all standards injected within 24 hr of BFB?					
3. Have the Entech position no. & vol. been verified with run log & sample vol. corrected if actual amount differs >5%?					
4. Was date/time of analysis verified between analysis header and logbook as correct?					
5. Was the CCAL compared to the correct ICAL?					
6. Is the %D = 30% for all target analytes? Up to 4 analytes allowed over 30% but = 40% D (Narrative req'd.).					
7. Have all peaks been auto identified? If not, list:					
8. If manual integrations were performed, are they clearly identified, initialed, dated and reason given?				Reasons: 1)Corrected split peak; 2)Unresolved peak; 3)tailing; 4)RT shift; 5)wrong peak selected; 6)other	
9. Have alternate hits/manual integrations been verified as correct and are correct RFs listed in CCAL summary?					
10. Is the first IS documented correctly on the log?					
11. Is the ICAL date & time on the CCAL correct?					
12. Elution order checked on isomeric pairs?					
• dichlorodifluoromethane / 1,2-dichlorotetrafluoroethane					
• trichlorofluoromethane / 1,1,2-trichlorotrifluoroethane					
• vinyl acetate / hexane					
• cis- and trans- isomers					
• ethyl benzene / m/p -xylene / o-xylene					
• 4-ethyl toluene/1,3,5-trimethylbenzene/1,2,4-trimethylbenzene					
• 1,3-, 1,4-, and 1,2-dichlorobenzene					
13. Did the LCS meet criteria (nonpolar target analytes 70-130%, with up to 2 nonpolars 60-140%; polar target analytes 60-140%, with up to 2 polars 45-155%)?				? [lcs6] LCS analyte(s) flagged as being outside control limits, but SOP allows 2 polars and 2 nonpolars outside 70-130%R.	
14. If criteria were not met, was a NCM generated, approved by supervisor, and copy included in folder?					
15. Does the CCAL folder contain **complete** data in the following order: data review checklist, a **complete** runlog, Entech report, tune pass/fail page, m/z list, tune chromatogram, Target CCAL summary, Quan report, chromatogram, manual integrations and leak check report.					

Analyst:	Date:	2nd Level Reviewer :	Date:
Comments:		Comments:	

Figure 2: Example Data Review Checklist (continued)

STL Knoxville GC/MS Air Data Review / Narrative Checklist **LOT/Project #_____**
Method: TO-14 and TO-15 - KNOX-MS-0001, Rev 9 **Page 1 of 1**

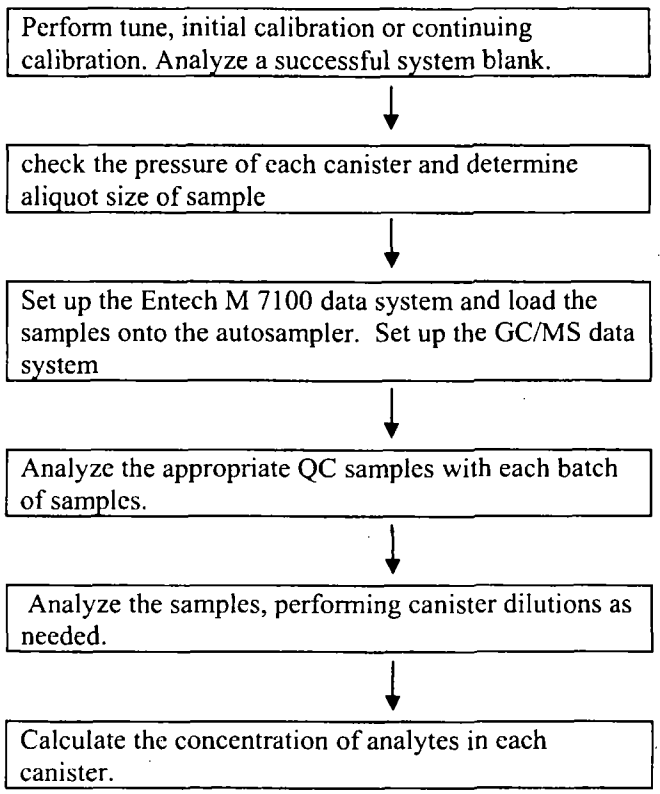
Instrument:	
Scanned File:	

Review Items **A. Tune / Continuing Calibration**	N/A	Yes	No	**Why is data reportable?**	2nd ✓
1. Were all samples injected within 24 hr of BFB?					
2. Has a Continuing Calibration Checklist been completed for each analytical batch?					
3. Was the correct ICAL used for quantitation?					
B. CLIENT SAMPLE AND QC SAMPLE Results	**N/A**	**Yes**	**No**	**Why is data reportable?**	
1. Were all special project requirements met?					
2. Were dilution factors/can prep information verified?					
3. Have the can number & lab ID been verified between the analysis log & sample prep log?					
4. Were samples received in cans?				↗ [Tedlar1] Samples rec'd on (date) in Tedlar bags & ana by TO-14 (TO-15) within 72 hours from sampling. ↗ [Tedlar2] Samples rec'd on (date) in Tedlar bags & transferred into Summa canisters within 72 hours.	
5. Sample analyses done within analytical holding time (HT)? *If no, list samples:* _____				↗ [ht2] Client requested analysis after HT expired. ↗ Other: _____	
6. Are surrogates and internal standards within QC limits? (70-130% R for surr.; 60-140%R from CCAL for IS) *If no, list samples/reason (e.g., surr):* Sample Reason Sample Reason _____ _____ _____ _____ _____ _____ _____ _____				↗ [surr1] DUP surr. %R demonstrated same effect. ↗ [surr2] Reanalysis demonstrated same effect. ↗ **[surr5] At client's request, data was flagged as estimated & released without further investigation.*** ↗ **[is1] Per client, reanalysis was not performed *** ↗ [is2] Reanalysis confirmed a matrix effect. ↗ Obvious matrix effect.	
7. Were all positive results and false negatives on quan report verified to be correct in LIMS?					
8. For dilutions, is highest concentration hit ≥ 20% cal range and not above calibration range? *List samples and reason (e.g., elev1).* Sample Reason Sample Reason _____ _____ _____ _____ _____ _____ _____ _____ _____ _____ _____ _____				↗ [elev1] Elevated RL for (ANALYTE) due to sample matrix interferences. ↗ [elev3] Elevated RLs for all analytes due to difficult sample matrix. ↗ [elev4] Elevated RLs based on screening ↗ [elev5] Elevated RLs for all analytes due to presence of non-target compounds.	
9. If manual integrations were performed, are they clearly identified, initialed, dated and reason given?				Reasons: 1)Corrected split peak; 2)Unresolved peak; 3)tailing; 4)RT shift; 5)wrong peak selected; 6)other	
10. Have alternate hits/manual integrations been verified as correct?					
C. Preparation QC					
1. System blank run every 24 hours prior to samples?					
2. System blank surrogate recoveries within QC limits (70-130% R) ?				↗ **[mb1] All sample surrogates OK and there is no analyte >RL in samples associated with blank.***	
3. Are all analytes present in the system blank < RL? *If no, list blank ID:* _____				↗ **[mb3] No analyte > RL in associated samples.*** ↗ **[mb4] Sample results > 20x higher than blank.**	
4. DUP done per 20 samples and are all RPDs within limits? (for target analytes >5x RL, <25% RPD; no criteria for methanol and n-butanol) *If no, list DUP ID:* _____					
5. Are all LCS analytes on final report within limits?				↗ [LCS6] Flagged out but within SOP limits. LCS ID: _____	
D. Other					
1. Final report acceptable? (Results correct, RLs calculated correctly, units correct, surrogate %R correct, appropriate flags used, dilution factor correct, analysis dates correct.)					
2. Are all nonconformances documented appropriately and copy included with deliverable?					
3. Were the standards scanned properly?					
4. Was a narrative prepared and all deviations noted?					
5. TO14A Autotext included in narrative (for TO14A samples only).				↗ [TO14]	
6. All target analytes on c.cal >30%D but <40%D noted in the narrative?				↗ [ccal] The ccal exhibited a %D ICAL >30% but ≤40% for the following analytes: _____	

Analyst:	**Date:**	**2nd Level Reviewer:**	**Date:**
Comments:		**Comments:**	

* Such action must be taken in consultation with client.

Figure 3: Flow Chart



Appendix III: Example Instrument parameters

```
                              TOPLEVEL PARAMETERS
                              -------------------

Method Information For: C:\MSDCHEM\1\METHODS\TO14.M

Method Sections To Run:

  ( ) Save Copy of Method With Data
  ( ) Pre-Run Cmd/Macro  *
  (X) Data Acquisition
  ( ) Data Analysis
  ( ) Post-Run Cmd/Macro =

Method Comments:
  TO14 METHOD USING HP-DB-5 60M X 0.32MM X 1.0 FILM THICKNESS

                              END OF TOPLEVEL PARAMETERS
                              --------------------------



                              INSTRUMENT CONTROL PARAMETERS
                              -----------------------------

Sample Inlet:       GC
Injection Source:   Manual
Injection Location: Front
Mass Spectrometer:  Enabled

================================================================================
                              HP6890 GC METHOD
================================================================================

OVEN
   Initial temp:  35 'C (On)                Maximum temp:  230 'C
   Initial time:  5.00 min                  Equilibration time:  0.00 min
   Ramps:
      #  Rate  Final temp  Final time
      1  6.00       65        0.00
      2 12.00      155        0.00
      3 25.00      220        7.00
      4   0.0(Off)
   Post temp:  35 'C
   Post time:  0.00 min
   Run time:  27.10 min

FRONT INLET (UNKNOWN)                    BACK INLET ()
   Mode:  Split
   Initial temp:  200 'C (On)
   Pressure:  7.89 psi (On)
   Split ratio:  2:1
   Split flow:  3.0 mL/min
   Total flow:  7.3 mL/min
   Gas saver:  Off
   Gas type:  Helium

COLUMN 1                                 COLUMN 2
   Capillary Column                         (not installed)
   Model Number:  HP 19091J-216
   HP-5 5% Phenyl Methyl Siloxane
   Max temperature:  325 'C
   Nominal length:  59.0 m
   Nominal diameter:  320.00 um
   Nominal film thickness:  1.00 um
   Mode:  constant flow
   Initial flow:  1.5 mL/min
   Nominal init pressure:  7.90 psi
   Average velocity:  31 cm/sec

Method: TO14.M            Wed Apr 30 14:03:13 2003            Page: 1
```

```
   Inlet:  Front Inlet
   Outlet:  MSD
   Outlet pressure:  vacuum

FRONT DETECTOR (NO DET)                 BACK DETECTOR (NO DET)

SIGNAL 1                                SIGNAL 2
   Data rate:  20 Hz                       Data rate:  20 Hz
   Type:  test plot                        Type:  test plot
   Save Data:  Off                         Save Data:  Off
   Zero:  0.0 (Off)                        Zero:  0.0 (Off)
   Range:  0                               Range:  0
   Fast Peaks:  Off                        Fast Peaks:  Off
   Attenuation:  0                         Attenuation:  0

COLUMN COMP 1                           COLUMN COMP 2
   (No Detectors Installed)                (No Detectors Installed)

THERMAL AUX 2
   Use:  MSD Transfer Line Heater
   Description:
   Initial temp:  150 'C (On)
   Initial time:  0.00 min
      #  Rate  Final temp  Final time
      1   0.0(Off)

                                        POST RUN
                                           Post Time: 0.00 min

TIME TABLE
   Time       Specifier                    Parameter & Setpoint

                            7673 Injector

     Front Injector:
         Injector not configured, use these parameters if it becomes configured
        Sample Washes                  2
        Sample Pumps                   4
        Injection Volume             1.0 microliters
        Syringe Size                10.0 microliters
        PostInj Solvent A Washes       4
        PostInj Solvent B Washes       0
        Viscosity Delay                0 seconds
        Plunger Speed               Fast

     Back Injector:
No parameters specified
                            MS ACQUISITION PARAMETERS

General Information
------- -----------

Tune File               : bfb.u
Acquistion Mode         : Scan


MS Information
-- -----------

Solvent Delay           : 3.80 min

EM Absolute             : False
EM Offset               : 0
Resulting EM Voltage    : 1858.8

[Scan Parameters]

Low Mass                : 28.5
High Mass               : 260.5
Threshold               : 200
Sample #                : 3       A/D Samples    8
Plot 2 low mass         : 28.5
Plot 2 high mass        : 260.5

[MSZones]

MS Quad                 : 106 C   maximum 200 C
MS Source               : 230 C   maximum 250 C

                              END OF MS ACQUISITION PARAMETERS

PostRun InstCntl macro(s) exist: msacq2.mac

                           END OF INSTRUMENT CONTROL PARAMETERS
```

Appendix IV: Recommended Calibration levels (normal reporting limit based on 200 mL sample analysis)

	Level, ppb v/v*								
Compound	**1**	**2**	**3**	**4**	**4A**	**5**	**6**	**7**	**8**
Bromochlormethane	10	10	10	10	10	10	10	10	10
1,4-Difluorobenzene	10	10	10	10	10	10	10	10	10
Chlorobenzene-d5	10	10	10	10	10	10	10	10	10
1,2-Dichloroethane-d4	10	10	10	10	10	10	10	10	10
Toluene-d8	10	10	10	10	10	10	10	10	10
4-Bromofluorobenzene	10	10	10	10	10	10	10	10	10
Chlorodifluoromethane	0.1	0.2	0.4	0.8	2.5	5	10	15	30
Dichlordifluoromethane	0.1	0.2	0.4	0.8	2.5	5	10	15	30
Chloromethane	-	-	0.4	0.8	2.5	5	10	15	30
1,2-Dichlorotetrafluoro-methane	0.1	0.2	0.4	0.8	2.5	5	10	15	30
Vinyl Chloride	0.1	0.2	0.4	0.8	2.5	5	10	15	30
Methanol	-	-	-	3.2	10	20	40	60	120
1,3-Butadiene	0.1	0.2	0.4	0.8	2.5	5	10	15	30
n-Butane	-	0.2	0.4	0.8	2.5	5	10	15	30
Bromomethane	0.1	0.2	0.4	0.8	2.5	5	10	15	30
Chloroethane	0.1	0.2	0.4	0.8	2.5	5	10	15	30
Trichlorofluoromethane	0.1	0.2	0.4	0.8	2.5	5	10	15	30
Acrolein	-	0.4	0.8	1.6	5.0	10	20	30	60
Acetonitrile	-	-	0.8	1.6	5.0	10	20	30	60
Acetone	-	-	-	1.6	5.0	10	20	30	60
Pentane	-	-	0.4	0.8	2.5	5	10	15	30
Ethyl Ether	-	0.4	0.8	1.6	5.0	10	20	30	60
1,1-Dichloroethene	0.1	0.2	0.4	0.8	2.5	5	10	15	30
Acrylonitrile	-	0.4	0.8	1.6	5.0	10	20	30	60
1,1,2-Trichlorotrifluoroethane	0.1	0.2	0.4	0.8	2.5	5	10	15	30
Methylene Chloride	-	-	0.4	0.8	2.5	5	10	15	30
3-chloropropene	0.1	0.2	0.4	0.8	2.5	5	10	15	30
Carbon Disulfide	-	0.2	0.4	0.8	2.5	5	10	15	30
Trans-1,2-Dichloroethene	0.1	0.2	0.4	0.8	2.5	5	10	15	30
Methyl-t-butyl Ether	0.1	0.4	0.8	1.6	5.0	10	20	30	60
1,1-Dichloroethane	0.1	0.2	0.4	0.8	2.5	5	10	15	30
Vinyl Acetate	-	0.4	0.8	1.6	5.0	10	20	30	60
2-Butanone	-	-	0.8	1.6	5.0	10	20	30	60
Hexane	0.1	0.2	0.4	0.8	2.5	5	10	15	30
cis-1,2-Dichloroethene	0.1	0.2	0.4	0.8	2.5	5	10	15	30
Chloroform	0.1	0.2	0.4	0.8	2.5	5	10	15	30
1,1,1-Trichloroethane	0.1	0.2	0.4	0.8	2.5	5	10	15	30
1,2-Dichloroethane	0.1	0.2	0.4	0.8	2.5	5	10	15	30
Benzene	0.1	0.2	0.4	0.8	2.5	5	10	15	30
1-Butanol	-	0.4	0.8	1.6	5.0	10	20	30	60
Cyclohexane	-	0.2	0.4	0.8	2.5	5	10	15	30
Carbon Tetrachloride	0.1	0.2	0.4	0.8	2.5	5	10	15	30
Heptane	0.1	0.2	0.4	0.8	2.5	5	10	15	30
1,2-Dichloropropane	0.1	0.2	0.4	0.8	2.5	5	10	15	30

Appendix IV: Recommended Calibration levels (normal reporting limit based on 200 mL sample analysis), continued

	Level, ppb v/v*								
Compound	**1**	**2**	**3**	**4**	**4A**	**5**	**6**	**7**	**8**
Trichloroethene	0.1	0.2	0.4	0.8	2.5	5	10	15	30
Dibromomethane	0.1	0.2	0.4	0.8	2.5	5	10	15	30
Bromodichloromethane	0.1	0.2	0.4	0.8	2.5	5	10	15	30
4-Methyl-2-Pentanone	-	0.4	0.8	1.6	5.0	10	20	30	60
cis-1,3-Dichloropropene	0.1	0.2	0.4	0.8	2.5	5	10	15	30
trans-1,3-Dichloropropene	0.1	0.2	0.4	0.8	2.5	5	10	15	30
Toluene	0.1	0.2	0.4	0.8	2.5	5	10	15	30
1,1,2-Trichloroethane	0.1	0.2	0.4	0.8	2.5	5	10	15	30
2-Hexanone	-	0.4	0.8	1.6	5.0	10	20	30	60
Octane	-	0.2	0.4	0.8	2.5	5	10	15	30
Dibromochloromethane	0.1	0.2	0.4	0.8	2.5	5	10	15	30
1,2-Dibromoethane	0.1	0.2	0.4	0.8	2.5	5	10	15	30
Tetrachloroethene	0.1	0.2	0.4	0.8	2.5	5	10	15	30
Chlorobenzene	0.1	0.2	0.4	0.8	2.5	5	10	15	30
Ethylbenzene	0.1	0.2	0.4	0.8	2.5	5	10	15	30
m/p-Xylene	0.1	0.2	0.4	0.8	2.5	5	10	15	30
Bromoform	0.1	0.2	0.4	0.8	2.5	5	10	15	30
Nonane	0.1	0.2	0.4	0.8	2.5	5	10	15	30
Styrene	0.1	0.2	0.4	0.8	2.5	5	10	15	30
o-Xylene	0.1	0.2	0.4	0.8	2.5	5	10	15	30
1,1,2,2-Tetrachloroethane	0.1	0.2	0.4	0.8	2.5	5	10	15	30
1,2,3-Trichloropropane	-	-	0.4	0.8	2.5	5	10	15	30
Cumene	0.1	0.2	0.4	0.8	2.5	5	10	15	30
n-Propylbenzene	0.1	0.2	0.4	0.8	2.5	5	10	15	30
4-Ethyltoluene	0.1	0.2	0.4	0.8	2.5	5	10	15	30
1,3,5-Trimethylbenzene	0.1	0.2	0.4	0.8	2.5	5	10	15	30
Alpha-Methylstyrene	-	0.2	0.4	0.8	2.5	5	10	15	30
Decane	-	0.2	0.4	0.8	2.5	5	10	15	30
1,2,4-Trimethylbenzene	-	0.2	0.4	0.8	2.5	5	10	15	30
1,3-Dichlorobenzene	-	0.2	0.4	0.8	2.5	5	10	15	30
Benzyl Chloride	-	0.2	0.4	0.8	2.5	5	10	15	30
1,4-Dichlorobenzene	-	0.2	0.4	0.8	2.5	5	10	15	30
1,2-Dichlorobenzene	-	0.2	0.4	0.8	2.5	5	10	15	30
Undecane	-	0.2	0.4	0.8	2.5	5	10	15	30
Dodecane	-	0.2	0.4	0.8	2.5	5	10	15	30
1,2,4-Trichlorobenzene	-	0.2	0.4	0.8	2.5	5	10	15	30
Naphthalene	-	0.2	0.4	0.8	2.5	5	10	15	30
Hexachlorobutadiene	-	0.2	0.4	0.8	2.5	5	10	15	30
Sec-butylbenzene	-	0.2	0.4	0.8	2.5	5	10	15	30
n-Butylbenzene	-	0.2	0.4	0.8	2.5	5	10	15	30
Vinyl Bromide	-	0.2	0.4	0.8	2.5	5	10	15	30
Tert-Butanol	-	0.4	0.8	1.6	5.0	10	20	30	60
2,2,4-Trimethylpentane	-	0.2	0.4	0.8	2.5	5	10	15	30
2-Chlorotoluene	-	0.2	0.4	0.8	2.5	5	10	15	30

* See section 10.3.11.

Appendix V: Recommended Low Level Calibration levels (normal reporting limit based on 500 mL sample analysis)

Compound	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6	Level 7
For compounds listed in Tables 1, 2, and 3 that are noted for Low Level analysis	0.010	0.020	0.040	0.100	0.200	0.500	1.0

STL KNOXVILLE

ATTACHMENT TO SOP KNOX-MS-0001

TITLE: PROJECT SPECIFIC ANALYTE LIST FOR GIVAUDAN

(SUPERSEDES: NONE)

Prepared By: _____

Reviewed By: _____ 7/21/05
Technical Specialist

Approved By: _____ 07/21/05
Quality Assurance Manager

Approved By: _____ 7-21-05
Environmental, Health and Safety Coordinator

Approved By: _____ 7-21-05
Laboratory Director

The following additional analytes will be target analytes for the Givaudan project.

CAS NUMBER	COMPOUNDS	REPORTING LIMITS (ppb, v/v)	MOLECULAR WEIGHT (ng/n mole)	SUGGESTED ION
79-29-8	2,3-Dimethyl butane	0.2	86.2	43
80-56-8	a-Pinene	0.2	136.2	93
79-92-5	Camphene	0.2	136.2	93
127-91-3	b-Pinene	0.2	136.2	93
5989-27-5	d-Limonene	0.2	136.2	68
99-87-6	p-Cymene	0.2	134.2	119
98-51-1	4-tert-Butyltoluene	0.2	148.2	133
464-49-3	Camphor*	5.0	152.2	95

* The initial demonstration of capability indicated poor precision for this analyte by this method as evidenced by the variable recovery of this compound. Any reported values for this analyte should be considered estimated.

TESTAMERICA KNOXVILLE

STANDARD OPERATING PROCEDURE

TITLE: SAMPLE RECEIPT AND LOG IN

(SUPERSEDES: KNOX-SC-0003, Rev. 11)

Prepared By: _____

Reviewed By: _____ 10/18/2007
Technical Specialist

Approved By: _____ 10/18/07
Quality Assurance Manager

Approved By: _____ 10-18-07
Environmental, Health and Safety Coordinator

Approved By: _____ 10-18-07
Laboratory Director

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1. Purpose

1.1. This standard operating procedure describes the receipt and log in activities that are the responsibility of the TestAmerica Knoxville sample receiving associates.

2. Responsibilities

2.1. It is the responsibility of the TestAmerica Knoxville sample receiving associates to perform the tasks as they are documented in this standard operating procedure.

2.2. It is the responsibility of the Laboratory Director and Customer Service Manager to supply adequate training, material and equipment to enable the associates to perform these tasks correctly.

3. Safety

3.1. Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document.

3.2. Procedures shall be carried out in a manner that protects the health and safety of all associates. Exposure to chemicals and samples will be maintained as low as reasonably achievable, therefore, unless they are known to be non-hazardous, all samples must be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made. The preparation of all standards, reagents and glassware cleaning procedures that involve solvents will be conducted in a fume hood with the sash closed as far as the operations will permit.

3.3. All work must be stopped in the event of a known or potential compromise to the health and safety of any associate. The situation must be reported **immediately** to a laboratory supervisor.

3.4. Sample receiving associates must wear gloves when handling samples and sample containers.

4. Procedure

4.1. Before samples arrive at the laboratory, the laboratory must provide to the sample collection personnel the sample acceptance policy. This is normally sent by the Project Manager to the client with the quote. See Appendix I.

4.2. Project Managers should make a reasonable effort to determine if samples to be received are radioactive in nature.

4.3. The shipping container is opened under a vented fume hood. If there are noxious fumes, work is stopped and the Health and Safety Coordinator is notified. If there are broken or leaking samples that are known or suspected to contain radioactive material, the work is stopped and the Radiation Safety Officer, or designee, is notified.

4.4. If the samples are known or suspected to contain radioactive material, the shipping containers and samples are surveyed according to the following.

NOTE: If radioactive samples are to be received, the Project Manager should make a reasonable effort to obtain screening data (either Gross Alpha/Gross Beta data (activity and specific activity), or specific radionuclide data (activity and specific activity)) from the client for each of the samples. The Radiation Safety Officer shall make a reasonable effort to ensure that any screening data received is acceptable.

4.4.1. If the package is labeled as a RADIOACTIVE MATERIAL shipment (as defined by 49 CFR 173.403), the sample control associate shall ensure that the external surfaces of the package are monitored by performing the following within 3 hours of receipt of the package, if received during the hours of 8:00 a.m. to 5:00 p.m. Monday through Friday, excluding holidays. If received at other times, the package shall be monitored within 3 hours after the beginning of the next working day.

4.4.2. Wipe Survey

4.4.2.1. Place a filter paper disc on the surface to be sampled.

4.4.2.2. Move the disc over an "s"-shaped area using moderate pressure, covering at least approximately 100 cm^2 (6 in^2), or at least approximately 20 inches in length, or the entire surface, if it is less than 100 cm^2 in area.

4.4.2.3. Place the disc smear in a container such that individual smears are separated from each other to prevent cross contamination.

4.4.2.4. Count each smear for alpha and beta activity in the Protean IPC9025 for five minutes. A shorter count time may be used if the count is long enough to have a detection limit below the contamination limit.

4.4.3. Exposure Rate

4.4.3.1. Measure the contact exposure rate of the package with a Ludlum Model 19 Micro-R Meter according to the TestAmerica Knoxville SOP KNOX-HS-0014, current revision, "Background and Source Check and Use of Portable Radiation Survey Instruments."

4.4.3.2. Measure the exposure rate of the package at 1 meter with a Ludlum Model 19 Micro-R Meter.

4.4.3.3. If the monitoring data of the package exceeds the site license criteria, contact the RSO, or designee.

4.5. The sample control associate shall open the package and ensure that the external surfaces of the containers are monitored by performing Section 4.4.2 on each container (or as a composite of any number of the containers), and Section 4.4.3 on each container.

4.6. If the monitoring data of any sample exceeds the site license criteria, contact the RSO, or designee.

4.7. Record all monitoring data, of both packages and containers, on a Radiological Survey form.

4.8. Classification of samples shall be performed according to TestAmerica Knoxville SOP KNOX-HS-0001, current revision, "Radiological Sample Screening and Classification".

4.9. The sample control associate shall ensure that all radiological documents are available for second level review by the RSO, or designee prior to release of the samples to the laboratory.

4.10. The sample control associate shall ensure that each container holding a radioactive sample is labeled/marked as CAT I or CAT II, as appropriate.

4.11. If the package is known to contain samples that are radioactive, but the package is not labeled as RADIOACTIVE MATERIAL, the following procedure is followed:

NOTE: The indication that a package contains radioactive samples may be through verbal or written communication from a client, historical knowledge of a site/project by a sample control associate, or through labeling/marking of containers within the package with a recognized radioactive label/marking. If a cooler is discovered to contain radioactive

samples it will not be moved until the cooler and sample containers can be surveyed.

4.11.1. The sample control associate shall open the package and ensure that the external surfaces of the containers are monitored by performing the following.

4.11.1.1. Wipe Survey

4.11.1.1.1. Perform the procedure specified in Section 4.4.2 on each container (or as a composite of any number of the containers).

4.11.1.2. Count Rate

4.11.1.2.1. Measure the count rate of the package with a Ludlum Model 3 with Model 44-9 Pancake G-M Detector according to TestAmerica Knoxville SOP, KNOX-HS-0014, current revision, "Background and Source Check and Use of Portable Radiation Survey Instruments".

4.11.2. If the monitoring data of any sample exceeds the site license criteria, contact the RSO, or designee. Additionally, the sample control associate shall proceed back to Section 4.4.2, and perform additional monitoring of packages and containers described in that section.

4.11.3. Record all container monitoring data on a Radiological Survey form.

4.11.4. Classification of samples shall be performed according to the TestAmerica Knoxville SOP KNOX-HS-0001, current revision, "Radiological Sample Screening and Classification".

NOTE: If historical screening information is available for a sample, this data may be used for sample classification.

4.11.5. The sample control associate shall ensure that all radiological documents are available for second level review by the RSO, or designee prior to release of the samples to the laboratory.

4.11.6. The sample control associate shall ensure that each container holding a radioactive sample is labeled/marked as CAT I or CAT II, as appropriate.

4.12. If the package is suspected to contain samples that are radioactive:

NOTE: Suspicion that a package contains samples that are radioactive can be the

result of keywords such as, but not limited to: FUSRAP, national laboratory, nuclear, uranium mine, Hanford, Las Vegas, Los Alamos, Mound, Oak Ridge, and Paducah. Additionally, shipping papers should be examined for contamination survey information, or screening data as an indication of the potential radioactive nature of samples.

4.12.1. Contact the RSO, or designee, who shall, working with information supplied by the Project Manager/client, determine whether or not the samples are to be processed as radioactive samples, or non-radioactive samples.

4.12.2. If the samples are determined to be radioactive, the sample control associate will proceed to process the samples as specified in Section 4.11.1

4.13. If the package is known or suspected to contain radioactive materials, and is treated as containing radioactive sample(s) based on the previous assessment(s) and the package or containers are crushed, wet, or damaged, the sample control associate shall proceed to monitor the packages and containers as specified in Section 4.4.2

4.14. The sample control associate will open and examine the shipping container and remove the enclosed sample documents. The following are recorded on the client's chain of custody form:

- Were custody seals present?
- The temperature of the cooler. If a temperature vial is present, it is used to take the temperature. Otherwise, the temperature is taken along the side of the bottle containers. The way the temperature was taken is recorded. The acceptable temperature range for sample coolers is above the freezing temperature of water to 6°C. The exceptions are samples from North Carolina and samples for Methods 1668 or 1613B (0-4 °C), VOST samples (up to 10 °C) and samples from Massachusetts (2-6 °C).
- The shipper's tracking number.
- Signature/initials and date.

4.14.1. If samples are delivered after normal business hours and a sample receiving associate is not present, the lab associate that receives the shipment will sign and date the chain of custody form to acknowledge receipt of the shipping container and take the temperature of the cooler, if

required. The lab associate will then store the shipping container in the proper location. The shipping container will remain there until the next business day; at that time, the sample receipt and login procedures will be completed.

4.15. The following information is then recorded on the Sample Receipt/Condition Upon Receipt Anomaly Checklist (See Appendix III):

- Presence of custody seals on the outside of the cooler.
- Presence of chain-of-custody forms inside the cooler.
- The chain-of-custody forms were properly filled out in ink.
- The chain-of-custody forms were signed and dated in the appropriate places.
- Presence of the shipper's packing slip and/or request for analysis.
- Conditions of samples at receipt (chilled, etc.). If a temperature vial is present, it is used to take the temperature. Otherwise, the temperature is taken along the side of the bottle containers. The way the temperature was taken is recorded. Summa canisters should be received at ambient temperature.
- Condition of bottles upon receipt (good condition, broken, etc.).
- Complete bottle labels (date, signed, analysis, and preservations).
- Information on bottle labels and tags agree with custody papers.
- Correct bottles used for the tests indicated.
- VOA bottles checked for the presence of air bubbles. If headspace is noted, the sample receiving associate will affix a round label (approximately ¾") and mark the vial with "HS" with indelible ink.
- Verify sample pH as appropriate (does not include VOAs). For each sample container use a new disposable Pasteur pipette to transfer a drop onto pH paper. Read the pH to the nearest pH unit and record the pH on the client's chain of custody form. If it is necessary for the laboratory to perform sample preservation, record the preservative used, the lot number of the preservative, analyst initials and the date and time on the COC or CUR. If samples for metals analysis are preserved in the laboratory, the

sample bottle is labeled with the date and time digestion may begin (at least 24 hours after preservation).

- Check samples for residual chlorine. For each sample, use a new disposable Pasteur pipette to transfer approximately 5 mL of sample to a residual chlorine strip. Note the reading on the client's chain of custody form. If residual chlorine is detected, the laboratory will add 2 mL of sodium thiosulfate solution to the sample and recheck for the presence of residual chlorine. If sodium thiosulfate is added to the sample, the lot number, analysts initials and date will be noted on the CUR or the chain of custody.

- Sufficient amount of sample sent for all analyses requested.

- Samples were verified received within holding time as specified in LQM.

- Samples were received via overnight courier, client drop off or other means.

4.16. The sample control associate then removes all sample containers. Any broken, leaking or dirty sample containers are placed inside the fume hood. Dirty sample containers are cleaned appropriately so as not to contaminate the sample storage area.

4.17. The sample control associate examines all documents and compares the information from the sample container labels and chain-of-custody records to ensure that there are no discrepancies between the documents and that all documents are properly completed and signed.

4.18. If any problems or discrepancies are noted during the sample receiving process, such as improper paperwork or broken or leaking samples, the sample control associate signs for the shipment and documents the problems on the Sample Receipt/Condition Upon Receipt Anomaly Checklist (CUR, see Appendix III). The sample control associate immediately notifies the project manager. The project manager contacts the client to rectify the situation.

4.19. If all samples recorded on the chain-of-custody record were received by the laboratory and there are no problems observed with the sample shipment, the sample control associate signs, dates and times the chain-of-custody record in the "Received for Laboratory by:" box on the document.

4.20. After the samples have been removed from shipping containers and organized according to the client's chain-of-custody form and the appropriate sample receipt paperwork (e.g., CUR, Sample Receipt Checklist) has been completed, the sample

control associate logs the samples into the LIMS using the quote number provided by the project manager.

4.20.1. If the quote number is unknown, the sample receiving associate contacts the project manager to obtain the appropriate quote number for the client samples.

4.20.2. If the project is an unusually complex project such as a source air trial burn, the sample receiving associate will typically request assistance from the project manager to ensure the client samples are logged in properly. This may include a physical review of the samples and chain of custody documentation by the project manager prior to sample log-in.

4.20.3. If there are questions or issues that prevent the sample receiving associate from logging the samples into the LIMS, and the project manager cannot review the sample receiving documentation immediately, the samples requiring temperature preservation are placed in a sample storage refrigerator (volatiles samples stored separately) until the project manager review is completed.

4.21. The project information is taken from the designated quote and the following information is entered into QuantIMS

- Date and time of receipt
- Client sample IDs
- Collection dates/times
- Storage location
- Test parameters (method codes and target analyte lists as defined by the Project Manager in the quote and requested by the client on the chain of custody)
- Sample Type (Refer to the QuantIMS checklist as defined by the PM)
- Refer to the QuantIMS general comments/checklist comments for any other fields that must be populated to meet electronic deliverable (EDD) requirements.

4.21.1.1. Some clients request that the samples be reported by Sample Delivery Group (SDG). The SDG is a group of samples received over a client-specified time period (therefore, different lots) that are reported together. The SDGs are tracked by sample receiving and documented in an Excel spreadsheet in Qmidtn01/public/SDG/numerical and/or alphabetic name of SDG.

4.21.1.2. All water samples requesting either total or dissolved/filtered metals analyses will be processed as follows:

- The sample receiving associate will assign the work order for total metals analysis SAC, and the work order for dissolved metals SAC from the quote. Note that the last three work order characters will be discreet for both SACs.
- The sample receiving associate will enter QIMS sample comments as either "field filtered" or "needs to be filtered at the lab".
- The sample receiving associate will either write on the container or affix a label on the filtered metals container as either "LF" for lab filtered or "FF" for field filtered.
- The samples needing to be lab filtered will be stored at $4^{\circ} \pm 2\,^{\circ}C$ until the metals group filters and preserves the samples; after filtering and preservation, the samples may be stored at room temperature.
- The sample receiving will verbally notify the metals group when the client requests the lab to filter samples.

4.22. QuantIMS assigns unique numbers and/or letter combinations to all projects, lots, samples and tests.

4.22.1. The first set of numbers/letters for a group of samples entering the laboratory is called the lot or lab ID number. Samples also receive a work order number that describes the type of test a sample will receive. As an analyst receives notice of the sample for their respective department, they batch groups of similar samples together and the samples are then assigned a batch number.

4.22.2. Each group of samples received or shipped from a specific site on the same day is logged in under a unique lot number. Each sample within a given lot receives a laboratory number or ID. Each lab ID is 12 of a possible 13 characters (H3A010121-001).

4.22.3. Lot number: The lot number is 9 characters long. Lot number **H1A010121**

is described as follows:

- **H** - the alpha character indicates the TestAmerica location where the samples were received. (H = Knoxville)
- **3** - the numeric character indicates the last digit of the year (i.e., 2003)
- **A** - the alpha character indicates the month (A = January, B = February, etc.)
- the next 2 numeric characters identify the day of the month, in this case the first day of the month.
- **0121**- the last 4 numeric characters are the sequential assignment of numbers specific to each lot received. Each day the first lot logged in receives the number 0001. Batch specific QC samples (method blanks, LCS, LCSD) receive a sequential assignment of 0000.

4.22.4. Sample Numbers: The samples in each lot are assigned a sample number that is attached to the lot number and are reset at each new lot. For example, the first and second samples in the lot above are labeled H3A010121-**001** and H3A010121-**002**.

4.22.5. Suffixes: Each sample also has a 1 character field (which may not be needed for all samples) called the suffix which identifies it as a:

Client sample - no suffix
Method blank - B
Check/Control Sample - C
Check dup/Dup control - L
Matrix spike (MS) - S
Matrix spike dup (MSD) - D
Sample dup/dup analysis - X
Serial dilution - P

4.22.6. 4.10.6 Each test has an 8 digit work order number. Work order number **A1234-2-01** is described as follows:

- **A1234** - The first 5 characters identify each sample.
- **2** - The 'modifier' indicates the type of run. In this case this is the second time the sample had to be run. If it needs reextraction/repreparation and run again the number would indicate a "3".
- **01** - The suffix is the test number of that specific sample. For example the "01" may indicate the 'silver' analysis, "02" may indicate the 'arsenic' analysis, an "03" may indicate a 'BOD', etc.
- The client requested analytical and preparatory methods and analyte lists defined by the project manager in the quote are linked to the work order number.

4.23. QuantIMS generates the sample labels based on the information from the quote and the login process. The sample containers are labeled, with the sample receiving associate carefully matching the client ID and analysis on the container with that on the QuantIMS label.

4.24. The samples that are to be analyzed at TestAmerica Knoxville are then placed in the sample storage refrigerators. Volatiles are stored separate from other analyses and metals samples are stored on shelves.

4.25. Samples that are to be subcontracted to another laboratory for analysis are packaged for shipment to the subcontract laboratory.

4.25.1. The sample control associate examines all documents and compares the information from the sample container labels and chain of custody records to verify that the appropriate samples are being prepared for shipment.

4.25.2. The containers are properly packaged to prevent breakage or leakage during shipment. All TestAmerica, DOT and IATA guidelines must be followed.

4.25.3. The cooler is lined with a plastic liner to prevent leakage from the cooler. If ice is needed, it is packed and sealed in heavy plastic bags.

4.25.4. The containers are wrapped in packing material and/or placed in plastic bags.

4.25.5. Once the cooler is packed and ready for shipment, the sample control associates signs and dates the chain of custody. A copy of the completed chain of custody record is made. The original is placed in a plastic bag in the cooler with the samples. The copy of the chain of custody record, along with the shipper's tracking number, is given to the project manager with the rest of the project documentation.

4.25.6. The cooler is sealed shut. All coolers are shipped with signed custody seals.

4.26. All sample receiving documents relevant to the lot are labeled with the lot number. All paperwork received from the client as well as that generated during sample login is filed in the lot project folder. Refer to the TestAmerica Knoxville SOP KNOX-AD-0002, "Project Records", current revision.

4.26.1. The login associate prints the referenced quote checklist and places it in the log folder for PM review.

4.27. Once the sample login process is complete, the project file is ready for the project manager to review and the samples are ready for analysis.

4.28. Any deviations from this procedure by TestAmerica associates must be documented as a nonconformance, with a cause and corrective action described.

5. Definitions

5.1. Definitions can be found in the TestAmerica Knoxville LQM glossary and in the TestAmerica Quality Management Plan.

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6.1.1. TestAmerica Quality Management Plan (QMP), current revision.

6.1.2. TestAmerica Knoxville Laboratory Quality Manual (LQM), current revision.

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6.3. Appendix III: Example Sample Receipt/Condition Upon Receipt Anomaly Checklist

Appendix II: Example Sample Acceptance Policy

TestAmerica Knoxville
Sample Acceptance Policy

The information below outlines the circumstances under which sample will be accepted by TestAmerica Knoxville. Failure to meet the following criteria will be noted in the project narrative. Please notify your PM with any questions.

Area of Concern
1. Proper, full and complete documentation, which includes sample identification, the location, data and time of collection, collector's name, preservation type, sample type, test requested and any special remarks concerning the samples shall be provided with the samples.
2. The samples shall be properly labeled to include unique identification. The labels must be durable (water resistant) and indelible ink must be used.
3. The samples shall be collected in the appropriate sample containers.
4. The samples shall arrive at the laboratory within the specified holding time for the analyses requested.
5. Sufficient sample volume must be available to perform the necessary tests.
6. The client will be notified upon sample receipt if the samples exhibit obvious signs of damage, contamination or inadequate preservation.

Appendix III: Example Sample Receipt/Condition Upon Receipt Anomaly Checklist

TESTAMERICA KNOXVILLE SAMPLE RECEIPT/CONDITION UPON RECEIPT ANOMALY CHECKLIST

Client: _____ **Project:** _____ **Lot Number:** _____

Review Items	Yes	No	NA	If No, what was the problem?	Comments/Actions Taken
1. Do sample container labels match COC? (IDs, Dates, Times)				☐ 1a Do not match COC ☐ 1b Incomplete information ☐ 1c Marking smeared ☐ 1d Label torn ☐ 1e No label ☐ 1f COC not received ☐ 1g Other:	
2. Is the cooler temperature within limits? (> freezing temp. of water to 6 °C; NC, 1668, 1613B: 0-4°C; VOST: 10°C; MA: 2-6 °C)				☐ 2a Temp Blank = _____ ☐ 2b Cooler Temp = _____	
3. Were samples received with correct chemical preservative (excluding Encore)?				☐ 3a Sample preservative =	
4. Were custody seals present/intact on cooler and/or containers?				☐ 4a Not present ☐ 4b Not intact ☐ 4c Other:	
5. Were all of the samples listed on the COC received?				☐ 5a Samples received-not on COC ☐ 5b Samples not received-on COC	
6. Were all of the sample containers received intact?				☐ 6a Leaking ☐ 6b Broken	
7. Were VOA samples received without headspace?				☐ 7a Headspace (VOA only)	
8. Were samples received in appropriate containers?				☐ 8a Improper container	
9. Did you check for residual chlorine, if necessary?				☐ 9a Could not be determined due to matrix interference	
10. Were samples received within holding time?				☐ 10a Holding time expired	
11. For rad samples, was sample activity info. provided?				☐ Incomplete information	
12. For SOG water samples (1613B, 1668A, 8290, LR PAHs), do samples have visible solids present?				If yes & appears to be >1%, was SOG notified? _____	
13. Are the shipping containers intact?				☐ 13a Leaking ☐ 13b Other:	
14. Was COC relinquished? (Signed/Dated/Timed)				☐ 14a Not relinquished	
15. Are tests/parameters listed for each sample?				☐ 15a Incomplete information	
16. Is the matrix of the samples noted?				☐ 15a Incomplete information	
17. Is the date/time of sample collection noted?				☐ 15a Incomplete information	
18. Is the client and project name/# identified?				☐ 15a Incomplete information	
19. Was the sampler identified on the COC?					

Quote #: _____ PM Instructions: _____

Sample Receiving Associate: _____ Date: _____

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B

ATTACHMENT B

ANALYTICAL DATA QUALITY ASSESSMENT AND VALIDATION-STANDARD OPERATING PROCEDURE (SOP)

CONFIDENTIAL

PROPRIETARY DOCUMENT

CONESTOGA-ROVERS
& ASSOCIATES

ANALYTICAL DATA QUALITY ASSESSMENT AND VALIDATION - STANDARD OPERATING PROCEDURE (SOP)

PREPARED BY:
CONESTOGA-ROVERS & ASSOCIATES
2055 NIAGARA FALLS BLVD., SUITE THREE
NIAGARA FALLS, NEW YORK 14304

OFFICE: 716-297-6150
FAX: 716-297-2265
WEB: CRAWORLD.COM

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ACRONYMS

A	Acid Fraction of SVOC
B/N	Base/Neutral Fractions of SVOC
CCAL	Continuing Calibration Standard
CCV	Continuing Calibration Verification
CFR	Code of Federal Regulations
CLP	Contract Laboratory Program
COC	Chain of Custody Form
COV	Coefficient of Variance
CRA	Conestoga-Rovers & Associates
CRDL	Contract Required Detection Limit
CVAA	Cold Vapor Atomic Absorption
DL	Dilution
%D	Percent Difference
DQO	Data Quality Objectives
DUP	Duplicate
EDD	Electronic Data Deliverables
EQL	Estimated Quantitation Limit
FDV	Full Data Validation
GC	Gas Chromatography
GC/MS	Gas Chromatography/Mass Spectrometry
HT	Holding Time
ICAL	Initial Calibration Standard
ICB	Initial Calibration Blank
ICP	Inductively Coupled Plasma
ICP/MS	Inductively Coupled Plasma/ Mass Spectrometry
ICS	Interference Check Sample
ICV	Initial Calibration Verification
IDL	Instrument Detection Limit
IS	Internal Standard
LCS	Laboratory Control Spike
LCSD	Laboratory Control Spike Duplicate

ACRONYMS

MD	Matrix Duplicate
MDL	Method Detection Limit
MS	Matrix Spike
MSD	Matrix Spike Duplicate
NA	Not Applicable
ND	Non-detect
NFG	National Functional Guidelines
PCB	Polychlorinated Biphenyls
QA	Quality Assurance
QC	Quality Control
QAPP	Quality Assurance Project Plan
RDV	Reduced Data Validation
REG 5	USEPA Region 5
RF	Response Factor
RRF	Relative Response Factor
RL	Report Limits
RPD	Relative Percent Difference
%RSD	Percent Relative Standard Deviation
SAP	Sampling and Analysis Plan
R^2	Correlation Coefficient
SOP	Standard Operating Procedures
SVOC	Semi-Volatiles Organic Compounds
TAL	Target Analyte List
TCL	Target Compound List
VOC	Volatile Organic Compounds
USEPA	United States Environmental Protection Agency

1.0 INTRODUCTION

The purpose of this Standard Operating Procedure (SOP) is to ensure that all analytical data quality assessment and validation (data validation) is performed by Conestoga-Rovers & Associates (CRA) in a consistent manner and in accordance with project-specific requirements. The purpose of data validation is to ensure that only those data that meet project-specific data quality objectives (DQO) are used for project decision making and reporting.

This SOP discusses data validation of the parameters associated with the following analytical techniques:

- Gas Chromatography/Mass Spectrometry (GC/MS) - volatile organic compounds (VOC) and semi-volatile organic compounds (SVOCs);
- GC - polychlorinated biphenyls (PCBs), chlorinated pesticides, VOCs, herbicides, etc;
- High Performance Liquid Chromatography (HPLC) - polynuclear aromatic hydrocarbons (PAH), carbamates, explosives, etc;
- Spectrometric - including inductively coupled plasma (ICP), inductively coupled plasma/mass spectrometer (ICP)/MS), cold vapor atomic absorption (CVAA);
- Spectrophotometry (Spec) - cyanide, sulfate, phenolics and other inorganics;
- Ion Chromatography (IC) - inorganic anions; and
- Titrimetric - chloride, etc.

The data validation procedures detailed in this SOP are based on guidance and quality control procedures established by the United States Environmental Protection Agency (USEPA) including the "USEPA Contract Laboratory Program National Functional Guidelines for Organic Data Review", USEPA-540/R-99/008, October 1999 and the "USEPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review", USEPA 540/R-94/013, February 1994, collectively referred to as NFGs throughout this SOP. Selected guidance for ICP/MS data review relies on the latest inorganic NFG, "USEPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review", USEPA 540/R-01/008, July 2002 referred to as NFG-2. In addition to the federal guidance data review follows other project specific guidance such as regional SOPs; analytical methods, and laboratory SOPs as defined in project

documentation (Quality Assurance Project Plan (QAPP), Sampling and Analysis Plan (SAP), Work Plan and Purchase Orders).

2.0 LEVELS OF ANALYTICAL DATA REVIEW AND ASSESSMENT

CRA completes several types or levels of data review and assessment including compliance assessment and data validation. Descriptions of these and the information reviewed are discussed below.

As defined by the USEPA, data verification is the process of evaluating the completeness, correctness, and conformance/compliance of a specific data set against the method, procedural, or contractual compliance[1]. Data validation is an analyte-specific and sample-specific process that extends the evaluation of data beyond method, procedural, or contractual compliance to determine the analytical quality of a specific data set[1].

This SOP addresses three levels of data validation, application of each is dependent on project-defined data quality objectives. For all samples sets, regardless of validation level employed, a compliance assessment must be completed. The compliance assessment includes an assessment of data package completeness and compliance with project requirements as outlined in the project Analytical Scope of Work.

The three levels of validation are as follows, the specific elements addressed for each level of review are presented in Table 2.1.

Reduced data validation (RDV), also referred to as data verification or Level III validation, entails the review of sample preservation and holding time compliance, as well as the lab and field quality control results (blank, spikes, surrogates, etc). It does not include the assessment of raw data, instrument calibration data, internal standard recoveries, interelement interference check standards, nor serial dilutions.

Full data validation (FDV), also referred to as Level IV validation, includes all steps of the RDV process as well as the review of raw data associated with sample and quality control results and confirmation of analyte quantitation and identification (e.g., sample calculations, mass spectra, chromatograms, etc) on a minimum of 10 percent of the laboratory data. FDV also includes the review of raw data and results for instrument

1 United States Environmental Protection Agency (USEPA) Guidance on Environmental Data Verification and Data Validation, USEPA QA/GA-8, November 2002.

calibration, (instrument performance, initial and continuing calibration), internal standards, interelement interference check standards, and serial dilutions.

A third level of validation is identified in the Region III document "Innovative Approaches to Data Validation, 1995". This level of validation (referred to as innovative approach) falls somewhere between FDV and RDV; it does not include the review of raw data, but it does include the assessment of all sample and QC results, including instrument calibration data, internal standard recoveries, interelement interference check standards, and serial dilutions.

For clients requesting FDV on 10 percent of their data, and a lesser validation level on the remaining data packages, the innovative approach is often used on the remaining 90 percent to ensure consistent qualifier application (this approach is referred to as 90/10). If FDV and RDV are used in this manor, the problem is that the package assessed using FDV may have calibration outliers and therefore data qualifications, while the same outliers would not yield data qualification in a RDV (e.g., calibration results are not assessed in RDV).

The innovative approach is similar to that used for projects requiring validation of New Jersey reduced deliverables.

Be aware that project-specific requirements may include data validation levels that differ from the three main types outlined above.

3.0 ELECTRONIC DATA FORMAT AND CODING

Data are received from the laboratory in hardcopy format and electronically as an EquIS® 4-file electronic data deliverable (EDD). A 10 percent manual check is performed to ensure that the EDD matches the hardcopy data. The data are imported into the database by the database analysts. For projects requiring data validation, the chemist is provided with an electronic output form the database (a flatfile workbook) for their use in reviewing the data and for communicating data qualifications back to the database analysts for import into the database.

The flatfile workbook consists of a sample summary worksheet, a flatfile, and a xtab.

3.1 SAMPLE SUMMARY WORKSHEET

The sample summary provides a snapshot of the type and number of sample results imported into the database for that sample set. This spreadsheet indicates the number of analytes reported for each sample/test as shown in the example below:

Sample_Name	*MADEP-VPH*	*SW-6010R*	*SW-7470R*	*SW-8015V*	*SW-8021 BTEX*	*SW-8260 BMTBE*
027626-032707-MW1					4	
027626-032707-MW11					4	
027626-032707-MW11 DUP					4	
027626-032707-MW12					4	
027626-032707-MW2					4	
027626-032707-MW4					4	
027626-032707-MW7					4	
027626-032707-MW8					4	
27626-051707-COMP1		7	1			
27626-051707-SB10 (10-12)				1		5
27626-051707-SB10 (14-15)				1		5
27626-051707-SB10(8-10)				1		5
27626-051707-SB2 (10-12)	3			1		5
27626-051707-SB4 (14-15)				1		5
27626-051707-SB4 (4-6)				1		5
27626-051707-SB4 (8-10)				1		5
27626-051707-SB5 (10-12)				1		5

The analytical Scope of Work and Chain of Custody or Field Key can be used to check that the proper number of analytes were reported and that the samples were analyzed for the required tests and that the proper number of results were reported.

If the sample summary shows that there were 26 VOCs reported for all samples except for one sample that had 24, the discrepancy should be checked.

This spreadsheet will summarize the number of results flagged as "reportable" by the laboratory. If the laboratory performs a dilution or reanalysis, they are directed to include both results in the EDD, but one should flagged as "Y" for reportable and the other "N". If the lab has failed to flag data for dilutions or re-analyses properly, the sample summary may show double the number of analytes for one or more of the samples. This is rectified by changing the reportable flags in the flatfile from "Y" to "N" for the appropriate results.

3.2 FLATFILE WORKSHEET

Any changes to be made to the database by the chemist are inputted into the flat file and imported back into the database.

3.2.1 FLATFILE FIELDS

The following are a list of fields included in the flatfile with descriptions.

sys_sample_code	sample code based on the Sample ID, including suffix for dilution and reanalysis
test_surrogate_key	sample/method code
cas_rn	analyte code based on CAS registry number including suffix for total or dissolved metals
lab_anl_method_name	analytical method code including suffix for listed parameters (i.e., Toxicity Characteristic Leaching Procedure [TCLP]) or holding time assuming one method produces multiple holding times
lab_prep_method_name	sample preparatory method code

lab_sample_id	laboratory sample ID
chemical_name	compound/analyte
loc_name	sample location
sample_name	sample identification number
parent_sample_code	"sys_sample_code" of parent sample for field duplicate (FD)/matrix spike (MS)/matrix spike duplicate (MSD)/LR/laboratory control sample duplicate (LCSD)
sample_matrix_code	sample matrix code
sample_type_code	original (N), field duplicate (FD), Trip Blank (TB),etc
start_depth	initial sample depth
end_depth	final sample depth
depth_unit	sample depth unit
sample_delivery_group	Laboratory SDG
instrument_id	instrument identifier
column_number	both columns are required when testing for PCBs and pesticides
test_batch_id	unique identifier for all lab batches
analysis_date	analysis date
analysis_time	analysis time
sample_date	sample collection date
dilution_factor	sample dilution factor
prep_date	sample prep date
result_value**	positive detection value (null if non-detect)
method_detection_limit**	MDL (unadjusted)
reporting_detection_limit**	report limit this field name is misleading, the values in this field are normally the sample-specific Practical Quantitation Limits (PQL) for organics and wet chemistry, and either the Contract Required Detection Limit (CRDL) or instrument detection limit (IDLs) for metals, depending on lab convention.
quantitation_limit**	sample-specific MDL/IDL - this field name is misleading, it has nothing to do with the quantitation limit.
result_unit**	units
lab_qualifiers**	laboratory qualifiers
validator_qualifiers**	validation qualifiers
detect_flag	**"Y" for positive detection, "N" for non-detects

qc_rpd_status	used to indicate whether the relative percent difference was within control limits
approval_a**	validation reason code
approval_b	DV guidance document code
collection_quarter	collection quarter
approval_code**	validation level code
organic_yn	indicates whether test was organic ("Y") or inorganic ("N")
result_type_code	Result type - "TRG" for a target or regular result, "TIC" for tentatively identified compounds, "SUR" for surrogates, "SC" for spiked compounds, or "IS" for internal standards (internal standards are not required in the deliverable)
sampling_reason	sample event identifier
result_comment	import metadata
fraction_code	test category of the analysis method. (e.g., VOCs, SVOCs, Wet, etc.)
percent_moisture	percent moisture of the sample portion used in this test; this value may vary from test to test for any sample
subsample_amount	amount of sample used for the test
subsample_amount_unit	unit of measurement for "subsample_amount"
final_volume	final sample volume
final_volume_unit	unit of measurement for "final_volume"
qc_original_conc	The concentration of the analyte in the original (unspiked) sample
qc_spike_added	The concentration of the analyte added to the original sample
qc_spike_measured	The measured concentration of the analyte
qc_spike_recovery	The percent recovery for the spike
qc_dup_original_conc	The concentration of the analyte in the original (unspiked) sample
qc_dup_spike_added	The concentration of the analyte added to the original sample
qc_dup_spike_measured	the measured concentration of the analyte in the duplicate
qc_dup_spike recovery	The duplicate percent recovery
qc_rpd	The relative percent difference between the spike and the spike duplicate
qc_spike_lcl	Lower control limit for spike recovery
qc_spike_ucl	Upper control limit for spike recovery
qc_rpd_cl	Relative percent difference control limit

qc_spike_status	Flag used to indicate whether the spike recovery was within control limits
qc_dup_spike status	Flag used to indicate whether the duplicate spike recovery was within control limit
reportable_result	Indicates whether sample result is to be reported - "Y" will allow for extraction, "N" will suppress

Fields that are color-coded are included for the chemist's information only. These fields should not be modified, as any changes will not be imported back into the database. If any changes are needed for these fields, please notify the database analyst.

Do not copy the data to another spreadsheet as data values *will* change at the discretion of the software. If copying data is necessary:

i) open a new spreadsheet;

ii) select entire spreadsheet;

iii) "Format/Cells/Number(tab)/Text";

iv) return to source spreadsheet and "Copy"; and

v) return to destination spreadsheet and "Paste Special/Text".

The user must select the entire spreadsheet prior to sorting a column, otherwise the data in column will sort within itself.

The flatfile provided should be in the "Autofilter" mode which enables the user to filter the data to view only those desired fields (e.g., view VOCs only by selecting 8260 in the method field, or view a single SDG, etc.).

The flatfile can be made more manageable by "hiding" columns not needed. To do this, right click on the column letter to highlight the entire column select "hide". You can highlight one or several columns before hiding them. To unhide, highlight the two visible columns adjacent to the hidden columns, right click and select "unhide". To unhide all columns at once, click on the top left-corner of the .xls sheet, which highlights the entire sheet, and go to "format", "columns" and select "unhide".

3.2.2 CHECK FLAT FILE PROGRAM

The Check Flatfile tab is located at the top of the flatfile worksheet includes three macros to be used on the flatfile including Convert Time, Run Flatfile Completeness Checker (covered later in this section), and Run Qualifier Copy (J, B, U).

Convert Time - All fields are submitted as text and must remain as text (to preserve significant digits in the database) with the exception of the "analysis_time" field which can be converted to standard time format (for sorting purposes). Use the "convert time" command under the "Check Flat File" tab at the top of the spreadsheet.

Run Qualifier Copy - For data that are validated, the validator qualifier field must include all lab qualifiers that should be applied to the final data set. This includes any lab qualifiers that would be preserved through validation (e.g. "U"). Prior to adding validator qualifiers to the flatfile, this program is used to copy pertinent lab qualifiers to the validator qualifier field as follows:

- U Qualifier - The program will ask "copy over U qualifiers?". If the user selects "yes", the program finds all instances of U in the "lab_qualifiers" field and inputs a "U" into the "validator_qualifier" field. The macro also inputs "PLU" (Preserve Lab U) into the "approval_code" field.

  If the user selects "no", the program does not do anything with lab "U" qualifiers.
- J Qualifier - When the program finds a "J" in the "lab_qualifiers" field it copies "J" into the "validator_qualifiers" field, and copies "BRL" (Below Reporting Limit) into the "approval_code" field. Note that some laboratories use the "J" flag to denote inorganic method blank contamination. Be sure to review inorganic "J" flags to ensure the flag reflects a value less than the reporting limit, and not method blank contamination. This is particularly true for TestAmerica Inc. The definition of the inorganic "J" flags must be verified by reviewing the laboratory report.
- B Qualifier – Most labs use the B qualifier differently for organic and inorganic tests, for organics, a B typically denotes blank contamination and for inorganics, a B typically denotes that a positive detection is less than the reporting limit (similar to how a "J" qualifier is used for organics). When the program finds a "B" in the "lab_qualifiers" field, it then looks at the "organic_yn" field. If the value in that field

is an "N", then it copies "J" into the "validator_qualifiers" field, and copies "BRL" into the "approval_code" field, if the value of the "organic_yn" field was a "Y", then it does nothing; no B is copied over.

3.2.3 DATA QUALIFICATION

Data qualifiers are inputted into the "validator_qualifier" field. Each "validator_qualifier" must have an associated reason for the data qualification that is inputted into the "approval_a" code field (see Section 5.0 for more information on reason codes). The addition of new valid values for reason codes must be submitted to Julie Lidstone for review and inclusion in the "approval_a" reference table.

All preserved laboratory qualifiers in the "validator_qualifier" field must also have an associated "approval_a" code. The "approval_a" code for the preserved lab qualifier of organic "J" and inorganic "B" is "BRL". The "approval_a" code for preserved laboratory qualifier "U" is "PLU".

To qualify for blank contamination, the value in the "result_value" field is removed, the "detect_flag" field is changed from "Y" to "N", the U qualifier is inputted into the "validator_qualifiers" field, the "quantitation_limit" field (remember, this field contains the sample-specific detection limit) is raised to the detected value, and the appropriate reason code is added to the "approval_a" field (e.g., MBK). If the original sample concentration was an estimated value (e.g., 6J), the "reporting_limit" field for the non-detect value will remain unchanged. If the analyte's concentration was not an estimated value, the value in the "reporting_limit" field must be elevated to the original sample concentration.

Samples may have more than one set of results due to dilutions and re-analyses completed by the laboratory. The EDD includes a field titled "reportable_result" which is populated with either "N" or "Y" for each result. When multiple analyses are performed, the laboratory will designate which result they feel is most usable based on quality control data. Any time there are multiple analyses for a sample, the data validator must determine which analysis best meets the project DQO. Consideration should be given to all quality control (QC) factors (e.g., surrogate recoveries, holding

times, internal standard recoveries, etc.), during this determination. If the validator chooses to report a result other than that selected by the lab, the "reportable_result" field is changed from "Y" to "N" for the value that the validator wishes not to report, and the "reportable_result" field is changed from "N" to "Y" for the value to be reported.

Due to the fact that some validation guidance documents include different qualifiers and vary in the application of qualifiers, each result in the database must include documentation of the guidance used for data validation. This information is stored in the "approval_b" field (see Section 4.0 for more information on "approval_b" codes); this field must be populated for all results.

All data in the database must show the level of validation applied. The "approval_code" value represents the level of validation. The "approval_code" will be defaulted to "4" upon opening the spreadsheet and must be revised after validation to the "approval_code" field prior to submittal for import into the database. Approval codes are summarized in Table 3.1.

Non-detect reporting limits are normally reported from the "reporting_detection_limit" field of the flatfile, which is typically the PQL for organics and the IDL or CRDL (depending on lab reporting convention) for inorganics.

If it is required that reporting limits other than those stored in the "reporting_detection_limit" field are required (e.g., IDLs be used for metals in place of CRDLs, or IDLs and MDLs across the board for risk assessment, or TRRP reporting), the reporting limits can be stored in an optional field called "custom_field_2". Prior to flatfile generation, the validator will inform the database analyst about where reporting limits for non-detect data are to be obtained and these values will be imported into the "custom"field"2" field of the flatfile.

If custom_field_2 is used, when changing reporting limits due to method blank concentrations, the validator must be sure to change the values in the "custom_field_2", "reporting_detection_limit" and "quantitation_limit" fields as appropriate.

3.2.4 FLATFILE COMPLETENESS CHECKER

This program is located under the Check Flatfile tab and is used to check the final flatfile for consistency and completeness. For example, the checker will identify inconsistencies like results that have "U" listed under "validator_qualifier" field, and a "Y" populated in the "detect_flag" field. This checker must be run and all errors addressed before submitting the flatfile back to database for import into the database.

3.2.5 SAVING THE UPDATED FLATFILE

Upon completion of validation, the "L" in the file name is changed to a "V" and the validator's initials are added to the end of the file name. The "peer" review person may also add their initials to the end of the file name.

3.3 XTAB GENERATION

Under the check flatfile tab, there is an option to prepare a crosstab (xtab) table of results. This table can be used by the chemist to review the final data and ensure that there are no missing results and that data appear to be reported correctly.

4.0 REVIEW OF APPLICABLE QUALITY CONTROL DOCUMENTS AND STANDARDS

Prior to commencing data validation, all applicable QC documents must be reviewed and understood. Where applicable, this includes the QAPP, DQO, region-specific or project-specific validation guidelines, permits, SOPs, and project SAPs, etc.

Unless otherwise specified, data validation is performed using the principles outlined in the USEPA NFG and the QC criteria outlined in the analytical methods. Project-specific quality documents will take precedence over all other guidance documents for decision-making purposes during analytical data review and assessment.

The data validation guidance document used to perform the validation must be recorded in the database. A two-digit code has been assigned to each document (see Table 4.1) and the appropriate code must be entered into the "approval_b" field of the flatfile.

5.0 REASON CODE ASSIGNMENT

As data are qualified throughout the data validation processes, a reason code is assigned to document the reason for the qualification. A list of reason codes and definitions are presented in Table 5.1. These reason codes are stored in the database in the "approval_a" field. For all data qualifications, the appropriate reason code must be entered into the "approval_a" field of the flatfile.

When a data value is qualified for multiple reasons, up to three reason codes (9 characters) can be assigned appending each to the primary qualifying code without separation. For example, if a data point is qualified for outlying surrogate and laboratory control sample (LCS) recoveries, the result is qualified with "LCSSUR".

6.0 DATA VALIDATION PROCEDURES

Data validation is performed in accordance with the USEPA NFGs (or other region- or project-specific validation guidance document) and any other project-specific quality control documents. The following sections detail the data validation procedures for each element.

During data validation, data qualifiers are applied to sample results to indicate potential biases in the data. The USEPA NFG data validation qualifier definitions are presented in Table 6.1. The CRA abbreviated data qualifier definitions are presented in Table 6.2. Either set of definitions can be used as appropriate based on agency and project-specific requirements.

6.1 DATA PACKAGE COMPLETENESS AND COMPLIANCE REVIEW

Prior to data quality assessment and validation, the data package must be checked to ensure that all elements are present. Data package completeness and compliance checklists are included as Appendices A-1 and A-2.

6.2 SAMPLE PRESERVATION AND HOLDING TIME ASSESSMENT

Holding times are defined as the amount of time that elapses between the collection of the appropriately preserved sample from the source in the field and the beginning of the analysis procedure (which may include extraction and a separate holding time period from extraction to analysis). The published sample container, preservation, and holding time requirements are presented in Table 6.3. Note that this table is to be used as guidance and could vary by method, region, agency, etc. If project-specific requirements differ from this table, project-specific requirements take precedence.

Sample holding times are verified by the Chain of Custody forms (COCs), laboratory custody records, and narrative to verify that samples were received at 4°C (±2°C) (if applicable), were properly preserved and analyzed within the method or project-specific holding times. For exceedances, qualify data as indicated in the following Sample Preservation and Holding Time (HT) Non-Compliance Action Table.

SAMPLE PRESERVATION AND HOLDING TIME NON-COMPLIANCE ACTION

		Action		
Assessment Element	*Failure*	*Non-Detects*	*Positive Results*	*Approval Code*
Holding Time [1]	Sample HT exceeds HT criteria by ≤2x (NFG) Sample HT exceeds HT criteria by >2x (NFG)	UJ R	J J	HTQ
Chemical Preservation	Not preserved in the field (NFG) (pH adjustments by lab are acceptable)	UJ	J	SPV
Inappropriate Container	Sample collected in inappropriate container (CRA)	Prof. Judgment	Prof. Judgment	SPV
Headspace (VOC Waters)	VOC vial contained headspace (CRA) (> pea-sized air bubble)	UJ	J	SPV
Sample/Cooler Temperature [2]	No Ice (CRA) and >6 and ≤10°C (CRA) No Ice (CRA) and >10 and ≤20°C (CRA) No Ice (CRA) and >20°C (CRA)	Prof. Judgement UJ R	Prof. Judgement J J	SPV SPV SPV

Notes:
1 Holding time criteria will incorporate professional judgement for certain parameter/matrices.
2 Sample/cooler temperature evaluation will include other considerations, such as the presence or absence of ice in the cooler, the number of days in transit and the specific parameters requested. Same day delivery of samples is exempt from receipt temperature requirements.

6.3 INSTRUMENT PERFORMANCE CHECK - ORGANICS BY GC/MS AND METALS BY ICP/MS

Tuning is a quality control performance check that is particular to the use of instruments having an MS as the detector. The MS functions by bombarding the target analytes with electrons as they enter the analyzer. The electrons collide with target analyte molecules causing them to ionize. The analyzer then performs a count of the ion abundance of each ion created with the compound molecules. The software used in conjunction with the mass analyzer prepares a plot of abundance versus mass of the ions, called a mass spectrum. The relative abundance of the ions created and detected from the compound molecules is dependent upon the electrical and magnetic properties of the mass analyzer.

The following items are evaluated as part of the instrument performance check during FDV with calculations spot-checked at a 10 percent frequency:

- Check tune summaries to ensure that instrument tune checks were performed every 12 hours (organics); and that all investigative samples are accounted for within those tune windows.
- Verify the tune checks were analyzed five times consecutively (ICP/MS only). If tune checks have not been performed at the required frequency, use professional judgement to determine whether associated sample results are valid.
- Check that all abundances are normalized to the proper m/z.
- Verify the ICP/MS percent relative standard deviation (%RSD) values were within the specified criteria.
- Check that the proper number of significant figures have been reported.
- Spot-check for transcription errors between raw data and tune summary form.
- Recalculate some of the relative ion abundance's to verify lab's calculations.
- Verify that spectra were obtained using accepted background subtraction techniques.
- Verify that appropriate (method- or QAPP-specific) ion abundance criteria were used.

If errors are noted, contact the laboratory and request a corrected re-submittal. If the lab cannot resubmit data, all associated data should be rejected (R).

Check all ion abundances against appropriate criteria. If outliers are noted, use professional judgement to determine whether the data are usable. If data are judged to be usable, the data validation report must clearly state the nature of the tune non-conformances. If the tune non-conformances are judged to impact data quality, qualify data as follows:

INSTRUMENT TUNE CRITERIA AND VALIDATION ACTION

		Action		
Assessment Element	*Criteria*	*Non-Detects*	*Positive Results*	*Approval Code*
VOC BFB Criteria (NFG)	50 8-40% of 95 * 174 50-120% of 95 75 30-60% of 95 * 175 4-9% of 174 95 Base Peak (100%) * 176 93-101% of 174 * 96 5-9% of 95 * 177 5-9% of 176 * 173 <2% of 174	* m/e non-compliant UJ (NFG)	* m/e non-compliant J (NFG)	TUN
	Incorrect base mass assignment	R (CRA)	R (CRA)	TUN
SVOC DFTPP Criteria (NFG)	51 30-60% of 198 *199 5-9% of 198 *68 <2% of 69 275 10-30% of 198 69 mass of 69 365 >1% of 198 *70 <2% of 69 *441 Present but <443 127 40-60% of 198 *442 >40% of 198 *197 <1% of 198 *443 17-23% of 442 *198 Base Peak (100%)	* m/e non-compliant UJ (NFG)	* m/e non-compliant J (NFG)	TUN
	Incorrect base mass assignment	R (CRA)	R (CRA)	TUN
Metals (NFG)	Analyzed 5 times consecutively	R (NFG)	R (NFG)	TUN
	Peak Width to 0.75 amu @ 5% peak height	UJ (NFG)	J (NFG)	TUN
	m/e ±0.1 amu over range of 6- 210 amu	UJ (NFG)	J (NFG)	TUN
	%RSD absolute signals <5%	UJ (NFG)	J (NFG)	TUN
Timeframe (NFG)	> 12 hour timeframe but ≤13 hours	UJ (CRA)	J (CRA)	TUN
	(from injection of tuning standard) (CRA)	R(CRA)	R(CRA)	TUN
	>13 hour timeframe			

6.4 INSTRUMENT CALIBRATION - ORGANICS

The following sections address initial and continuing instrument calibration for organic analyses. Instrument calibration data are reviewed during FDV only.

6.4.1 INITIAL INSTRUMENT CALIBRATION - ORGANICS

Calibration is the establishment of a quantitative relationship between the response of the analytical procedure and the concentration of the target analyte. The initial calibration (ICAL) is the procedure that functions as the calibration curve for the target analytes. A necessary prerequisite is that a confident identification of the target analyte has already been established.

To assess ICAL data:

- Check lab data to ensure that initial calibration standards were analyzed at the proper frequency.
- Verify a minimum of five standards were utilized and were analyzed at the appropriate concentrations.
- Check that the ICAL was analyzed prior to all samples associated with it.
- Verify that the ICAL met the minimum average relative response factors (RRF) and %RSD criteria identified in the NFG unless alternate method criteria are specified.
- Check lab data to ensure that the compounds identified were within the retention time (RT) criteria.
- Verify that at least three peaks were used in the calibration of each Aroclor during PCB analysis.

If the calibration standards were not analyzed at the proper frequency, use professional judgement to determine the usability of the data.

- Spot check calculations (10 percent) for RRF or response factors (RF) for methods not using internal standards.
- Spot-check calculations (10 percent) of the calibration curve. If various calculation methods were used (e.g., average RRF, linear regression, quadratic, etc.), results reported using each calculation must be verified.
- For GC methods, spot-check the calculation of retention time windows.
- Spot-check %RSD, correlation coefficient (R^2) calculations if used.

If errors are identified, contact the lab to have the data package corrected and resubmitted.

- Check the linearity or the calibration curve (%RSDs $\leq$30 percent for GC/MS, %RSDs $\leq$20 percent for GC, R^2 values >0.99).
- For methods using internal standards, check analyte sensitivity; average RRF must be $\geq$0.05.

If linearity or sensitivity criteria are not met, qualify data as follows:

ORGANIC INITIAL CALIBRATION CRITERIA AND VALIDATION ACTION

Method	*Assessment Element*	*Criteria*	*Failure*	*Action*		*Reason Code*
				Non-Detects	*Positive Results*	
GC/MS (VOC & SVOC)	Minimum Average Relative Response Factor (RRF) (NFG)	0.05 (NFG)	<0.05	R	J	ICL
	Relative Standard Deviation (%RSD) (NFG)	≤30.0%	>30.0%	UJ (CRA)	J (CRA)	ICL
	Quadratic Coefficient of Determination (R^2) (SW846)	≥0.99 (SW846)	<0.99 (SW846)	UJ (CRA)	J (CRA)	ICL
	Linear Correlation Coefficient (R) (SW846)	≥0.995 (CRA)	<0.995	UJ(CRA)	J(CRA)	ICL
GC & HPLC (PCB, Pest., VOCs, SVOCs) [1]	% Relative Standard Deviation (%RSD) (SW-846) or	≤ 20% (SW-846)	>20%	UJ [2]	J [2]	ICL
	Linear Correlation Coefficient (R) (SW846)	≥0.995 (CRA)	<0.995	UJ [2] (CRA)	J [2] (CRA)	ICL

Notes:
1 Multi-component analyte %RSD limits are based on average of all peaks used in calibration.
2 CRA modification of NFG qualification:
- Aroclor 1016 Non-compliance is representative of Aroclor 1221 through 1248
- Aroclor 1260 Non-compliance is representative of Aroclor 1254 through 1268

6.4.2 CONTINUING INSTRUMENT CALIBRATION - ORGANICS

The continuing calibration verification (CCAL) is used to verify that the initial calibration is maintained and correct while the instrument is used to process samples. The CCAL also serves to determine that the identification criteria are still being met. Valid sample results will always be preceded by an acceptable CCAL analysis for GC/MS methods and are bracketed by acceptable CCAL analyses for GC methods.

- Check lab data to ensure that continuing calibration standards were analyzed at the proper frequency.
- Verify that calibration standards were at the appropriate concentrations.
- Compare %Drift values to those compounds quantitated utilizing a quadratic curve.

- Check that the GC/MS CCAL met the minimum RRF and maximum percent difference (%D)/%Drift criteria.

If calibration standards were not analyzed at the proper frequency, use professional judgement to determine the usability of the data.

- Spot-check calculations (10 percent) for RRF or RF for methods not using internal standards.
- Spot check calculations (10 percent) for RRF or RF, and %D/%Drift.
- For GC, verify that the analyte retention times fall within the established retention time windows.

If errors are identified, contact the lab to have the data package corrected and resubmitted.

- Check the linearity (%D/% Drift $\leq$25 percent (GC/MS), %D $\leq$15 percent GC)
- For methods using internal standards, check analyte sensitivity; average RRF must be $\geq$0.05

If linearity or sensitivity criteria are not met, qualify data as follows:

ORGANIC CONTINUING CALIBRATION CRITERIA AND VALIDATION ACTION

Method	*Assessment Element*	*Criteria*	*Failure*	*Action*		*Reason Code*
				Non-Detects	*Positive Results*	
GC/MS (VOC & SVOC)	Minimum Average Relative Response Factor (RRF) (NFG)	≥0.05 (NFG)	<0.05	R (NFG)	J (NFG)	CCL
	Percent Difference (%D) (NFG)	≤25% (NFG)	> 25%	UJ (NFG)	J (NFG)	CCL
	Percent Drift (%Drift) (SW846)	≤25% (SW846)	> 25%	UJ (CRA)	J (CRA)	CCL
GC & HPLC (PCB, pest, VOCs, SVOCs) [1]	Percent Difference (%D) (NFG) or Percent Drift (%Drift) (SW846)	≤15% (SW-846)	> 15%	UJ [2] (CRA)	J [2] (CRA)	CCL
		≤15% (SW846)	> 15%	UJ [2] (CRA)	J [2] (CRA)	CCL
	Retention Time Window SW846)	±0.07 Min of Standard (SW846)	Outside Window	Prof. Judgment (CRA)	Prof. Judgment (CRA)	CCL

Notes:
(1) Multi-component analyte %D and % Drift limits are based on average of all peaks or concentrations used in calibration.
(2) CRA modification of NFG qualification:
- Aroclor 1016 Non-compliance is representative of Aroclor 1221 through 1248
- Aroclor 1260 Non-compliance is representative of Aroclor 1254 through 1268

6.5 INSTRUMENT CALIBRATION - INORGANICS

The following sections address initial and continuing instrument calibration for inorganic analyses. Instrument calibration data are reviewed during FDV only.

6.5.1 INITIAL INSTRUMENT CALIBRATION - INORGANICS

Calibration is the establishment of a quantitative relationship between the response of the analytical procedure and the concentration of the target analyte. The initial calibration (ICAL) is the procedure that functions as the calibration curve for the target analytes. A necessary prerequisite is that a confident identification of the target analyte has already been established.

If required by the method or QAPP, the CRDL must be verified with a standard (CRI) at 2 times (x) the CRDL or 2x the instrument detection limit (IDL), whichever is greater.

- Check that the ICAL was analyzed prior to all samples associated with it.
- Check lab data to ensure that the ICALs were analyzed at the proper concentration and frequency.
- Verify the initial calibration verification (ICV) was analyzed at the proper concentration and frequency.
- Check the linearity coefficient of variance (COV) $\geq$0.995.
- Check lab data to ensure the CRI was analyzed at the proper frequency, if required.

If calibration standards were not analyzed at the proper frequency, use professional judgement to determine the usability of the data.

- Spot-check calculations for calibration curves at a frequency of 10 percent. Results using calibration curve must be verified.

If errors are identified, contact the lab to have the data package corrected and resubmitted.

INORGANIC INITIAL CALIBRATION CRITERIA AND VALIDATION ACTION

Method	*Assessment Element*	*Criteria*	*Failure*	*Action* [1]		*Reason Code*
				Non-Detects	*Positive Results*	
ICP, ICP/MS, CVAA, Spec., IC	COV (Metals, Mercury, Gen. Chem.)	≥0.995 (NFG)	COV < 0.995	Prof. Judgement (NFG)	J (NFG)	ICL
ICP, ICP/MS (Metals)	Initial Calibration Verification (ICV)	± 10% of true value (NFG)	< 90% but ≥ 75% < 75% > 110% but ≤125% > 125%	UJ (NFG) R (NFG) None None	J (NFG) R (NFG) J (NFG) R (NFG)	ICL ICL ICL ICL
CVAA (Mercury)	ICV	± 20% of true value (NFG)	< 80% but ≥ 65% < 65% > 120% but ≤135% > 135%	UJ (NFG) R (NFG) None None	J (NFG) R (NFG) J (NFG) R (NFG)	ICL ICL ICL ICL
Spec. & IC (Gen. Chem.)	ICV	± 15% of true value (NFG)	< 85% but ≥ 70% < 70% > 115% but ≤130% > 130%	UJ (NFG) R (NFG) None None	J (NFG) R (NFG) J (NFG) R (NFG)	ICL ICL ICL ICL
ICP, CVAA ICP/MS Spec. (Metals, Mercury Gen. Chem.)	CRI [2]	Beginning of Analysis (if applicable) ± 20% of true value (±30% for ICP/MS) (NFG-2)	< LCL but ≥ 50% < 50% > UCL	UJ (NFG-2) R (NFG-2) None	J (if <2x RL) (NFG-2) J (if <2x RL) (NFG-2) J (if <2x RL) (NFG-2)	CRA CRA CRA

Notes:
1 All samples prepared within the analytical batch are affected.
2 The 2002 NFG for inorganics will be used to evaluate the CRI standard if CRI data is required.

6.5.2 CONTINUING INSTRUMENT CALIBRATION - INORGANICS

The continuing calibration verification (CCV) is used to verify that the ICAL is maintained and correct while the instrument is used to process samples. The CCV also serves to determine that the identification criteria are still being met. Valid sample results will always be bracketed in time by acceptable CCV analyses.

- Check lab data to ensure that continuing calibration standards were analyzed at the proper frequency.
- Verify that calibration standards were at the appropriate concentrations.

If calibration standards were not analyzed at the proper frequency, use professional judgement to determine the usability of the data.

INORGANIC CONTINUING CALIBRATION CRITERIA AND VALIDATION ACTION

Method	*Assessment Element*	*Criteria*	*Failure*	*Action* [1]		*Reason Code*
				Non-Detects	*Positive Results*	
ICP, ICP/MS (Metals)	Continuing Calibration Verification (CCV)	After every 10 samples ± 10% of true value (NFG)	<90% but ≥75% < 75% >110% but ≤125% >125%	UJ (NFG) R (NFG) None None	J (NFG) R (NFG) J (NFG) R NFG)	CCL CCL CCL CCL
CVAA (Mercury)	CCV	After every 10 samples ± 20% of true value (NFG)	<80% but ≥65% < 65% >120% but ≤135% > 135%	UJ (NFG) R (NFG) None None	J (NFG) R (NFG) J (NFG) R (NFG)	CCL CCL CCL CCL
Spec. & IC (Gen. Chem.)	CCV	After every 10 samples ± 15% of true value (NFG)	<85% but ≥70% < 70% >115% but ≤130% >130%	UJ (NFG) R (NFG) None None	J (NFG) R (NFG) J (NFG) R (NFG)	CCL CCL CCL CCL
Spec. (Gen. Chem.)	Distillation Check	Midrange CN standard distilled (± 15% of undistilled std) (NFG) if applicable	>115% <85%	None UJ (NFG)	J (NFG) J (NFG)	CCL CCL

Notes:
[1] All samples between non-compliant CCVs within the analytical sequence are affected.

6.6 BLANKS (METHOD BLANKS, INSTRUMENT BLANKS, CALIBRATION BLANKS AND FIELD BLANKS)

Blank samples are prepared, collected and analyzed to determine if contamination of samples is potentially introduced during the collection and analysis process. Sources of sample contamination can include the containers and equipment used to collect the samples, preservatives added to the samples, other samples in transport coolers and laboratory sample storage refrigerators, standards and solutions used to calibrate instruments, glassware and reagents used to process samples and the analytical instrument sample introduction equipment. Each area of analysis has its own particular suite of common laboratory contaminants.

Method blanks apply to all samples belonging to the same sample preparation batch, or in the case of VOC, all samples analyzed on the same instrument on the same day. Inorganic initial calibration blanks (ICBs) apply to all samples after while continuing calibration blanks (CCBs) apply to all samples analyzed immediately before and after. Field blanks (trip blanks, rinse blanks, equipment blanks, filter blanks, etc.) are intended to identify contamination introduced during sample collection and/or storage and should be applied only to those samples collected at the same time as, and with the same equipment as the field blanks (see sample collection note, COC, sample key or field personnel to determine which field blanks apply to which samples). Trip blanks are applied to all VOC samples transported to the laboratory in the same shipping cooler as the trip blank.

If blanks were not analyzed at the proper frequency, potential contamination cannot be assessed for the corresponding investigative samples. This should be noted in the data validation report.

- Check the extraction logs, run-logs, and method blank summary forms to ensure that method blanks were prepared and analyzed with samples at the required frequency (typically one method blank per analytical batch).
- Check the sample run-log to ensure that instrument blanks were analyzed after any sample having significantly high target analyte concentrations.
- Check the run-log to ensure that ICBs and CCBs were analyzed at the proper frequency for inorganic analyses (typically every 10 samples).
- Review blank raw data for target analytes.

If target analytes are detected in the blanks, detection of these analytes in associated investigative samples may reflect contamination, and must be qualified as indicated in the table below. For assessing contamination in soil samples, individual sample weights (dry or wet) must be applied to the blank result before comparing it to the sample result. Soil samples with associated field blank contamination less than the reporting limits will be documented in the validation text without qualification. Significant field blank contamination for soils will require qualification. Sample preparation and dilution

factors for laboratory blanks (ICBs, CCBs, and method blanks) must also be applied to the blank results.

For sample results qualified non-detect (U) to reflect contamination, change the "detect" field in the flatfile from "Y" to "N", raise the report limit (RL) to the sample analyte concentration (when above the RL) and delete.

BLANK VALIDATION ACTION

Assessment Element	*Failure*	*Action* [1]			*Reason Code*
		Non-Detects	*Positive Results (RL Reporting)*	*Positive Results (MDL Reporting)*	
Method Blank Contamination	Target analytes detected <5x blank value or <10x for common lab contaminants [2] (NFG)	NA	< RL qualify U at RL > RL qualify U at value	< RL qualify UJ at value > RL qualify U at value	MBK
ICB and CCB Contamination	Target analytes detected <5x blank (NFG)	NA	< RL qualify U at RL > RL qualify U at value	< RL qualify UJ at value > RL qualify U at value	CBK CBK
Field Blank Contamination	Target analytes detected <5x blank value or <10x for common lab contaminants (CRA) (waters only)	NA	< RL qualify U at RL > RL qualify U at value	< RL qualify UJ at value > RL qualify U at value	TBK, FBK, RBK, FIL

Notes:
1 Hierarchy of qualifying data due to blank contamination is MBK, CBK, TBK, FBK, RBK, FIL. (CRA)
2 Common laboratory contaminants include: VOC - acetone, 2-butanone, methylene chloride and cyclohexane and SVOC - phthalates.

6.7 SYSTEM MONITORING COMPOUNDS (SURROGATES) - ORGANICS

Surrogates are non-target compounds added to every sample at the beginning of the sample preparation to monitor the success of the sample preparation on an individual sample basis.

For PCB analysis tetrachloro-m-xylene (TCMX) the more volatile of the two surrogates, is more volatile than any of the target analytes of this method. The recoveries of TCMX are linked to the lowest volume to which the sample extract was concentrated and target compounds such as Aroclor 1221 and Aroclor 1232. Samples with higher weight PCBs

contain substantial portions of decachlorobiphenyl (DCB), which will effect the calculated recovery of this surrogate when these analytes are present in the sample.

- Check surrogate summary forms to verify that all investigative samples have been accounted for.
- Spot-check raw data to verify the recoveries on the surrogate summary form.
- Spot-check calculations of the surrogate recoveries.
- Check that the control limits used are the appropriate limits for the project.
- Check surrogate recoveries against the laboratory control limits.

If any errors are found in the surrogate summaries, or are determined in the calculations, contact the laboratory and request the forms and any affected data pages are resubmitted with corrections.

If outliers are noted, verify that samples were re-analyzed. If surrogate recoveries for extractable parameters are still outside of the control limits, verify that the laboratory re-extracted the samples to confirm matrix interference. When there are unacceptable surrogate recoveries, followed by acceptable re-analyses, verify that the designated successful analysis was reported in the flatfile.

Sample data with outlying surrogate recovery should be qualified as summarized below. SVOC surrogate recoveries are assessed by fraction (base/neutral or acid) and only those analytes within that fraction affected by outlying surrogate recoveries are qualified.

Interferences and/or sample dilutions can prohibit surrogate recovery assessment. In such cases, it should be noted in the data validation report that surrogate recoveries could not be assessed.

SURROGATE CRITERIA AND VALIDATION ACTION

Assessment Element	*Failure*	*Action*		*Reason Code*
		Non-Detects	*Positive Results*	
GC, GC/MS & HPLC (excluding SVOC analysis)	If one or More Surrogates:			
	%R > UCL (NFG)	None	J (NFG)	SUR
	%R <LCL but ≥10% (NFG)	UJ (NFG)	J (NFG)	SUR
	%R <10% (NFG)	R (NFG)	J (NFG)	SUR
	Diluted (≥ 1:5) (CRA)	None	None	None
GC/MS SVOC Surrogate Recovery	1 out in a fraction > 10%	None	None	SUR
	≥2 out of a fraction %R > UCL (NFG)	None	J (NFG)	
	≥2 out of a fraction %R <LCL but ≥10% (NFG)	UJ (NFG)	J (NFG)	SUR
	One %R <10% NFG)	R (NFG)	J (NFG)	SUR
	Diluted (≥ 1:5) (CRA)	None	None	None

If the surrogates in method blanks and/or laboratory control samples (LCS) are as low as sample surrogate recoveries, matrix effects cannot be assumed and the overall extraction efficiency is in question. The problem should be noted in the data validation notes, and the laboratory should be contacted to provide an explanation and corrective actions for future analyses.

6.8 MATRIX SPIKE/MATRIX SPIKE DUPLICATES - ORGANICS

An MS consists of a sample fortified with a known amount of a target analyte and is typically analyzed in duplicate (MS/MSD). Analysis of the MS/MSD and comparison with the unspiked sample result provides the ability to assess accuracy and precision of the method on a given sample matrix. MS/MSD recoveries are used for a qualitative indication of accuracy due to matrix effects. The relative percent difference (RPD) between the recoveries is used for a qualitative indication of precision.

- Verify that MS/MSDs were prepared and analyzed at the proper frequency (typically one per sample batch, up to 20 samples).

If MS/MSDs were not prepared and analyzed at the proper frequency, note this in the data validation report.

- Spot-check MS/MSD recovery calculations from raw data.

- Spot check RPD calculations.

If errors are determined in the calculations, contact the laboratory and request that the forms and any affected data pages be resubmitted with corrections.

- Assess recoveries against control limits.

If outlying analyte recoveries are identified, qualify all associated results for that sample only as summarized below. MS/MSD outliers observed in the organic analyses are associated with the parent sample only. Outlying results for multiple MS/MSD sample recoveries can indicate a systematic error (e.g., recoveries for multiple MS/MSDs show similar biases). In such cases, results for all associated samples in that batch may be qualified.

In cases where the original sample concentrations are significantly greater than the spiking concentrations (>4x), matrix spike recoveries cannot be assessed. This should be noted in the data validation report, and the associated samples are not qualified.

- Assess RPD values against laboratory established control limits.

If outlying MS/MSD percent recoveries or RPDs are identified, qualify all associated positive results for that sample only as follows:

MS/MSD - ORGANICS VALIDATION ACTION

Assessment Element	*Failure* [1]	*Action* [2]		*Reason Code*
		Non-Detects	*Positive Results*	
MS/MSD Accuracy (Recovery)	%R > UCL (Reg. 5) (Both MS & MSD)	None	J	MSD
	%R <LCL but ≥10% (Reg. 5) (Both MS & MSD)	UJ	J	MSD
	%R <10% (Reg. 5) (Either MS or MSD)	R	J	MSD
MS/MSD Precision	RPD > Criteria (Reg. 5)	None	J	MSD

Notes:

1 List of target compounds the laboratory will utilize are presented with each sample delivery group. The criteria used in validation will be those limits statistically generated by the laboratory, and may change periodically. Therefore the limits used for validation are referred to as the upper control limit (UCL) or lower control limit (LCL).

2 CRA Modification to NFG Qualifications:
- Aroclor 1016 Non-compliance is representative of Aroclor 1221 through 1248
- Aroclor 1260 Non-compliance is representative of Aroclor 1254 through 1268

6.9 MATRIX SPIKE/MATRIX SPIKE DUPLICATES OR MATRIX SPIKE/MATRIX DUPLICATE - INORGANICS

An MS is a sample fortified with a known amount of a target analyte and is typically analyzed in duplicate (MS/MSD). Analysis of the MS/MSD and comparison with the unspiked sample results provides the ability to assess accuracy and precision of the method on a given sample matrix. Precision may also be assessed through analysis of a matrix duplicate (MD). MS/MSD recoveries are used for a qualitative indication of accuracy (bias) due to matrix effects. The RPD between the recoveries (MS/MSD) or the results (MD) is used to assess precision. Only project specific sample matrix spikes are considered when evaluating and qualifying samples.

- Verify that MS/MSD or MS/MD were prepared and analyzed at the proper frequency (typically one per sample batch).

If MS/MSD or MS/MD were not prepared and analyzed at the proper frequency, note this in the data validation notes.

- Spot-check MS/MSD recovery calculations from raw data (FDV only).
- Spot-check RPD calculations.

If errors are determined in the calculations, contact the laboratory and request that the forms and any affected data pages be revised and resubmitted.

- Assess recoveries against control limits.

If outlying analyte recoveries are observed, qualify results for all associated samples (samples prepared in the same analytical batch).

In cases where the original sample concentrations are significantly greater than the spiking concentrations (>4x), MS recoveries cannot be assessed. Since the accuracy cannot be adequately determined, accuracy is considered not calculable (NC).

- Assess RPD values against control limits. If control limits are not specified for the project, use 20 percent for water samples and 35 percent for soil samples with results greater than five (5) times the RL. For sample results less than five (5) times the RL, precision is assessed by comparing the difference between the two results to a control limit of plus or minus (±) the RL amount for water samples and ±2 times the RL amount for soil samples.
- If one result from the sample/MD set is non-detect, precision is calculated using the analyte reporting limit for the non-detect results.

If MS/MSD or MS/MD data do not meet the above criteria, qualify all associated positive results as follows.

MS/MSD & MD - INORGANICS VALIDATION ACTION

Assessment Element	*Failure* [1]	*Action*		*Reason Code* [2]
		Non-Detects	*Positive Results*	
MS or MS/MSD Accuracy (Recovery)	%R ≥125% (NFG) (MS and MSD)	NA	J	MSQ or MSD
	%R ≥30% and <75% (NFG) MS and MSD	UJ	J	MSQ or MSD
	%R <30% (NFG) MS or MSD	R	J	MSQ or MSD
MS/MSD or MD Precision	RPD (if both values are >5X RL, Waters >20%, Soils >35%	NA	J	MSD or DUP
	RL (if either value is <5X RL), Waters >1X RL value (Reg. 5), Soils >2X RL value (Reg. 5)	J	J	MSD or DUP

Notes:
1 Laboratory may develop specific ICP/MS criteria.
2 Use MSD reason code for any data qualifications related to MS/MSD accuracy and/or precision. Use the MSQ reason code for any data qualifications related to accuracy when MS only is analyzed. Use the DUP reason code for any data qualifications related to precision when MD is analyzed.

6.10 LABORATORY CONTROL SPIKE/LABORATORY CONTROL SPIKE DUPLICATE SAMPLES

A LCS consists of a portion of analyte-free water or solid phase sample that is spiked with target analytes at a known concentration. The LCS is processed through the entire method procedure with each sample batch; the results are examined for target analyte recovery. In analytical batches where an MS/MSD sample is not available the LCS may be analyzed in duplicate. The LCS/laboratory control sample duplicate (LCSD) can be used by the laboratory in cases where the MS/MSD failed to achieve acceptable recovery and/or precision. If the LCS/LCSD fails to generate acceptable results, this should cause concern about the validity of the results for all samples in the batch.

- Verify that LCS or LCS/LCSD were prepared and analyzed at the proper frequency (typically one per sample batch).

If LCS or LCS/LCSD were not prepared and analyzed at the proper frequency, note this in the data validation narrative.

- Spot-check LCS or LCS/LCSD recovery calculations from raw data (FDV only).
- Check that the control limits used are the appropriate limits for the project.

If errors are determined in the control limits or calculations, contact the laboratory and request that the forms and any affected data pages be resubmitted with corrections.

- Assess recoveries against control limits.

If outlying analyte recoveries are identified, qualify all associated sample results in that sample batch as summarized below. If the LCS or LCSD recoveries indicate a systematic error (e.g., recoveries for all spiking compounds are low), qualifications of all compounds (spiking and non-spiking compounds) can be performed.

LCS/LCSD VALIDATION ACTION

Assessment Element	*Failure* [1]	*Action* [2]		*Reason Code* [3]
		Non-Detects	*Positive Results*	
LCS or LCSD Accuracy	%R >UCL (NFG)	None	J	LCQ or LCD
	Organics %R ≥10% but <LCL (Reg. 5)	UJ	J	LCQ or LCD
	Inorganics %R ≥50% but < 79% (NFG)	UJ	J	LCQ or LCD
	Organics %R <10% (Reg. 5)	R	J	LCQ or LCD
	Inorganics %R < 50 % (NFG)	R	J	LCQ or LCD
LCS/LCSD Precision	RPD > Lab control Limit (CRA)	NA	J	LCD

Notes:

1 Organic LCS Criteria - List of target compounds the laboratory will utilize are presented with each sample delivery group. The criteria used in validation will be those limits statistically generated by the laboratory, and may change periodically. Therefore the limits used for validation are referred to as the upper control limit (UCL) or lower control limit (LCL).

2 CRA Modification to NFG Qualifications:
- Aroclor 1016 Non-compliance is representative of Aroclor 1221 through 1248
- Aroclor 1260 Non-compliance is representative of Aroclor 1254 through 1268

3 Use LCD reason code for any data qualifications related to LCS/LCSD accuracy and/or precision. Use LCQ reason code for any data qualifications related to accuracy when LCS only is analyzed.

6.11 INTERNAL STANDARDS

Internal standards (IS), assessed during FDV only, are used as the quantitation and relative retention time standard for the target analytes analyzed by MS. Low area counts for the internal standards translate into falsely high reported values for target

analytes in the samples. Anyreported value for an analyte is an estimate when high or low IS area counts are reported.

- Verify that all samples are accounted for on the IS review forms.
- Spot check for transcription errors between the IS area counts reported on the summary form, and the raw data from calibration and sample analyses.
- Spot check the IS area range calculations.
- Spot check IS recoveries for the samples.

If there are errors in the IS summaries, or errors are determined in the calculations, contact the laboratory and request that the forms and any affected data pages be resubmitted with corrections.

- Check IS recoveries against control limits of 50-200 percent (GC/MS) or 30-120 percent (ICP/MS). If outliers are noted, verify that samples were re-injected. Where there are unacceptable IS recoveries, followed by acceptable re-analyses, verify that the designated successful analysis was reported in the flatfile.
- Verify that all internal standards were recovered.
- Check that the IS brackets the masses of target analytes (ICP/MS).
- Verify when outliers are observed during ICP/MS analysis, a two fold dilution is performed and a reanalysis of the calibration blank is performed.
- For IS recoveries outside of the control limits, only results for those analytes calculated from the outlying ISs will be affected as follows:

INTERNAL STANDARD CRITERIA AND VALIDATION ACTION

Assessment Element	*Failure*	*Action*		*Reason Code*
		Non-Detects	*Positive Results*	
IS Recovery (GC/MS)	>200% (NFG)	NA	J	IST
	<50% but ≥25% (NFG)	UJ	J	IST
	<25% (NFG)	R	J	IST
IS Recovery (ICP/MS)	Sample IS >120% (NFG-2)	NA	J	IST
	Sample IS <30% (NFG-2)	UJ	J	IST
	CCB, CCV IS >120% (SW-846)	NA	J	IST
	CCB, CCV <80% (SW-846)	UJ	J	IST
	Reanalysis of CCB, CCV not performed for outliers (NFG-2)	R	R	IST

6.12 INTERFERENCE CHECK SAMPLE - METALS

The interference check samples ICS (ICSA and ICSAB), assessed during FDV only, are analyzed at the completion of daily calibration and at the end of operation (minimum of two analyses per 8 hours of run time). The ICS data should be carefully checked for positive and negative target analyte results greater than the absolute value of the IDL for elements not included in the ICSA or ICSAB solutions. Positive results are an indication of either laboratory contamination of the ICS test solutions or an improperly generated interelement correction factor for that element. The latter situation can lead to false positive results on samples.

Aqueous samples that exhibit levels of the four ICSA interferents (Al, Ca, Fe and Mg) at least as high as those present in the ICSAB (500, 500, 200, and 500 milligrams per liter [mg/L], respectively) can be examined for potential false positive and false negative results based on interference correction factor deficiencies. Application of these guidelines to soil samples requires that reduced sample size and dilution effects upon the levels of the four ICSA elements is taken into account. These calculate to be 100,000 milligrams per kilogram (mg/kg) for Al, Ca and Mg, and 40,000 mg/kg for Fe. If the low-level concentrations are used for the ICSA, then the guidelines apply to all recoveries, regardless of the sample concentrations of the interfering elements. The guidelines, which apply, are noted below.

- Check lab data to ensure that the interference check samples were analyzed at the proper frequency.

- Spot check for transcription errors between the ICS recoveries reported on the summary form, and the raw data. Recalculate from the raw data one or more of the analyte percent recoveries and compare to the laboratory reported recovery on the summary form.
- Evaluate the ICS raw data for results with an absolute value greater than the IDL for those analytes that are not present in the ICS solution. If results greater than the IDL are observed an evaluation of the associated sample data for the affected elements should be made. If aluminum (Al), calcium (Ca), iron (Fe), and magnesium (Mg) equals ICS levels, a potential for false positive results exist and professional judgement should be used.

If interference check samples were not analyzed at the proper frequency, use professional judgement to determine the usability of the data.

ICSA/ICSAB CRITERIA AND VALIDATION ACTION

Assessment Element	*Failure*	*Action* [1]		*Reason Code*
		Non-Detects	*Positive Results*	
Accuracy	% Recovery <50% (NFG)	R	J	ICS
	% Recovery >120% (NFG)	NA	J	ICS
	% Recovery 50%-79% (NFG)	UJ	J	ICS
Spectral Interference (non-blank qualified hits in ICSAB)	Positive values	NA	J	ICS
	Negative values (>RL) (NFG)	R	J	ICS

Notes:
1 Action is based on the fact that Al, Ca, Fe, or Mg are present at least as high as ICSAB solution Al, Ca, Mg (500 mg/L or 100,000 mg/kg) and Fe (200 mg/L or 40,000 mg/kg)

6.13 SERIAL DILUTION SAMPLE - INORGANICS

The serial dilution of samples quantitated by ICP and ICP/MS determines whether or not significant physical or chemical interferences exist due to sample matrix. A serial dilution of 1:5 must be performed on at least one sample from every batch of analyses by ICP and ICP/MS to determine if physical or chemical interferences exist in the analyte determinations. Field blanks cannot be used to fulfill the serial dilution requirement. If the analyte in the sample is at least 50 times the value of the IDL, then the percent

difference between the value obtained from the 1:5 dilution and the undiluted value must be within 10 percent. Serial dilution data assessment is completed during FDV only.

- Check lab data to ensure that the serial dilution samples were analyzed at the proper frequency.
- Check the raw data and recalculate the percent difference (%D). Verify that the serial dilution analysis results and the calculated % D agree with the values reported on the summary form.
- Check the raw data for any evidence of negative interference (results from the diluted sample that are significantly higher than the original sample), possibly due to high levels of dissolved solids in the sample, etc.

SERIAL DILUTION CRITERIA AND VALIDATION ACTION

Assessment Element	*Failure*	*Action*		*Reason Code*
		Non-Detects	*Positive Results*	
% Difference	% Difference >10% (Detects >50x IDL) (NFG)	Not Applicable	J (all in batch of similar matrix/concentration)	ISD

6.14 TENTATIVELY IDENTIFIED COMPOUNDS - GC/MS

Tentatively identified compounds (TICs) are only provided upon request and are reviewed during FDV only. TICs are found in the samples that elute from the GC/MS as defined peaks, yet are not calibrated analytes. Up to 30 peaks (10 per VOC and 20 per SVOC fractions) greater than 10 percent in area or height of the nearest internal standard are candidate TICs. The following cautions are appropriate when considering spectral matches from these libraries:

- Library spectra used may not be obtained from mass spectrometers tuned to meet BFB/DFTPP acceptance criteria.
- The source of the compound/spectra in the library may be of questionable integrity (identifications are simply wrong).

- Some of the spectra may have been background corrected to remove artifact signals and others have not.
- In the interest of conservation of storage space, the spectra have been reduced to eliminate many of the small signals, leaving just the major signals.

Check that all TICs include a raw spectra, an enhanced spectra and library matches.

For TICs that are not reported as "unknown":

- Review mass spectra for each TIC identified and compare to the library match selected by the laboratory.
- Ensure that major ions are present in the sample mass spectra.
- Spot-check relative intensities of major ions to verify that they are within 20 percent of the expected values.
- Check to see that all positive identifications have library matches greater than 85 percent.

If there are questions regarding compound identification, contact the laboratory to discuss and obtain corrected forms if needed.

If TICs are identified in blanks at concentrations similar to those in the samples, these TICs should be considered contamination and identified by the laboratory as such.

If any target analytes from another fraction are identified as TICs (e.g., naphthalene in the VOC analysis), check to see that the compound was reported as a target analyte with the proper fraction. If the analyte was reported with the proper fraction, disregard it as a TIC in the other fraction; do not report the analyte in both fractions.

The following TICs are common laboratory artifacts or analytical by-products. If these compounds are not of specific interest to the site, the presence of these compounds should be noted in the data validation memo and they should be disregarded as TICs.

- Common laboratory contaminants: CO_2, siloxanes, diethyl ether, hexane, certain freons, and low level phthalates.

- Solvent preservatives such as cyclohexane and its related by-products (cyclohexanone, cyclohexanol, chlorocyclohexane and chlorocyclohexanol).
- Aldol condensation products (4-hydroxy-4-methyl-2-pentanone, 4-methyl-2-pentene-2-one, and 5,5-dimethyl-2(5H)-furanone).

All TIC data must be qualified as estimated (J). TICs that are identified by the laboratory with a specific compound name, a Chemical Abstracts Service Registry Number (CASRN), and meet the review criteria above are qualified with "NJ", indicating that presumptive evidence of the compound exists and the reported concentration is estimated.

It should be noted that the laboratory may have a more extensive list of calibrated compounds than the requested compound list, and these calibrated compounds may be reported as TICs. Non-target, calibrated compounds reported as TICs are qualified as estimated (J) because they have not been reviewed in the same manner as the target compounds. The data validation report should include a discussion and tabular summary (if appropriate) of these TICs.

6.15 ANALYTE IDENTIFICATION - ORGANICS

Spot check positive sample results to ensure that retention times are within the established retention time windows at a 10 percent frequency.

For GC/MS, spot-check mass spectra at a 10 percent frequency during FDV as follows:

- Perform a visual comparison of sample mass spectra against reference spectra to ensure a general match.
- Verify that all major ions are present and their intensities are within 20 percent of the expected values.
- Review ions in the sample with >10 percent abundance that are not in the reference spectra.

If there are any discrepancies in analyte identification, the laboratory must be contacted for resolution and corrected forms submitted if necessary. Qualification of data due to analyte identification discrepancies are summarized below.

ANALYTE IDENTIFICATION APPROVAL CODES

Assessment Element	*Failure*	*Action*		*Reason Code*
		Non-Detects	*Positive Results*	
Second Column confirmation (1)	%D > 40% ≤80% %D >80%	None None	J NJ	DCD DCD
GC Degradation	> 15 %for GC	None	J	DEG
Chromatography	Poor chromatography	Prof. Judgement	Prof. Judgement	QUA
Carry over contamination	Suspected instrumental carryover	Prof. Judgement	Prof. Judgement	SIC

Notes: (1) If reported result <RL and %D >50, qualify as non-detect at the RL.

6.16 ANALYTE QUANTITATION

Analyte quantitation is verified at a 10 percent frequency during FDV with the following checks:

- Spot check sample report limits for non-detected analytes (for organics and general chemistry analytes, use the lowest calibration standard to verify the quantitation limit; for metals, use the IDL to verify the report limit), making sure that report limits reflect individual original sample weights/volumes, final volumes, percent moisture (where applicable), dilutions, etc.
- Spot-check random positive sample results.
- Note in the data validation text whether values below the report limit were reported and qualified as estimated (lab "J" or "B" flagged values). These analytes are qualified as J values with the BRL reason code.
- If the project requires detection limit reporting (sample data are reported non-detect to the laboratory sample specific MDLs) all non-detect data should be qualified as estimated values (UJ) with the DLR reason code.

- Review replicate or quadruplicate results as specified in methods (graphite furnace, total organic carbon [TOC], and total organic halides [TOX]).
- Note in the data validation text whether soil results were reported on a dry- or wet-weight basis.
- If dilutions were performed, ensure that values above the calibration range (E values) are not used unless absolutely necessary (these values should be qualified as estimated). Compare original and diluted results to ensure that they are compared.

If there are any discrepancies in analyte quantitation, the laboratory must be contacted for resolution and corrected forms submitted if necessary. Qualification of data based on analyte quantitation discrepancies observed are summarized below.

ANALYTE QUANTITATION APPROVAL CODES

Assessment Element	*Failure*	*Action*		*Reason Code*
		Non-Detects	*Positive Results*	
Exceeds Calibration Range	Sample results exceeds instrument calibration range	None	J	EXE
Method of Standard Addition	Percent recovery outside method criteria	UJ	J	MSA
Variability	Variability in replicate results	Prof. Judgement	Prof. Judgement	REP
Precision-Metals	%RSD outside criteria for replicate aspiration	Prof. Judgement	Prof. Judgement	RSP
Percent Solids	Percent solids less than 50%	Prof. Judgement	Prof. Judgement	SLD
Variability in Sample Results	Dissolved analyte result significantly greater than total	Prof. Judgement	Prof. Judgement	TVD
Dilutions	Validator's choice of dilution	Prof. Judgement	Prof. Judgement	VCD
Reanalysis	Validator's choice of reanalysis	Prof. Judgement	Prof. Judgement	VCR

6.17 FIELD DUPLICATES

Overall precision for the sampling event and laboratory procedures is monitored through the collection and analysis of field duplicate sample sets.

- Compare results for original sample and field duplicate and calculate the RPD. If one or more results are non-detect, use the report limit or MDL value to calculate the RPD.
- Compare the RPDs to the project control limits. If limits have not been established, use default limits of 50 percent for water and 100 percent for soil samples if the sample results are greater than five times the RL. If sample results are less than 5 times the RL, precision is assessed by comparing the difference between the two results to a control limit of plus or minus one time the RL value for water samples and two time the RL value for soil samples.

If outlying RPDs are identified, qualify all associated positive results for that sample and it's duplicate as summarized below. If the field duplicate results show drastic differences, check with the sampler to ensure proper field duplicate identification, then have the laboratory verify proper sample labeling and analyte quantitation.

FIELD DUPLICATE SAMPLE ASSESSMENT

Assessment Element	*Failure*	*Action*		*Reason Code*
		Non-Detects	*Sample Detections*	
Precision				
Sample or duplicate concentrations > 5X RL	Water sample RPD > 50%	None (CRA)	J (CRA)	FDP
	Soil sample RPD > 100%	None (CRA)	J (CRA)	FDP
Sample or duplicate concentrations < 5X RL	Water sample difference >1X RL	None (CRA)	J (CRA)	FDP
	Soil sample difference >2X RL	None (CRA)	J (CRA)	FDP

7.0 LAB RESUBMISSION DOCUMENTATION

Corrections to laboratory reports must be requested in writing and a hardcopy of this request must be stored with the project files. Obsolete sample pages must be stamped "Corrected" and signed and dated by the data validator. The corrected pages are to be inserted in the original data package.

If a complete package resubmission is requested, the obsolete package must be marked "obsolete" and the new package include a summary of the changes in the report narrative.

8.0 FLAT FILE CHECKS

Prior to extracting an analytical table from the flatfile, the following checks must be performed:

i) ensure for each sample that there is only one result designated "reportable" for all associated analyte;

ii) verify that acceptance codes for all results reflect the level of data review performed by the validator;

iii) ensure that all lab qualifiers have been addressed and converted if necessary to data validation qualifiers (e.g., B, E, *, etc.).

iv) ensure that all validation qualifications have appropriate Reason Codes

Ensure that all results qualified "U" or "UJ" have "N" in the detected field.

9.0 REPORT FORMAT

Data validation report should include the following:

i) an introduction detailing the objective of the sampling and analysis program; general sample collection information; the analytical methods used; and a reference of all pertinent quality documents;

ii) text describing the elements of the data package that were reviewed, the findings for each, and the impact each finding had on the overall data usability;

iii) a sampling and analysis summary table; and

iv) tables summarizing all data qualification and the rationale for each.

An example data validation report (FDV) is presented in Appendix B.

10.0 REFERENCES

- "USEPA Contract Laboratory Program National Functional Guidelines for Organic Data Review", USEPA-540/R-99/008, October 1999
- "USEPA Contract Laboratory Program National Functional Guidelines for Inorganic Review", USEPA-540/R-94/013, February 1994.
- "USEPA Contract Laboratory Program National Functional Guidelines for Inorganic Review", USEPA-540/R-01/008, July 2002.
- "Region III Modifications to National Functional Guidelines for Organic Data Review", USEPA, September 1994.
- "Region 5 Standard Operating Procedure for Validation of CLP Organic Data", USEPA February 1997.
- "Quality Assurance/Quality Control Guidance for Removal Activities, Sampling QA/QC Plan and Data Validation Procedures", USEPA/540/G-90/004, OSWER Directive 9360.4-01, dated April 1990.
- USEPA Guidance on Environmental Data Verification and Data Validation, USEPA QA/GA-8, November 2002.
- "Quality Assurance Associates Standard Operating Procedure for the Data Quality Review (DQR) of Organic and Inorganic Data", October 1999.
- "USEPA Guidance for Quality Assurance Project Plans", December 2002, USEPA/240/R-02/009.
- Environmental Protection Agency, Region III. Innovative Approaches to Data Validation. 1995. U.S. Environmental Protection Agency, Region III. USEPA Region III QA Directives. U.S.

11.0 GLOSSARY OF TERMS

Accuracy	A measure of overall agreement of a measurement to a known value. Accuracy is assessed by means of percent recoveries and reference samples.
Assessment	The evaluation process used to measure the performance or effectiveness of a system and its elements.
Action Level	The concentration level that is high enough to warrant action. Action levels are generally regulatory levels that are determined by a regulatory agency.
Analyte	The element or compound to be determined.
Blank	A purified sample matrix subjected to the usual analytical or measurement process. A blank should not contain analytes of interest. A blank is used to detect contamination during sampling, handling, preparation, and/or analysis.
Calibration Curve	The relationship between instrument response and analyte concentration. The "curve" may be linear or non-linear.
Calibration Factor	The response factor for external standard analyses expressed as peak area (or height) per nanogram of analyte injected.
Calibration Range	The concentration range bounded by the lowest and highest concentration calibration standards used in the equation for the calibration curve.
Continuing Calibration	The daily standard when it is used to update the response factors for sample quantitation.
Chain of Custody	An unbroken trail of accountability that ensures the physical security of samples, data, and records.
Comparability	A measure of the confidence with which one data set or method can be compared to another.
Completeness	A measure of the amount of valid data obtained from a measurement system.
Compliance Review	Compliance review is the assessment of data package completeness and compliance with project requirements as outlined in the project Analytical Scope of Work.
Daily Standard	A single calibration standard, normally at a concentration near the middle of the calibration range, that is analyzed at the beginning of each analysis shift.

Data Quality	A measure of the degree of acceptability or utility of data for a particular purpose.
Data Validation	Data validation is an analyte-specific and sample-specific process that extends the evaluation of data beyond method, procedural, or contractual compliance to determine the analytical quality of a specific data set.
Data Validation-Reduced or Data Verification	Reduced Data Validation (RDV) is assessment of data and quality control deliverables provided in a standard summary laboratory report. Qualification of sample results is based on sample holding time periods, sample preservation, and laboratory batch quality control sample results (method blank, laboratory control samples, matrix spike/matrix spike duplicate or matrix spike/matrix duplicate, and surrogates) in accordance with U.S. USEPA's National Functional Guidelines, the analytical methods, and project quality assurance documents.
Data Validation-Full	Full Data Validation (FDV) is assessment of data and quality control deliverables provided in an expanded laboratory report . Qualification of sample results is based on sample holding time periods, sample preservation, laboratory batch quality control sample results (method blank, laboratory control samples, matrix spike/matrix spike duplicate or matrix spike/matrix duplicate, and surrogates), instrument calibration data, analyte identification and quantitation, additional method-specific quality control results (as appropriate), and raw data in accordance with U.S. USEPA's National Functional Guidelines, the analytical methods, and project quality assurance documents. FDV consists of reviewing and assessing all sample results and quality control data reported in summary tables and a 10 percent spot check of laboratory calculations and analyte identification from the raw data.
Field Duplicate	A second aliquot of a sample collected in the field that is treated the same as the original in order to determine the precision of the sampling and analysis.
Field Blank (Trip, Rinsate)	A blank that measures contamination possibly introduced in the field or during transportation. It also includes any contamination introduced during sample handling, preparation and/or analysis.

Initial Calibration Verification	The daily standard when it is used to verify that the calibration curve is still valid for sample quantitation (see also continuing calibration standard).
Inorganics	Inorganics as specified within this document are metals and cyanide.
Instrument Detection Limit	The minimum concentration of a target analyte, determined by various means, that can be measured above the instrument background noise.
Laboratory Control Sample	An aliquot of a clean matrix, spiked with known quantities of selected analytes.
Matrix	The predominant material of which the sample is composed. Matrix is not a synonymous phase.
Matrix Duplicate	A second aliquot of a sample that is treated the same as the original in order to determine the precision of the method.
Matrix Spike/Spike Duplicate	An aliquot of a sample spiked in duplicate with known quantities of selected analytes.
Method	A body of procedures and techniques for performing an activity, systematically presented in the order in which they are to be executed.
Method Blank	A blank prepared to represent the sample matrix as closely as possible and analyzed exactly like the calibration standards, samples, and QC samples. Results of method blanks provide an estimate of the within-batch variability of the blank response and an indication of bias introduced by the analytical procedure.
Method Detection Limit	The statistically derived lowest level of an analyte in a sample that will result in a signal different than zero as specified in 40 CFR 136, Appendix B.
Organics	Organics as specified within this document are volatile organic compounds, semi-volatile organic compounds, and polychlorinated biphenyls.
Parent Sample	The sample from which an aliquot was taken by the laboratory to prepare a matrix spike or analyzed as a matrix duplicate. This also refers to the investigative sample and field duplicate relationship.
Percent (%) Difference	A parameter used to compare the daily standard to the initial calibration when a calibration or response factor is

	used, comparing the difference of the factors. It indicates both the direction and the magnitude of the comparison.
Percent (%) Drift	A parameter used to compare the daily standard to the initial calibration when a linear calibration curve is used, comparing the % difference of the determined concentrations. It indicates both the direction and the magnitude of the comparison.
Precision	A measure of agreement among repeated measurements of the same property under identical, of substantially similar, conditions. Precision is assessed by means of duplicate/replicate sample analysis.
Quality Assurance	A system of management activities involving planning, implementation, assessment, reporting, and quality improvement to ensure that a process, item, or service is of the type and quality needed and expected by the client.
Quality Control	A set of measures and activities that are used to fulfill the need for quality.
QC Sample	An uncontaminated sample matrix spiked with known amounts of analytes from a source independent of 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.
Quantitation	The degree to which the instrument measures the concentration of target analytes.
Quantitation Limit	The minimum concentration that a target analyte can be measured within specified limits of precision and accuracy. Quantitation limits are generally 5-10x the method detection limit.
Re-analysis	The process of repeating a sample that includes both a new sample preparation and analysis.
Recovery	The act of determining whether or not the methodology measures all of the analyte contained in a sample.
Re-injection	The process of repeating a sample that does not include a new sample preparation. It is a re-injection of an existing extract.
Reported Result	The concentration or a target analyte in a given sample that is reported by the laboratory on the analysis results form. A

	positive result that is below the report limit may or may not be a reported result depending on the client's request.
Report Limit	The detection limit or quantitation limit (depending on the client's request) for a target analyte in a given sample that is reported by the laboratory on the analysis results form. The value includes adjustment for any sample dilution or method factor.
Representativeness	The measure of the degree to which data accurately and precisely represent a characteristic of a population, parameter variations at a sampling point, a process condition, or an environmental condition.
Sample	An environmental sample that is not a QC sample and any re-analysis or re-injection thereof.
Sensitivity	The capability of a method or instrument to discriminate between measurement responses representing different levels of a variable of interest.
Spike	A substance that is added to an environmental sample to increase the concentration of the target analyte by a known amount. A laboratory control spike or matrix spike is used to measure accuracy. A spike duplicate is used to measure precision.
Split Samples	Two or more representative portions taken from one sample in the field or in the laboratory and analyzed by different analysts or laboratories. Split samples are quality control samples that are used to assess analytical variability and comparability.
Standard Operating Procedure	A document that details the method for an operation, analysis, or action which thoroughly describes the techniques and steps to be followed. It is officially approved as the method for performing certain routine or repetitive tasks.
Target Analyte	An analyte specifically reported for a given analysis.

TABLE 2.1

DATA REVIEW AND VALIDATION LEVELS

Item Reviewed	*Compliance Review*	*Reduced Data Validation*	*Innovative Validation*	*Full Data Validation*
General Report Deliverables				
Sample ID Check (COC versus Lab Deliverables)	X	X	X	X
Methods/Procedures	X	X	X	X
Parameter List	X	X	X	X
Report/Detection Limits	X	X	X	X
Documentation/Deliverables	X	X	X	X
Sample Specific and Batch QC Results				
Sample Preservation and Holding Times		X	X	X
Method Blanks		X	X	X [1]
Field Blanks (Trip and Rinsate Blanks)		X	X	X [1]
System Monitoring Compounds (Surrogates)		X	X	X [1]
MS/MSD - Organics		X	X	X [1]
MS/MSD, MS/MD - Inorganics		X	X	X [1]
Laboratory Control Sample (LCS)		X	X	X [1]
Field Duplicates		X	X	X [1]
Expanded Data Elements				
Instrument Performance Check (GC/MS & ICP/MS)			X	X [1]
Initial Calibration - Organics			X	X [1]
Continuing Calibration - Organics			X	X [1]
Initial Calibration Verification - Inorganics			X	X [1]
Continuing Calibration Verification - Inorganics			X	X [1]
Internal Standards (GC/MS & ICP/MS)			X	X [1]
Instrument Blanks - Inorganics			X	X [1]
ICP/MS Internal Standards			X	X [1]
ICP Interference Check Samples			X	X [1]
Serial Dilutions			X	X [1]
Compound Identification				X [1]
Chromatography				X [1]
Compound/Analyte Quantitation (raw data)				X [1]
Report Limit Verification				X [1]

Notes:

[1] Raw data review including calculation checks and chromatography review will be completed on 10 percent of the sample data unless data warrants otherwise.

GC Gas Chromatograph.

ICP Inductively Coupled Plasma.

MS Matrix Spike.

MSD Matrix Spike Duplicate.

TABLE 3.1

DATA VALIDATION LEVELS - "APPROVAL_CODES"

Approval Code	*Description*
0	Validation Status Unknown
1	No Review Performed
2	Reduced Validation/Verification Performed
3	Full Validation Performed
4	Lab Qualified Result, in the process of Verification/Validation
5	Do not use
6	Compliance Check
8	Full Validation Performed by External Consultant
9	Reduced Validation/Verification Performed by External Consultant
10	Innovative Approach Validation (Forms Review includes NJ Reduced)

TABLE 4.1

DATA VALIDATION GUIDANCE DOCUMENTS - "APPROVAL_b"

Guidance Code[1]	*Data Validation Guidance Document(s)*
01	National Functional Guidelines in conjunction with CRA SOP
02	CRA Analytical Data Quality Assessment and Validation SOP 2004
03	NJDEP Guidance Documents in conjunction with CRA SOP
04	Region II Guidance Documents in conjunction with CRA SOP
05	Region III Guidance Documents in conjunction with CRA SOP
06	Region I Guidance Documents in conjunction with CRA SOP
07	Region 5 Guidance Documents in conjunction with CRA SOP
08	Texas Commission on Environmental Quality) Regulatory Guidance Texas Risk Reduction Program (TRRP-13) in
09	Canadian Validation Procedural Review
10	Guidance Document Unavailable (professional judgement used for data validation)
11	National Functional Guidelines in conjunction with CRA SOP and QAPP
97	Unknown DV Guidance Document
98	Not applicable. Data not validated
99	Predates population of approval_b field as of October 26, 2005

Note:

[1] Guidance codes are identified as Approval_b codes in the database and flat files

CRA Conestoga-Rovers & Associates.

DV Data Validation.

NJDEP New Jersey Department of Environmental Protection.

SOP Standard Operating Procedure.

TABLE 5.1

DATA VALIDATION REASON CODES - "APPROVAL_a"

Reasons for Data Qualification	*Reason Code*
Analyte present, quantitation may be biased high due to presence of co-eluting target analyte(s).	ABH
Result reported is below calibration level; quantitation may not be accurate.	BCL
Breakthrough of Aromatic Compounds into the Aliphatic Fraction	BKR
Below Reporting Limit (for preserving laboratory organic Js and inorganic Bs)	BRL
Qualified due to blank spike outlier	BSQ
Inorganics calibration blank contamination - initial or continuing	CBK
Continuing Calibration Outlier	CCL
CRA/Contract Required Detection Limit (CRDL) Outlier	CRA
Dual column discrepancy (for GC analyses only)	DCD
Qualified due to high degradation (GC pest analysis only)	DEG
Detection Limit Reporting	DLR
Duplicate Variability	DUP
Exceeds calibration range	EXE
Field Blank Contamination	FBK
Field Duplicate Variability	FDP
Filter Blank Contamination	FIL
Holding Time Exceedance	HTQ
Dioxin/Furan Ion Abundance Ratio Violation	IBA
Initial Calibration Outlier	ICL
Inductively Coupled Plasma (ICP) Calibration Stability (instrument drift)	ICS
ICP Serial Dilution	ISD
ICP Interference Check Sample Outlier	ISI
Internal Standard Outlier	IST
Laboratory Control Sample (LCS) Percent Recovery Outlier	LCQ
Laboratory Control Sample/Laboratory Control Sample Duplicate (LCS/LCD) Outlier	LCD
Method Blank Contamination	MBK
Method of Standard Additions Outlier (Metals)	MSA
Matrix Spike/Matrix Spike Duplicate (MS/MSD) Outlier	MSD
Matrix Spike (MS) Percent Recovery Outlier	MSQ
Nitrite results greater than combined nitrate/nitrite result	NNQ
Preservation of laboratory qualifier	PLQ
Preservation of laboratory U qualifier	PLU
Post Digestion Spike Outlier	PSP
Analyte present, the reported value may not be accurate or precise due to poor chromatography. The sample chromatogram exhibits baseline interference that impacted sample quantitation.	QUA
Rinse Blank Contamination	RBK
Variability in replicate results	REP
Percent Relative Standard Deviations (% RSDs) out for replicate aspiration	RSP
Suspected Instrumental Carryover	SIC
Percent Solids less than 50%	SLD
Sample preservation violation due to - temperature, preservative and pH	SPV
Sample Receipt Nonconformance	SRN
Surrogate Outlier	SUR
Trip Blank Contamination	TBK

TABLE 5.1

DATA VALIDATION REASON CODES - "APPROVAL_a"

Reasons for Data Qualification	*Reason Code*
Tentatively Identified Compound (TIC)	TIC
Total dioxins and/or furans are reported as estimated due to the nature of the quantitation.	TOT
Tune Nonconformance	TUN
Dissolved analyte result is significantly greater than the associated total analyte result	TVD
Validator's Choice of Columns for reporting GC results	VCC
Validator's choice of dilutions for when the dilution on the flat file is not the one you want to report	VCD
Validator's choice of method	VCM
Validator's choice of reanalysis	VCR

TABLE 6.1

DATA VALIDATION QUALIFIER DEFINITION

Qualifier[1]	*Definition*
Organics	
U	The analyte was analyzed for, but was not detected above the reported sample quantitation limit.
J	The analyte was positively identified; the associated numerical value is the approximate concentration of the analyte in the sample (for detected
N	The analysis indicates the presence of an analyte for which there is presumptive evidence to make a "tentative identification".
NJ	The analysis indicates the presence of an analyte that has been "tentatively identified" and the associated numerical value represents its approximate concentration.
R	The sample results are rejected due to serious deficiencies in the ability to analyze the sample and meet quality control criteria. The presence or absence of the analyte cannot be verified.
UJ	The analyte was not detected above the reported sample quantitation limit. However, the reported quantitation limit is approximate and may or may not represent the actual limit of quantitation necessary to accurately and precisely
Inorganics	
U	The material was analyzed for, but was not detected above the level of the associated value. The associated value is either the sample quantitation limit or the sample detection limit.
J	The associated value is an estimated quantity.
R	The data are unusable. (Note: Analyte may or may not be present).
UJ	The material was analyzed for, but was not detected. The associated value is an estimate and may be inaccurate or imprecise

Notes:

[1] Qualifier codes identified are based on the following guidance documents.

Organics "USEPA Contract Laboratory Program National Functional Guidelines for Organic Data Review, USEPA 540/R-99/008, October 1999.

Inorganics "USEPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review, USEPA 540/R-94/013, February 1994.

TABLE 6.2

ABBREVIATION OF DATA VALIDATION QUALIFIER DEFINITIONS

Qualifier[1]	*Definition*
	Organics & Inorganics
J	Estimated Concentration
N	TIC Presumptively Present
NJ	TIC Presumptively Present, Estimated Concentration
R	Rejected
U	Not Detected
UJ	Not Detected, Estimated Reporting Limit

Notes:

[1] Qualifier codes identified are based on the following guidance documents.

Organics "USEPA Contract Laboratory Program National Functional Guidelines for Organic Data Review, USEPA 540/R-99/008, October 1999.

Inorganics "USEPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review, USEPA 540/R-94/013, February 1994.

TIC Tentatively Identified Compound.

TABLE 6.3

SAMPLE PRESERVATION AND HOLDING TIME REQUIREMENTS

Analyses	*Sample Containers*[1]	*Preservation*	*Maximum Holding Time from Sample Collection*[2] *40 CFR*	*SW-846*	*Volume of Sample*
WATER ***Organic Tests***					
VOC	Three 40 mL teflon-lined septum vials per analysis	HCl to pH < 2 Iced, 4 ± 2° C	14 days for analysis	14 days for analysis	Fill completely, no air bubbles
VOC-unpreserved	Three 40 mL teflon-lined septum vials per analysis	Iced, 4 ± 2° C	7 days for analysis	7 days for analysis	Fill completely, no air bubbles
PCB as Aroclors	Two 1 liter amber glass bottles per analysis	Iced, 4 ± 2° C	1 year until extraction, 1 year after extraction	None	Fill to neck of bottle
Polynuclear Aromatic Hydrocarbons (PAH) or Base-Neutral/Acid Extractables (BNA)	Two 1 liter amber glass bottles per analysis	Iced, 4 ± 2° C	7 days for extraction 40 days after extraction for analysis	7 days for extraction 40 days after extraction for analysis	Fill to neck of bottle
Pesticides	Two 1 liter amber glass bottles per analysis	Iced, 4 ± 2° C	7 days for extraction 40 days after extraction for analysis	7 days for extraction 40 days after extraction for analysis	Fill to neck of bottle
Herbicides	Two 1 liter amber glass bottles per analysis	Iced, 4 ± 2° C	7 days for extraction 40 days after extraction for analysis	7 days for extraction 40 days after extraction for analysis	Fill to neck of bottle
PCDD/PCDF (Dioxins/Furans)	Two 1 liter amber glass bottles per analysis	Iced, 4 ± 2° C	1 year	None	Fill to shoulder of jar
Formaldehyde	Two 1 liter amber glass bottles per analysis	Iced, 4 ± 2° C	-	3 days for extraction; 3 days from extraction to analysis	

TABLE 6.3

SAMPLE PRESERVATION AND HOLDING TIME REQUIREMENTS

Analyses	*Sample Containers*[1]	*Preservation*	*Maximum Holding Time from Sample Collection*[2] *40 CFR*	*SW-846*	*Volume of Sample*
Organic Tests (Cont'd.)					
TPH as Gas Range	Three 40 mL teflon-lined septum vials per analysis	Iced, 4 ± 2° C	-	14 days for analysis	Fill completely, no air bubbles
TPH as Diesel Range	Two 1 liter amber glass bottles per analysis	HCl to pH < 2 Iced, 4 ± 2° C	-	7 days for extraction 40 days after extraction for analysis	Fill to neck of bottle
Inorganic Tests					
Acidity	One 250 ml plastic bottle	Iced, 4 ± 2° C	14 days for analysis	-	Fill to neck of
Alkalinity	One 250 ml plastic bottle	Iced, 4 ± 2° C	14 days for analysis	-	Fill to neck of bottle
Ammonia, nitrogen	One 500 ml plastic bottle	H_2SO_4 to pH < 2 Iced, 4 ± 2° C	28 days for analysis	-	Fill to neck of bottle
Biochemical Oxygen Demand (BOD)	One 1 liter amber glass bottle	Iced, 4 ± 2° C	48 hours to initiate analysis	-	Fill to neck of bottle
Bromide	One 250 ml plastic bottle	Iced, 4 ± 2° C	28 days for analysis	28 days for analysis	Fill to neck of bottle
Chloride	One 250 ml plastic bottle	Iced, 4 ± 2° C	28 days for analysis	28 days for analysis	Fill to neck of bottle
Chemical Oxygen Demand (COD)	One 250 ml plastic bottle	H_2SO_4 to pH < 2 Iced, 4 ± 2° C	28 days for analysis	-	Fill to neck of bottle
Hexavalent Chromium	One 250 ml plastic bottle	Iced, 4 ± 2° C pH=9.3-9.7, cool ≤6°C	24 hours for analysis 28 days for analysis	-	Fill to neck of bottle

TABLE 6.3
SAMPLE PRESERVATION AND HOLDING TIME REQUIREMENTS

Analyses	*Sample Containers*[1]	*Preservation*	*Maximum Holding Time from Sample Collection*[2] *40 CFR*	*SW-846*	*Volume of Sample*
Inorganic Tests (Cont'd.)					
Coliform, Total/Fecal	One 250 ml plastic bottle (sterile)	Iced, 4 ± 2° C	6 hours for analysis	6 hours for analysis	Fill to neck of bottle
Color	One 250 ml plastic bottle	Iced, 4 ± 2° C	48 hours for analysis	-	Fill to neck of bottle
Cyanide (total, free or amenable)	One 250 ml plastic bottle	NaOH to pH>12 Iced, 4 ± 2° C	14 days for analysis	14 days for analysis	Fill to neck of bottle
Fluoride	One 250 ml plastic bottle	Iced, 4 ± 2° C	28 days for analysis	28 days for analysis	Fill to neck of bottle
Hardness	One 250 ml plastic bottle	HNO_3 to pH < 2 Iced, 4 ± 2° C	6 months	6 months	Fill to neck of bottle
Metals	One 1 liter plastic bottle	HNO_3 to pH < 2 Iced, 4 ± 2° C	6 months	6 months	Fill to neck of bottle
Mercury	One 1 liter plastic bottle	5ml/L 12N HCl or BrCl	90 days	28 days for analysis	
Low Level Mercury[3]	Four 40 mL teflon-lined septum vials per analysis	Iced, 4 ± 2° C	-	48 hours until laboratory preservation with BrCl, 28 days from collection until analysis	Fill completely, no air bubbles
Nitrogen, Kjeldahl (TKN)	One 250 ml plastic bottle	H_2SO_4 to pH < 2 Iced, 4 ± 2° C	28 days for analysis	-	Fill to neck of bottle
Nitrate or Nitrite	One 250 ml plastic bottle	Iced, 4 ± 2° C	48 hours for analysis	48 hours for analysis	Fill to neck of bottle

TABLE 6.3

SAMPLE PRESERVATION AND HOLDING TIME REQUIREMENTS

Analyses	*Sample Containers*[1]	*Preservation*	*Maximum Holding Time from Sample Collection*[2] 40 CFR	SW-846	*Volume of Sample*
Inorganic Tests (Cont'd.)					
Nitrate plus Nitrite	One 250 ml plastic bottle	H_2SO_4 to pH < 2 Iced, 4 ± 2° C	28 days for analysis	28 days for analysis	Fill to neck of bottle
Oil & Grease	One 1 liter amber glass bottle	H2SO4 or HCl to pH<2 Iced, 4 ± 2° C	28 days for analysis	28 days for analysis	Fill to neck of bottle
Phenols	One 500 ml glass bottle	H_2SO_4 to pH < 2 Iced, 4 ± 2° C	28 days for analysis	28 days for analysis	Fill to neck of bottle
Phosphate	One 250 ml plastic bottle	Iced, 4 ± 2° C	28 days for analysis	48 hours for analysis	Fill to neck of bottle
Phosphorus (total)	One 500 ml plastic bottle	H_2SO_4 to pH < 2 Iced, 4 ± 2° C	28 days for analysis	-	Fill to neck of bottle
ortho-Phosphate	One 250 ml plastic bottle	Iced, 4 ± 2° C	48 hours for analysis	-	Fill to neck of bottle
Paint Filter	One 500 ml glass bottle	Iced, 4 ± 2° C	-	None	Fill to neck of bottle
pH	One 250 ml plastic bottle	Iced, 4 ± 2° C	15 minutes	-	Fill to neck of bottle
Radiochemistry:					
Alpha, Beta, Radium	Two 1 liter plastic bottles	HNO_3 to pH < 2, Iced, 4 ± 2° C	6 months for analysis	-	Fill to neck of bottle
Tritium	One 250 ml glass amber bottle	Iced, 4 ± 2° C	6 months for analysis	-	Fill to neck of bottle
Radon	Three 40 mL glass vials	Iced, 4 ± 2° C	4 days for analysis	-	Fill to neck of bottle
I-131	One 1 liter plastic bottle	NaOH to pH>8 Iced, 4 ± 2° C	16 days for analysis	-	Fill to neck of bottle

TABLE 6.3

SAMPLE PRESERVATION AND HOLDING TIME REQUIREMENTS

Analyses	*Sample Containers*[1]	*Preservation*	*Maximum Holding Time from Sample Collection*[2] *40 CFR*	*SW-846*	*Volume of Sample*
Inorganic Tests (Cont'd.)					
Silica	One 250 ml plastic bottle	Iced, 4 ± 2° C	28 days for analysis	-	Fill to neck of bottle
Solids Total Dissolved Solids (TDS) Total Solids(TS) Total Suspended Solids (TSS) Suspended Solids (SS)	One 250 ml plastic bottle	Iced, 4 ± 2° C	7 days for analysis	-	Fill to neck of bottle
Sulfide, Total or Reactive	One 500 ml plastic bottle	Zn Acetate/NaOH, pH>9 Iced, 4 ± 2° C	7 days for analysis	7 days for analysis	Fill to neck of bottle
Sulfate	One 250 ml plastic bottle	Iced, 4 ± 2° C	28 days for analysis	28 days for analysis	Fill to neck of bottle
Sulfite	One 250 ml plastic bottle	Iced, 4 ± 2° C	15 minutes	-	Fill to neck of bottle
Surfactants	One 250 ml plastic bottle	cool, ≤6°C	48 hours for analysis	-	
Specific Conductance	One 250 ml plastic bottle	Iced, 4 ± 2° C	28 days for analysis	-	Fill to neck of bottle
Turbidity	One 250 ml plastic bottle	Iced, 4 ± 2° C	48 hours for analysis	-	Fill to neck of bottle
Total Organic Carbon (TOC)	One 500 ml plastic bottle	H_2SO_4 to pH < 2 Iced, 4 ± 2° C	28 days for analysis	28 days for analysis	Fill to neck of bottle
Total Organic Halogens (TOX)	One 500 ml amber glass bottle	H_2SO_4 to pH < 2 Iced, 4 ± 2° C	-	28 days for analysis	Fill to neck of bottle
Recoverable	One 1 liter amber	HCl to pH < 2	28 days for analysis	-	Fill to neck of
Total Petroleum Hydrocarbons (TPH)	glass bottle	Iced, 4 ± 2° C			bottle

TABLE 6.3
SAMPLE PRESERVATION AND HOLDING TIME REQUIREMENTS

Analyses	*Sample Containers*[1]	*Preservation*	*Maximum Holding Time from Sample Collection*[2] *40 CFR*	*SW-846*	*Volume of Sample*
SOLID (Soil/Sediment)					
VOC[4,5]	One 25g En Core Sampler™ per analysis or field-preserve w/ methanol	Iced, 4 ± 2° C	-	48 hours for extraction(En Core 14 days for analysis	Fill completely
PCB as Aroclors	One 4-ounce glass jar	Iced, 4 ± 2° C	-	none	Fill to shoulder of jar
Pesticides	One 4-ounce glass jar	Iced, 4 ± 2° C	-	14 days for extraction 40 days after extraction for analysis	Fill to shoulder of jar
Polynuclear Aromatic Hydrocarbons (PAH) or Base-Neutral/Acid Extractables (BNA)	One 4-ounce glass jar	Iced, 4 ± 2° C	-	14 days for extraction 40 days after extraction for analysis	Fill to shoulder of jar
Herbicides	One 4-ounce glass jar	Iced, 4 ± 2° C	-	14 days for extraction 40 days after extraction for analysis	Fill to shoulder of jar
PCDD/PCDF (Dioxins/Furans)	One 4-ounce glass jar	Iced, 4 ± 2° C	-	none	Fill to shoulder of jar
Metals	One 4-ounce glass jar	Iced, 4 ± 2° C	-	180 days (mercury 28 days) for analysis	Fill to shoulder of jar
Cyanide (total)	One 4-ounce glass jar	Iced, 4 ± 2° C	-	14 days for analysis	Fill to shoulder of jar
Hexavalent Chromium	One 4-ounce glass jar	Iced, 4 ± 2° C	-	30 days for extraction 168 hours for analysis	Fill to shoulder of jar

TABLE 6.3
SAMPLE PRESERVATION AND HOLDING TIME REQUIREMENTS

Analyses	*Sample Containers*[1]	*Preservation*	*Maximum Holding Time from Sample Collection*[2] *40 CFR*	*SW-846*	*Volume of Sample*
TCLP					
VOC	One 4-ounce glass jar	Iced, 4 ± 2° C	-	14 days from collection to TCLP extraction; 14 days from extraction to analysis	Fill to shoulder of jar
SVOC	One 4-ounce glass jar	Iced, 4 ± 2° C	-	14 days from collection to TCLP extraction; 7 days from TCLP extraction to prep extraction; 40 days from prep extraction to analysis	Fill to shoulder of jar
Metals	One 4-ounce glass jar	Iced, 4 ± 2° C	-	180 days from collection to TCLP extraction; 180 days from extraction to analysis	Fill to shoulder of jar
Mercury	One 4-ounce glass jar	Iced, 4 ± 2° C	-	28 days from collection to TCLP extraction; 28 days from extraction to analysis	Fill to shoulder of jar

Notes:
[1] - Multiple parameters on a single sample with identical preservation requirements may be combined into one single sample container.
[2] - These are technical holding times, i.e., are based on time elapsed from time of sample collection.
[3] - Sample containers must be fluoropolymer or borosilicate glass.
[4] - If Encore™ samples cannot be analyzed within 48 hours, they can be frozen at -10 degrees Celcius.
[5] - If no other samples are submitted with solid VOCs a separate container must be included for percent moisture.

APPENDIX A-1

LABORATORY REPORT DELIVERABLES CHECKLIST - QC SUMMARY REPORT

APPENDIX A-1

LABORATORY REPORT DELIVERABLES CHECKLIST - ORGANIC DATA

Case Narrative:

	Case Narrative Present

Quality Control Summary Package:

	Data Summary Sheets
	Matrix Spike/Spike Duplicate Recoveries
	Laboratory Control Sample Recoveries
	Method Blank Summaries
	GC/MS Tuning and Mass Calibration
	Initial Calibration Data
	Continuing Calibration Data
	Surrogate Compound Recovery Summary
	Internal Standard Area Summary

Sample and Blank Data Package Section

	Reconstructed Ion Current (RIC) Chromatogram
	Quantitation Reports
	Raw and Enhanced Mass Spectra
	Reference Mass Spectra for Target Compounds
	Mass Spectral Library Search for TICs

Raw QC Data Package Section

	DFTPP and/or BFB mass spectra and mass listings
	RIC Chromatogram for Standards, LCS, and MS/MSD
	Quantitation Reports for Standards, LCS, and MS/MSD
	List of Instrument Detection Limits
	Chain of Custody Records
	Sample Preparation and Analysis Run Logs

APPENDIX A-1

LABORATORY REPORT DELIVERABLES CHECKLIST - INORGANIC DATA

Case Narrative:

	Case Narrative present

Quality Control Summary Package:

	Data Summary sheets
	Initial and Continuing Calibration results
	CRDL Standard results
	Preparation Blank and Calibration Blank results
	ICP Interference Check Sample results
	Matrix Spike recoveries
	Matrix Duplicate results
	Laboratory Control Sample recoveries
	Method of Standard Additions results
	ICP Serial Dilution results
	Instrument Detection Limits
	ICP Interelement Correction Factors
	ICP Linear Ranges
	Preparation Log
	Analysis Run Log

Raw QC Data Package Section

	Chain of Custody Records
	Instrument Printouts
	Sample Preparation Notebook Pages
	Logbook and Worksheet Pages
	Percent Solids Determination

APPENDIX A-2

LABORATORY REPORT DELIVERABLES CHECKLIST –
EXPANDED DELIVERABLE REPORT

APPENDIX A-2
LABORATORY REPORT DELIVERABLES CHECKLIST
EXPANDED DATA REPORT

Laboratory Name: _____
Date and Report No.: _____

	Report Item	*Complete Yes/No*	*Comments*
A.	**REPORT COVER PAGE**		
1.	CRA Project reference number.		
2.	CRA Project name.		
3.	CRA Work Order representative.		
4.	Purchase Order number.		
5.	Laboratory Short Form representative - Laboratory Project Manager.		
6.	Approval signature.		
7.	Report date.		
B.	**PROJECT SUMMARY/NARRATIVE**		
1.	Summarize project and all Quality Control compliance issues.		
C.	**SUPPORTING DOCUMENTATION**		
1.	employed for the analyses.		
2.	identification numbers.		
3.	Qualifying codes glossary - Define any qualifying codes utilized in report.		
D.	**TABULATED DATA**		
	The sample result section of the report shall include the following information for each sample (one		
1.	CRA sample identification number.		
2.	Laboratory sample identification number.		
3.	Sample collection date and time.		
4.	Dates - Sample collected, Sample Receipt, prepared and analyzed.		
5.	Sample matrix.		
6.	Parameter units of measure.		
7.	Specific analytical methodology.		
8.	QC batch identifier number.		
9.	Percent dry weight (solid samples).		
10.	Dilution factors.		
11.	Test parameters or analytes.		
12.	Analytical results, original and reanalysis due to QC criteria failure or dilutions.		
13.	Sample specific reporting limits.		
14.	Qualifying codes, as required.		

APPENDIX A-2
LABORATORY REPORT DELIVERABLES CHECKLIST
EXPANDED DATA REPORT

Laboratory Name: _____
Date and Report No.: _____

Report Item	*Complete Yes/No*	*Comments*
E. QUALITY CONTROL NARRATIVE		
For each sample for which QA/QC problems are encountered, the following specific information shall be		
1. CRA and Laboratory sample identification numbers affected.		
2. Sample matrix.		
3. Parameters affected.		
4. Data acceptance criteria exceeded.		
5. Specific analytical problems that occurred.		
6. Corrective actions(s) taken, or attempted, to resolve the problems.		
F. QUALITY CONTROL RESULTS SUMMARY		
1. Laboratory method blank results.		
2. Laboratory control sample or QC check sample - Percent recoveries and acceptance		
3. Matrix Spike/Matrix Spike Duplicate or Matrix Spike/Matrix Duplicate - Amount in		
4. Surrogate compounds - Percent recoveries and laboratory control limits (may be included		
5. QC batch identification numbers.		
G. GC/MS DATA		
1. Initial and continuing calibration results and summary, including compound relative		
2. Tuning results and summary report.		
3. Internal standard response and retention times summary.		
4. Sample preparation documentation.		
5. Instrument run logs.		
6. Labeled and dated chromatograms/spectra of sample results, all laboratory		
7. Results of tentatively identified compounds, if requested.		
H. GC DATA		
1. Initial and continuing calibration results and summary, including compound response		
2. Chlorinated pesticide breakdown report (if applicable).		
3. Sample preparation documentation.		
4. Instrument run logs.		
5. Labeled and dated chromatograms of samples and all laboratory calibration/QC checks.		
I. ICP DATA		
1. Initial and continuing calibration standard and blank results and summary.		
2. Low level check standard (CRQL) results and summary.		
3. Interference check sample results and summary.		
4. Serial dilutions and post digestion spike results and summary		
5. Sample preparation records.		
6. Instrument run logs.		
7. Inter-element and background correction factors.		
8. Instrumental data records.		

APPENDIX A-2
LABORATORY REPORT DELIVERABLES CHECKLIST
EXPANDED DATA REPORT

Laboratory Name: _____
Date and Report No.: _____

	Report Item	Complete Yes/No	Comments
J. ICP/MS DATA			
1.	Initial and continuing calibration standard and blank results and summary.	_____	_____
2.	Low level check standard (CRQL) results and summary.	_____	_____
3.	Internal standard intensities.	_____	_____
4.	Tune results and summary.	_____	_____
5.	Interference check sample results and summary.	_____	_____
6.	Serial dilutions and post digestion spike results and summary	_____	_____
7.	Sample preparation records.	_____	_____
8.	Instrument run logs.	_____	_____
9.	Inter-element and background correction factors.	_____	_____
10.	Instrumental data records.	_____	_____
K. OTHER METALS DATA			
1.	Initial and continuing calibration standard and blank results and summary.	_____	_____
2.	Dilution tests and post digestion spike results.	_____	_____
3.	Sample preparation records.	_____	_____
4.	Instrument run logs.	_____	_____
5.	Instrumental data records.	_____	_____
L. INORGANIC DATA			
1.	Initial and continuing calibration standard and blank results summary.	_____	_____
2.	Calibration verification.	_____	_____
3.	Sample preparation records.	_____	_____
4.	Run logs.	_____	_____
5.	Instrumental data records.	_____	_____
M. DOCUMENT CONTROL			
1.	Fully executed original CRA Chain of Custody	_____	_____
2.	Complete internal laboratory custody documentation.	_____	_____
3.	Copy of Work Order.	_____	_____

Review Completed By: _____ Date: _____

APPENDIX B-1

FULL DATA VALIDATION REPORT TEMPLATE

CONESTOGA-ROVERS
& ASSOCIATES

PROPRIETARY DOCUMENT

E-Mail Date:
E-Mail To:
c.c.:

E-Mail and Hard Copy if Requested

ANALYTICAL DATA ASSESSMENT AND VALIDATION
SUPPLEMENTAL REMEDIAL INVESTIGATION
SITE NAME
SITE LOCATION
SAMPLING DATE

PREPARED BY:
CONESTOGA-ROVERS & ASSOCIATES

2055 Niagara Falls Blvd., Suite #3
Niagara Falls, New York 14304
Telephone: 716-297-6150 Fax: 716-297-2265
Contact: Paul McMahon [jbh]
Date: December 5, 2005
www.CRAworld.com

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1.0 INTRODUCTION

The following document details an assessment and validation of analytical results for samples collected in _____. Analyses were provided by _____Laboratories in _____. Sample identifications (ID), times, dates of collection, and parameters analyzed are summarized in Table 1. A summary of the analytical methods is presented in Table 2. Summaries of the analytical results are presented in Tables 3A, 3B, and 3C.

Evaluation of the data was based on information obtained from the finished data sheets, raw data, Chain of Custody forms, blank data, duplicate data and recovery data for matrix, blank, and surrogate spikes. The assessment of analytical and in-house data included checks for: data consistency (by observing comparability of duplicate analyses); adherence to accuracy and precision criteria; transmittal errors; and anomalously high and low parameter values.

The quality assurance/quality control (QA/QC) criteria by which these data have been assessed are outlined in the analytical methods referenced in Table 2 and the documents entitled:

i) "USEPA Contract Laboratory Program National Functional Guidelines for Organic Data Review", United States Environmental Protection Agency (USEPA) 540/R-99-008, October 1999;

ii) "USEPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review", USEPA 540/R-94-013, February 1994; and

iii) "Quality Assurance Project Plan (QAPP)", October 2005.

Items i) and ii) will hereinafter be referred to as the "Guidelines".

Full deliverables (including raw data) were provided by _____ for the program. The data quality assessment and validation presented in the following subsections were performed based on the sample results and supporting QA/QC provided.

2.0 SAMPLE HOLDING TIMES

The holding time criteria for the analyses are specified in the QAPP.

Sample Chain of Custody documents and analytical reports were used to determine sample holding times. Most samples were prepared and analyzed within the required holding times. Due to laboratory error, six samples requiring polychlorinated biphenyls (PCB) analyses were not extracted within the holding times. The associated sample results were qualified as estimated, based on the potential low bias (see Table 4).

All samples were properly cooled after sampling and upon receipt at the laboratory.

3.0 GAS CHROMATOGRAPH / MASS SPECTROMETER (GC/MS) TUNING AND MASS CALIBRATION - VOLATILES AND SEMI-VOLATILES

Prior to analysis, GC/MS instrumentation is tuned to ensure optimization over the mass range of interest. To evaluate instrument tuning, Methods TO-15/8260B and 8270C require the analysis of specific tuning compounds bromofluorobenzene (BFB) and decafluorotriphenylphosphine (DFTPP), respectively. The resulting spectra must meet the criteria cited in the methods before analysis is initiated. Analysis of the tuning compound must then be repeated every 12 hours throughout sample analysis to ensure the continued optimization of the instrument.

Tuning compounds were analyzed at the required frequency throughout the volatile and semi-volatile analysis periods. All tuning criteria were met, indicating that proper optimization of the instrumentation was achieved.

4.0 INSTRUMENT CALIBRATION

4.1 GC/MS CALIBRATION - VOLATILES AND SEMI-VOLATILES

4.1.1 INITIAL CALIBRATION

In order to quantify compounds of interest in samples, calibration of the GC/MS over a specific concentration range must be performed. Initially, a minimum of a five-point calibration curve containing all compounds of interest is analyzed. In accordance with the SW-846 methods, linearity of the curve and instrument sensitivity are evaluated against the following criteria:

i) all relative response factors (RRFs) must be greater than or equal to 0.05; and

ii) percent relative standard deviation (%RSD) values must not exceed 30 percent.

Method TO-15 initial calibrations were evaluated using the method criteria. All initial calibration data were reviewed and most met the above criteria. Results associated with outlying RSDs were qualified as estimated (see Table 5).

4.1.2 CONTINUING CALIBRATION

To ensure that instrument calibration is acceptable throughout the sample analysis period, continuing calibration standards must be analyzed and compared to the initial calibration curve every 12 hours. In accordance with the SW-846 methods, the following criteria are employed to evaluate continuing calibration data:

i) all RRF values must be greater than or equal to 0.05; and

ii) percent difference (%D) values must not exceed 25 percent.

Method TO-15 continuing calibrations were evaluated using the method criteria. Most continuing calibration results were acceptable. Results associated with outlying %Ds were qualified as estimated (see Table 6).

4.2 GC CALIBRATION - TOTAL CHLORINATED PESTICIDES/PCBs

To ensure that instrument performance was acceptable throughout the pesticide/PCB analysis, the criteria outlined in the methods for initial and continuing instrument calibration have been evaluated.

4.2.1 INSTRUMENT PERFORMANCE

4.2.1.1 PERFORMANCE EVALUATION MIXTURES (PEM)

The PEM is analyzed at the beginning and end of the initial calibration sequence and throughout the analytical sequence. The results of these analyses are used to evaluate dichlorodiphenyltrichloroethane (DDT)/endrin breakdown, using the Method 8081A degradation criteria of $\leq$15 percent. PEM standards were analyzed at the required frequency throughout sample analysis and all method performance criteria were met.

4.2.1.2 INITIAL CALIBRATION

In order to quantify compounds of interest, calibration of the gas chromatograph/electron capture detector (GC/ECD) over a specific concentration range must be performed. Initially, a calibration curve consisting of a minimum of five concentration levels is analyzed for all single component compounds of interest and for Aroclors 1016 and 1260. A single calibration standard is analyzed for all other multi-response compounds. Linearity of the calibration curves is acceptable if all RSD values are less than or equal to 20.0 percent.

Retention time windows are also calculated from the initial calibration analyses. These windows are then used to identify all compounds of interest in subsequent analyses.

All initial calibration standards were analyzed at the required frequencies. All retention time, peak resolution and linearity criteria were satisfied as specified in the methods.

4.2.1.3 CONTINUING CALIBRATION

To ensure that the calibration of the instrument is valid throughout the sample analysis period, continuing calibration standards are analyzed and evaluated on a regular basis.

To evaluate the continued linearity of the calibration, %D values are calculated for each compound. As specified in the methods, all %D values should be less than 15 percent.

To ensure that compound retention times do not vary over the analysis period, all retention times for continuing calibration compounds must fall within the established retention time windows.

All continuing calibration standards were analyzed at the required frequency. Most %D values and all compound retention times met the above criteria indicating acceptable instrument calibration throughout the analysis period. Results associated with outlying %Ds were qualified as estimated (see Table 6).

4.3 INORGANICS CALIBRATION

4.3.1 INSTRUMENT CALIBRATION

4.3.1.1 INITIAL CALIBRATION

Initial calibration of the instruments ensures that they are capable of producing satisfactory quantitative data at the beginning of a series of analyses. For Inductively Coupled Plasma (ICP) analysis, a calibration blank and at least one standard must be analyzed at each wavelength to establish the analytical curve. For mercury Atomic Absorption (AA) analyses, a calibration blank and a minimum of five standards must be analyzed to establish the analytical curve and resulting correlation coefficients must be at least 0.995. For cyanide analyses, a calibration blank and a minimum of four standards must be analyzed to establish the analytical curve and resulting correlation coefficients must be at least 0.995.

After the analyses of the calibration curves, an Initial Calibration Verification (ICV) standard must be analyzed to verify the analytical accuracy of the calibration curves. All analyte recoveries from the analyses of the ICVs must be within the following control limits.

Analytical Method	*Parameter*	*Control Limits*
ICP/AA	Metals	90 - 110%
Cold Vapor AA	Mercury	80 - 120%
Instrumental Wet Chemistry	Cyanide	85 - 115%

Upon review of the data, it was determined that the calibration curves and ICVs were analyzed at the proper frequencies and that all of the above-specified criteria were met. The laboratory effectively demonstrated that the instrumentation used for metals and cyanide analyses was properly calibrated prior to sample analyses.

4.3.1.2 CONTINUING CALIBRATION

To ensure that instrument calibration is acceptable throughout the sample analysis period, Continuing Calibration Verification (CCV) standards are analyzed on a regular basis. Each CCV is deemed acceptable if all analyte recoveries are within the control limits specified above for the ICVs. If some of the CCV analyte recoveries are outside the control limits, samples analyzed before and after the CCV, up until the previous and proceeding CCV analyses, are affected.

For this study, CCVs were analyzed at the proper frequency. All analyte recoveries reported for the CCVs were within the specified limits.

5.0 INTERNAL STANDARDS ANALYSES

Internal standard data were evaluated for all total volatile and semi-volatile samples.

5.1 VOLATILES

To ensure that changes in the GC/MS sensitivity and response do not affect sample analysis results, internal standard compounds are added to each sample prior to analysis. All results are then calculated as a ratio of the internal standard responses.

The sample internal standard results for Method 8260B were evaluated against the following criteria:

i) the retention time of the internal standard must not vary more than ±30 seconds from the associated calibration standard; and

ii) internal standard area counts must not vary by more than a factor of two (-50 percent to +100 percent) from the associated calibration standard.

Method TO-15 internal standards were evaluated using the method criteria. Most internal standard recoveries associated with the reported sample results and retention times reported met the above criteria. Results associated with outlying area counts were qualified as estimated (see Table 7).

5.2 SEMI-VOLATILES

To ensure that changes in the GC/MS sensitivity and response do not affect sample analysis results, internal standard compounds are added to each sample prior to analysis. All results are then calculated as a ratio of the internal standard responses.

The sample internal standard results were evaluated against the following criteria:

i) the retention time of the internal standard must not vary more than ±30 seconds from the associated calibration standard; and

ii) internal standard area counts must not vary by more than a factor of two (-50 percent to +100 percent) from the associated calibration standard.

Most associated internal standard recoveries and retention times reported met the above criteria. A poor chrysene-d12 response was reported for sample W-42271-110405-WA-09, and the associated non-detect sample results were rejected. Remaining results associated with outlying area counts were qualified as estimated (see Table 7).

6.0 SURROGATE SPIKE RECOVERIES

In accordance with the methods employed, all samples, blanks and standards analyzed for volatile organic compounds (VOCs), semi-volatile organic compounds (SVOCs), chlorinated pesticides, and PCBs were spiked with surrogate compounds prior to sample extraction and/or analysis. Surrogate recoveries provide a means to evaluate the effects of individual sample matrices on analytical efficiency. Non-detect sample results associated with high surrogate recoveries were not qualified, as the indicated high bias would not impact the data. All other surrogate recoveries were evaluated as specified below.

6.1 VOLATILES

All samples submitted for VOC determinations were spiked with surrogate compounds prior to sample analysis. All surrogate recoveries were within the laboratory control limits.

6.2 SEMI-VOLATILES

All samples submitted for analysis were spiked with surrogate compounds prior to sample extraction and analysis. According to the "Guidelines", up to one outlying surrogate in the base/neutral or acid fractions is acceptable as long as the recovery is at least 10 percent.

All sample analyses yielded acceptable recoveries.

6.3 CHLORINATED PESTICIDES/PCBs

All investigative samples submitted for chlorinated pesticide/PCB determinations were spiked with the surrogate compounds tetrachloro-m-xylene (TCMX) and decachlorobiphenyl (DCB) prior to sample preparation. Surrogate recoveries could not be assessed for some analyses due to necessary sample dilutions. All remaining results associated with outlying DCB and TCMX surrogate recoveries were qualified as estimated (see Table 8).

7.0 LABORATORY BLANK ANALYSES

The purpose of assessing the results of laboratory blank analyses is to determine the existence and magnitude of sample contamination introduced during analysis. Laboratory blanks are prepared and analyzed as samples.

For this study, laboratory blanks were analyzed at a minimum frequency of one per 20 investigative samples and/or one per analytical batch.

7.1 VOLATILES

Most volatile analytes of interest were reported as non-detect in the method blanks. Low VOC concentrations were reported for some analyses. All associated samples with similar concentrations were qualified as non-detect (see Table 9).

7.2 SEMI-VOLATILES

Most semi-volatile analytes of interest were reported as non-detect in the method blanks. Low SVOC concentrations were reported for some analyses. All associated samples with similar concentrations were qualified as non-detect (see Table 9).

7.3 CHLORINATED PESTICIDES/PCBs

Analysis of the laboratory blanks yielded non-detect results for all pesticides and PCBs indicating contamination was not a factor for this analysis.

7.4 INORGANIC ANALYSES

Upon review of the initial calibration blanks, continuing calibration blanks and preparation blanks, it was noted that metal concentrations were observed above the instrument detection limit (IDL). Most investigative samples associated with contaminated laboratory blanks yielded either non-detect concentrations or concentrations greater than five times the associated laboratory blank concentrations for the analytes of interest. These sample results were not impacted by the contamination detected. Associated sample results that were impacted were qualified as non-detect (see Table 9).

8.0 LABORATORY CONTROL SAMPLE (LCS) ANALYSES

LCS and/or laboratory control sample duplicates (LCSD) are prepared and analyzed as samples to assess the analytical efficiencies of the methods employed, independent of sample matrix effects.

LCS analyses were performed for all parameters at a minimum frequency of one per 20 investigative samples.

8.1 VOLATILES

Blank samples were spiked with the specified compounds. Most blank spike sample analyses yielded recoveries within the laboratory control limits. Low 1,2,4-trichlorobenzene recoveries were reported for the air analyses, and the associated sample results were qualified as estimated (see Table 10).

8.2 SEMI-VOLATILES

Blank samples were spiked with the specified SVOC compounds prior to extraction. All recoveries reported for the blank spikes were within the control limits, indicating that acceptable laboratory accuracy was achieved during the analysis.

8.3 CHLORINATED PESTICIDES/PCBs

LCS samples were spiked with the specified compounds. All recoveries reported for the blank spikes were within the control limits, indicating acceptable analytical accuracy.

8.4 INORGANICS

The LCS serves as a monitor of the overall performance of all steps in the analysis, indicating the sample preparation. LCSs were analyzed using the same sample preparation, analytical methods, and QA/QC procedures employed for the inorganic samples.

All LCS samples yielded recoveries within the established control limits, indicating acceptable laboratory performance.

9.0 MATRIX SPIKE/MATRIX SPIKE DUPLICATE (MS/MSD) ANALYSES

To evaluate the effects of sample matrices on the extraction or digestion process, measurement procedures, and accuracy of a particular analysis, samples are spiked with a known concentration of the analyte of concern and analyzed as MS/MSD samples. The relative percent difference (RPD) between the MS and MSD are used to assess analytical precision. Non-detect sample results associated with high MS/MSD recoveries were not qualified, as the indicated high bias would not impact the data. MS/MSD analyses were performed as specified in Table 1.

9.1 VOLATILES

The MS/MSD samples were spiked with representative compounds. Most percent recoveries and RPD values were within the laboratory control limits. Results associated with outlying MS/MSD recoveries were qualified as estimated (see Table 11).

9.2 SEMI-VOLATILES

The MS/MSD samples were spiked with representative compounds prior to extraction. Most percent recoveries and RPD values were within the laboratory control limits. Results associated with outlying MS/MSD recoveries were qualified as estimated (see Table 11).

9.3 CHLORINATED PESTICIDES/PCBs

The MS/MSD samples were spiked with representative chlorinated pesticide compounds. No qualification of sample data was necessary for this analysis.

9.4 INORGANICS

The MS/MSD samples were spiked with cyanide and the metals of interest. Per the "Guidelines", the data cannot be assessed if the sample concentration exceeds four times the spike concentration.

Most MS/MSD recoveries were acceptable. Results associated with outlying MS/MSD recoveries were qualified as estimated (see Table 11).

10.0 ICP SERIAL DILUTION

The serial dilution determines whether significant physical or chemical interferences exist due to sample matrix. A minimum of one per 20 investigative samples or at least one per analytical batch must be analyzed at a five-fold dilution. For samples yielding analyte concentrations greater than 50 times the IDL, the serial dilution results must agree within 10 percent of the original results.

A serial dilution was performed on the MS sample. Most results met the criteria above. Results associated with outlying analyses were qualified as estimated (see Table 12).

11.0 ICP INTERFERENCE CHECK SAMPLE ANALYSIS (ICS)

To verify that the laboratory has established proper interelement and background correction factors, ICSs are analyzed. These samples contain high concentrations of aluminum, calcium, magnesium and iron and are analyzed at the beginning and end of each sample analysis period.

ICS analysis results were evaluated for all samples. All ICS recoveries were within the established control limits of 80-120 percent.

12.0 FIELD QA/QC

12.1 FIELD DUPLICATES

To assess the analytical and sampling protocol precision, five field duplicates (as identified in Table 1) was collected and submitted "blind" to the laboratory. The results were evaluated using the criteria in the QAPP. Most field duplicate results showed adequate reproducibility outside of the estimated region of detection. Results that did show variability were qualified as estimated (see Table 13).

12.2 RINSE BLANKS

To assess contamination from field equipment cleaning activities, two rinse blanks were collected as identified in Table 1. Most sample results were non-detect for the analytes of interest. Results impacted by rinse blank contamination were qualified as non-detect (see Table 14).

12.3 TRIP BLANKS

Trip blanks are transported, stored, and analyzed with the investigative samples to identify potential cross-contamination of VOCs. Three trip blanks were collected as identified in Table 1. Most sample results were non-detect for the analytes of interest. Results impacted by trip blank contamination were qualified as non-detect (see Table 15).

13.0 SAMPLE QUANTITATION

All soil results were reported on a dry weight basis.

The laboratory confirmed all detected pesticide/PCB results using a second column. In some instances, there was notable variability between the results from each column. In these cases, the higher of the two results was reported, and the associated sample results were qualified as estimated (see Table 16).

14.0 TENTATIVELY IDENTIFIED COMPOUNDS (TICs)

Chromatographic peaks recorded during volatile and semi-volatile sample analyses that are not target compounds, surrogates, or internal standards, are potential TICs.

Summaries of the TICs reported by the laboratory are presented in Tables 17A and 17B.

15.0 CONCLUSION

Based on this QA/QC assessment, the data produced by ____ are acceptable with the specific exceptions and qualifications noted.

TABLES

PROPRIETARY DOCUMENT

TABLE 1

SAMPLE COLLECTION AND ANALYSIS SUMMARY
SUPPLEMENTAL REMEDIAL INVESTIGATION

Sample ID	Location ID	Matrix	Collection Date (mm/dd/yy)	Collection Time (hr:min)	Analysis/Parameters: TCL VOCs + TICs	TCL SVOCs + TICs and Dioxin Screen	TCL Pesticides/PCBs	TAL Metals/Cyanide	TO-15 VOCs	Comments
W-42271-102505-WA-01	SV-18	Soil/waste	10/25/05	16:30	X	X	X	X	X	
S-42271-102605-WA-02	SV-17	Soil/surface	10/26/05	10:15	X	X	X	X	X	
S-42271-102605-WA-03	SV-17	Soil/fill	10/26/05	10:25	X	X	X	X	X	
W-42271-102605-WA-04	SV-17	Soil/waste	10/26/05	10:35	X	X	X	X	X	
S-42271-102605-WA-06	MW-3-05	Soil/surface	10/26/05	13:05	X	X	X	X	X	
W-42271-102605-WA-07	MW-3-05	Soil/waste	10/26/05	13:23	X	X	X	X	X	
S-42271-102605-WA-08	MW-5-05	Soil/surface	10/26/05	14:35	X	X	X	X	X	
S-42271-102705-WA-09	SV-16	Soil/surface	10/27/05	8:45	X	X	X	X	X	
S-42271-102705-WA-09-D	SV-16	Soil/surface	10/27/05	8:50	X	X	X	X	X	Field Duplicate of S-42271-102705-WA-09
W-42271-102705-WA-10	SV-16	Soil/waste	10/27/05	9:20	X	X	X	X	X	
W-42271-102705-WA-10-D	SV-16	Soil/waste	10/27/05	9:20	X	X	X	X	X	Field Duplicate of W-42271-102705-WA-10

Notes:

- Not applicable.
MS Matrix Spike.
MSD Matrix Spike Duplicate.
SVOCs Semi-Volatile Organic Compounds.
TAL Target Analyte List.
TCL Target Compound List.
TICs Tentatively Identified Compounds.
VOCs Volatile Organic Compounds.

PROPRIETARY DOCUMENT

TABLE 2

ANALYTICAL METHODS SUMMARY
SUPPLEMENTAL REMEDIAL INVESTIGATION

Analytical Parameters	*Analytical Method*
TCL VOCs (Plus TICs)	8260 [1]
TCL SVOCs (with 1,4-Dioxane, TICs, and Dioxin Screen)	8270 [1]
TCL Pesticides/PCBs	8081/8082 [1]
TAL Inorganics (Soil)	6010/7471/9012 [1]
TAL Inorganics (Water)	6010/7470/9012 [1]
Percent Solids	160.3 [2]
VOCs	TO-15 [3]

Notes:

(1) "Test Methods for Evaluating Solid Waste", SW-846, 3rd Edition (with revisions).

(2) "Methods for the Chemical Analysis of Water and Wastes", USEPA 600/4-79-220, March 1983 (with revisions).

(3) "Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air", January 1999.

PCBs Polychlorinated Biphenyls.
SVOCs Semi-Volatile Organic Compounds.
TAL Target Analyte List.
TCL Target Compound List.
TICs Tentatively Identified Compounds.
VOCs Volatile Organic Compounds.

ANALYTICAL RESULTS SUMMARY - SOIL SAMPLING
SUPPLEMENTAL REMEDIAL INVESTIGATION

	Sample Location:	MW-3-05	MW-3-05	MW-5-05	MW-7-05	MW-9-05	POND	Low lying area near RCR Yacht
	Sample ID:	S-42271-102605-WA-06	S-42271-102605-WA-07	S-42271-102605-WA-08	S-42271-110105-WA-21	S-42271-110105-WA-18	S-42271-110305-WA-027	S-42271-110305-WA-025
	Sample Date	10/26/2005	10/26/2005	10/26/2005	11/1/2005	11/1/2005	11/3/2005	11/3/2005
Parameter	Units							
Volatile Organic Compounds								
1,1,1-Trichloroethane	µg/kg	5.3 U	320 U	5.8 U	5.6 U	5.5 U	7.5 U	7.5 U
1,1,2,2-Tetrachloroethane	µg/kg	5.3 U	320 U	5.8 U	5.6 U	5.5 U	7.5 U	7.5 U
1,1,2-Trichloroethane	µg/kg	5.3 U	320 U	5.8 U	5.6 U	5.5 U	7.5 U	7.5 U
1,1-Dichloroethane	µg/kg	5.3 U	320 U	5.8 U	5.6 U	5.5 U	7.5 U	7.5 U
1,1-Dichloroethene	µg/kg	5.3 U	320 U	5.8 U	5.6 U	5.5 U	7.5 U	7.5 U
1,2,4-Trichlorobenzene	µg/kg	5.3 U	320 U	5.8 UJ	5.6 U	5.5 U	7.5 UJ	7.5 UJ
1,2-Dibromo-3-chloropropane (DBCP)	µg/kg	11 UJ	640 U	12 UJ	11 UJ	11 UJ	15 UJ	15 UJ
1,2-Dibromoethane (Ethylene Dibromide)	µg/kg	5.3 U	320 U	5.8 U	5.6 U	5.5 U	7.5 U	7.5 U
1,2-Dichlorobenzene	µg/kg	5.3 U	24 J	5.8 UJ	5.6 U	5.5 U	7.5 UJ	7.5 UJ
1,2-Dichloroethane	µg/kg	5.3 U	320 U	5.8 U	5.6 U	5.5 U	7.5 U	7.5 U
1,2-Dichloropropane	µg/kg	5.3 U	320 U	5.8 U	5.6 U	5.5 U	7.5 U	7.5 U
1,3-Dichlorobenzene	µg/kg	5.3 U	320 U	5.8 UJ	5.6 U	5.5 U	7.5 UJ	7.5 UJ
1,4-Dichlorobenzene	µg/kg	5.3 U	320 U	5.8 UJ	5.6 U	5.5 U	7.5 UJ	7.5 UJ
2-Butanone (Methyl Ethyl Ketone)	µg/kg	21 U	1300 U	23 U	22 U	9.5 J	23 J	3.9 J
2-Hexanone	µg/kg	21 U	1300 U	23 U	22 U	22 U	30 UJ	30 UJ
4-Methyl-2-Pentanone (Methyl Isobutyl Ketone)	µg/kg	21 U	1300 U	23 U	22 U	22 U	30 U	30 U
Acetone	µg/kg	21 U	1300 U	23 U	22 U	22 U	21 J	15 J
Benzene	µg/kg	5.3 U	320 U	5.8 U	5.6 U	5.5 U	7.5 U	0.75 J
Bromodichloromethane	µg/kg	5.3 U	320 U	5.8 U	5.6 U	5.5 U	7.5 U	7.5 U
Bromoform	µg/kg	5.3 UJ	320 U	5.8 UJ	5.6 UJ	5.5 UJ	7.5 U	7.5 U
Bromomethane (Methyl Bromide)	µg/kg	5.3 UJ	320 U	5.8 UJ	5.6 UJ	5.5 UJ	7.5 U	7.5 U
Carbon disulfide	µg/kg	5.3 U	25 J	5.8 U	5.6 U	5.5 U	7.5 U	7.5 U
Carbon tetrachloride	µg/kg	5.3 U	320 U	5.8 U	5.6 U	5.5 U	7.5 U	7.5 U
Chlorobenzene	µg/kg	5.3 U	320 U	5.8 U	5.6 U	5.5 U	7.5 U	7.5 U
Chloroethane	µg/kg	5.3 UJ	320 U	5.8 UJ	5.6 UJ	5.5 UJ	7.5 U	7.5 U
Chloroform (Trichloromethane)	µg/kg	5.3 U	320 U	5.8 U	5.6 U	5.5 U	7.5 U	7.5 U
Chloromethane (Methyl Chloride)	µg/kg	5.3 U	320 U	5.8 U	5.6 U	5.5 U	7.5 U	7.5 U
cis-1,2-Dichloroethene	µg/kg	5.3 U	320 U	5.8 U	5.6 U	5.5 U	7.5 U	7.5 U
cis-1,3-Dichloropropene	µg/kg	5.3 U	320 U	5.8 U	5.6 U	5.5 U	7.5 U	7.5 U
Cyclohexane	µg/kg	11 U	640 U	12 U	11 U	11 U	15 U	15 U
Dibromochloromethane	µg/kg	5.3 U	320 U	5.8 U	5.6 U	5.5 U	7.5 U	7.5 U
Dichlorodifluoromethane (CFC-12)	µg/kg	5.3 U	320 U	5.8 U	5.6 U	5.5 U	7.5 U	7.5 U
Ethylbenzene	µg/kg	5.3 U	320 U	5.8 U	5.6 U	5.5 U	7.5 U	7.5 U
Isopropylbenzene	µg/kg	0.67 J	320 U	5.8 U	5.6 U	5.5 U	7.5 U	7.5 U
Methyl acetate	µg/kg	11 U	640 U	12 U	11 U	11 U	15 U	15 U
Methyl cyclohexane	µg/kg	11 U	640 U	12 U	11 U	11 U	15 U	15 U
Methyl Tert Butyl Ether	µg/kg	21 U	1300 U	23 U	22 U	22 U	30 U	30 U
Methylene chloride	µg/kg	5.3 U	320 U	5.8 U	5.6 U	5.5 U	7.5 U	7.5 U
Styrene	µg/kg	5.3 U	320 U	5.8 U	5.6 U	5.5 U	7.5 U	7.5 U
Tetrachloroethene	µg/kg	0.98 J	320 U	5.8 U	5.6 U	5.5 U	7.5 U	7.5 U
Toluene	µg/kg	5.3 U	20 J	5.8 U	5.6 U	5.5 U	6.5 J	0.44 J
trans-1,2-Dichloroethene	µg/kg	5.3 U	320 U	5.8 U	5.6 U	5.5 U	7.5 U	7.5 U
trans-1,3-Dichloropropene	µg/kg	5.3 U	320 U	5.8 U	5.6 U	5.5 U	7.5 U	7.5 U
Trichloroethene	µg/kg	5.3 U	320 U	5.8 U	5.6 U	5.5 U	7.5 U	7.5 U
Trichlorofluoromethane (CFC-11)	µg/kg	5.3 UJ	320 U	5.8 UJ	5.6 U	5.5 U	7.5 U	7.5 U

TABLE 3A

ANALYTICAL RESULTS SUMMARY - SOIL SAMPLING
SUPPLEMENTAL REMEDIAL INVESTIGATION

	Sample Location:	MW-3-05	MW-3-05	MW-5-05	MW-7-05	MW-9-05	POND	Low lying area near RCR Yacht
	Sample ID:	S-42271-102605-WA-06	S-42271-102605-WA-07	S-42271-102605-WA-08	S-42271-110105-WA-21	S-42271-110105-WA-18	S-42271-110305-WA-027	S-42271-110305-WA-025
	Sample Date	10/26/2005	10/26/2005	10/26/2005	11/1/2005	11/1/2005	11/3/2005	11/3/2005
Parameter	Units							
Wet Chemistry								
Cyanide (total)	mg/kg	2.1	0.44 J	0.23 J	1.2	0.61	7.6	11.5 J
Total Solids	%	80.1	78.7	84.8	82.5	91.6	64.4	61.2

Notes:

J Estimated.

U Non-detect at associated value.

UJ The analyte was not detected above the sample quantitation limit. The reported quantitation limit is an estimated quantity.

TABLE 4

QUALIFIED SAMPLE RESULTS DUE TO HOLDING TIME EXCEEDANCES
SUPPLEMENTAL REMEDIAL INVESTIGATION

Parameter	*Sample ID*	*Holding Time (days)*	*Holding Time Criteria (days)*	*Analyte*	*Sample Results*	*Units*	*Qualifier*
PCBs	S-42271-102705-WA-12	21	10	Aroclor-1232 (PCB-1232)	48 U	µg/Kg	UJ
				Aroclor-1248 (PCB-1248)	48 U	µg/Kg	UJ
				Aroclor-1016 (PCB-1016)	48 U	µg/Kg	UJ
				Aroclor-1242 (PCB-1242)	48 U	µg/Kg	UJ
				Aroclor-1260 (PCB-1260)	48 U	µg/Kg	UJ
				Aroclor-1254 (PCB-1254)	17 J	µg/Kg	J
				Aroclor-1221 (PCB-1221)	48 U	µg/Kg	UJ
PCBs	S-42271-102705-WA-13	21	10	Aroclor-1260 (PCB-1260)	39 U	µg/Kg	UJ
				Aroclor-1254 (PCB-1254)	39 U	µg/Kg	UJ
				Aroclor-1221 (PCB-1221)	39 U	µg/Kg	UJ
				Aroclor-1232 (PCB-1232)	39 U	µg/Kg	UJ
				Aroclor-1248 (PCB-1248)	39 U	µg/Kg	UJ
				Aroclor-1016 (PCB-1016)	39 U	µg/Kg	UJ
				Aroclor-1242 (PCB-1242)	39 U	µg/Kg	UJ
PCBs	S-42271-102805-WA-14	21	10	Aroclor-1260 (PCB-1260)	53 U	µg/Kg	UJ
				Aroclor-1254 (PCB-1254)	53 U	µg/Kg	UJ
				Aroclor-1221 (PCB-1221)	53 U	µg/Kg	UJ
				Aroclor-1232 (PCB-1232)	53 U	µg/Kg	UJ
				Aroclor-1248 (PCB-1248)	53 U	µg/Kg	UJ
				Aroclor-1016 (PCB-1016)	53 U	µg/Kg	UJ
				Aroclor-1242 (PCB-1242)	53 U	µg/Kg	UJ
PCBs	S-42271-103105-WA-15	21	10	Aroclor-1260 (PCB-1260)	37 U	µg/Kg	UJ
				Aroclor-1254 (PCB-1254)	37 U	µg/Kg	UJ
				Aroclor-1221 (PCB-1221)	37 U	µg/Kg	UJ
				Aroclor-1232 (PCB-1232)	37 U	µg/Kg	UJ
				Aroclor-1248 (PCB-1248)	37 U	µg/Kg	UJ
				Aroclor-1016 (PCB-1016)	37 U	µg/Kg	UJ
				Aroclor-1242 (PCB-1242)	37 U	µg/Kg	UJ
PCBs	S-42271-103105-WA-16	21	10	Aroclor-1260 (PCB-1260)	41 U	µg/Kg	UJ
				Aroclor-1254 (PCB-1254)	41 U	µg/Kg	UJ
				Aroclor-1221 (PCB-1221)	41 U	µg/Kg	UJ
				Aroclor-1232 (PCB-1232)	41 U	µg/Kg	UJ
				Aroclor-1248 (PCB-1248)	41 U	µg/Kg	UJ
				Aroclor-1016 (PCB-1016)	41 U	µg/Kg	UJ
				Aroclor-1242 (PCB-1242)	41 U	µg/Kg	UJ
PCBs	S-42271-103105-WA-17	21	10	Aroclor-1260 (PCB-1260)	40 U	µg/Kg	UJ
				Aroclor-1254 (PCB-1254)	40 U	µg/Kg	UJ
				Aroclor-1221 (PCB-1221)	40 U	µg/Kg	UJ
				Aroclor-1232 (PCB-1232)	40 U	µg/Kg	UJ
				Aroclor-1248 (PCB-1248)	40 U	µg/Kg	UJ
				Aroclor-1016 (PCB-1016)	40 U	µg/Kg	UJ
				Aroclor-1242 (PCB-1242)	40 U	µg/Kg	UJ

Notes:
J Estimated.
PCBs Polychlorinated Biphenyls.
U Non-detect at associated value.
UJ The analyte was not detected above the sample quantitation limit. The reported quantitation limit is an estimated quantity.

PROPRIETARY DOCUMENT

TABLE 5

QUALIFIED SAMPLE RESULTS DUE TO OUTLYING INITIAL CALIBRATION RESULTS
SUPPLEMENTAL REMEDIAL INVESTIGATION

Parameter	*Compound*	*Calibration Dates*	*%RSD*	*Associated Sample ID*	*Sample Results*	*Units*	*Qualifier*
VOCs in Air	2-Butanone (Methyl Ethyl Ketone)	11/03/05	33	A-42271-JC-001	0.88 J	ppbv	J
				A-42271-JC-002	1.0 J	ppbv	J
				A-42271-JC-003	2.8 J	ppbv	J
				A-42271-JC-004	2.5 U	ppbv	UJ
				A-42271-JC-005	16 J	ppbv	J
				A-42271-JC-006	0.82 J	ppbv	J
				A-42271-JC-007	0.50 U	ppbv	UJ
				A-42271-JC-008	5.0 U	ppbv	UJ
				A-42271-JC-009	5.0 U	ppbv	UJ
				A-42271-JC-010	0.50 U	ppbv	UJ
				A-42271-JC-011	0.50 U	ppbv	UJ
				A-42271-JC-012	5.0 U	ppbv	UJ
				A-42271-JC-013	3.0 J	ppbv	J
				A-42271-JC-014	0.50 U	ppbv	UJ
				A-42271-JC-015	1.5 U	ppbv	UJ
				A-42271-JC-016	21 U	ppbv	UJ
				A-42271-JC-017	5.0 U	ppbv	UJ
				A-42271-JC-018	3.6 J	ppbv	J
				A-42271-JC-019	0.50 U	ppbv	UJ
				A-42271-JC-020	0.50 U	ppbv	UJ

Notes:
%RSD Percent Relative Standard Deviation.
J Estimated.
U Non-detect at associated value.
UJ The analyte was not detected above the sample quantitation limit. The reported quantitation limit is an estimated quantity.
VOCs Volatile Organic Compounds.

PROPRIETARY DOCUMENT

TABLE 6

QUALIFIED SAMPLE RESULTS DUE TO OUTLYING CONTINUING CALIBRATION RESULTS
SUPPLEMENTAL REMEDIAL INVESTIGATION

Parameter	*Calibration Date*	*Compound*	*%D*	*Associated Sample ID*	*Sample Results*	*Units*	*Qualifier*
VOCs in Air	11/12/05	Acetone	31	A-42271-JC-016	210 U	ppbv	UJ
Volatiles	11/07/05	Bromomethane (Methyl Bromide)	-61	W-42271-102505-WA-01	6.0 U	µg/Kg	UJ
				S-42271-102605-WA-02	5.9 U	µg/Kg	UJ
				S-42271-102605-WA-03	7.1 U	µg/Kg	UJ
				S-42271-102605-WA-06	5.3 U	µg/Kg	UJ
				S-42271-102605-WA-08	5.8 U	µg/Kg	UJ
Volatiles	11/07/05	Chloroethane	-43	W-42271-102505-WA-01	6.0 U	µg/Kg	UJ
				S-42271-102605-WA-02	5.9 U	µg/Kg	UJ
				S-42271-102605-WA-03	7.1 U	µg/Kg	UJ
				S-42271-102605-WA-06	5.3 U	µg/Kg	UJ
				S-42271-102605-WA-08	5.8 U	µg/Kg	UJ
Volatiles	11/07/05	Trichlorofluoromethane (CFC-11)	-29	W-42271-102505-WA-01	6.0 U	µg/Kg	UJ
				S-42271-102605-WA-02	5.9 U	µg/Kg	UJ
				S-42271-102605-WA-03	7.1 U	µg/Kg	UJ
				S-42271-102605-WA-06	5.3 U	µg/Kg	UJ
				S-42271-102605-WA-08	5.8 U	µg/Kg	UJ
Volatiles	11/07/05	Bromoform	31	W-42271-102505-WA-01	6.0 U	µg/Kg	UJ
				S-42271-102605-WA-02	5.9 U	µg/Kg	UJ
				S-42271-102605-WA-03	7.1 U	µg/Kg	UJ
				S-42271-102605-WA-06	5.3 U	µg/Kg	UJ
				S-42271-102605-WA-08	5.8 U	µg/Kg	UJ
Volatiles	11/07/05	1,2-Dibromo-3-chloropropane (DBCP)	36	W-42271-102505-WA-01	12 U	µg/Kg	UJ
				S-42271-102605-WA-02	12 U	µg/Kg	UJ
				S-42271-102605-WA-03	14 U	µg/Kg	UJ
				S-42271-102605-WA-06	11 U	µg/Kg	UJ
				S-42271-102605-WA-08	12 U	µg/Kg	UJ
Volatiles	11/08/05	Bromomethane (Methyl Bromide)	-51	S-42271-102705-WA-09-D	6.9 U	µg/Kg	UJ
				S-42271-102605-WA-04	6.6 U	µg/Kg	UJ
Volatiles	11/08/05	Chloroethane	-42	S-42271-102705-WA-09-D	6.9 U	µg/Kg	UJ
				S-42271-102605-WA-04	6.6 U	µg/Kg	UJ
Volatiles	11/08/05	Trichlorofluoromethane (CFC-11)	-27	S-42271-102705-WA-09-D	6.9 U	µg/Kg	UJ
				S-42271-102605-WA-04	6.6 U	µg/Kg	UJ
Volatiles	11/09/05	Bromomethane (Methyl Bromide)	-36	S-042271-102705-WA-09	6.5 U	µg/Kg	UJ
				S-42271-102705-WA-10	6.2 U	µg/Kg	UJ
				S-42271-102705-WA-12	7.1 U	µg/Kg	UJ
				S-42271-103105-WA-15	5.4 U	µg/Kg	UJ

Notes:
%D Percent Difference.
J Estimated.
U Non-detect at associated value.
UJ The analyte was not detected above the sample quantitation limit. The reported quantitation limit is an estimated quantity.
VOCs Volatile Organic Compounds.

PROPRIETARY DOCUMENT

TABLE 7

QUALIFIED SAMPLE RESULTS DUE TO OUTLYING INTERNAL STANDARD (IS) RECOVERIES
SUPPLEMENTAL REMEDIAL INVESTIGATION

Parameter	*Sample ID*	*IS*	*IS Area Count (percent)*	*Control Limits (percent)*	*Analytes*	*Sample Results*	*Units*	*Qualifier*
Volatiles	S-42271-110305-WA-025	1,4-Dichlorobenzene-d4	42	50-200	1,4-Dichlorobenzene	7.5 U	µg/Kg	UJ
					1,2,4-Trichlorobenzene	7.5 U	µg/Kg	UJ
					1,3-Dichlorobenzene	7.5 U	µg/Kg	UJ
					1,2-Dichlorobenzene	7.5 U	µg/Kg	UJ
					1,2-Dibromo-3-chloropropane (DBCP)	15 U	µg/Kg	UJ
Volatiles	S-42271-110305-WA-026	1,4-Dichlorobenzene-d4	39	50-200	1,4-Dichlorobenzene	8.1 U	µg/Kg	UJ
					1,2,4-Trichlorobenzene	8.1 U	µg/Kg	UJ
					1,3-Dichlorobenzene	8.1 U	µg/Kg	UJ
					1,2-Dichlorobenzene	8.1 U	µg/Kg	UJ
					1,2-Dibromo-3-chloropropane (DBCP)	16 U	µg/Kg	UJ
Volatiles	S-42271-110305-WA-027	1,4-Dichlorobenzene-d4	48	50-200	1,4-Dichlorobenzene	7.5 U	µg/Kg	UJ
					1,2,4-Trichlorobenzene	7.5 U	µg/Kg	UJ
					1,3-Dichlorobenzene	7.5 U	µg/Kg	UJ
					1,2-Dichlorobenzene	7.5 U	µg/Kg	UJ
					1,2-Dibromo-3-chloropropane (DBCP)	15 U	µg/Kg	UJ
Volatiles	S-42271-110105-WA-19	1,4-Dichlorobenzene-d4	42	50-200	1,4-Dichlorobenzene	5.5 U	µg/Kg	UJ
					1,2,4-Trichlorobenzene	5.5 U	µg/Kg	UJ
					1,3-Dichlorobenzene	5.5 U	µg/Kg	UJ
					1,2-Dichlorobenzene	5.5 U	µg/Kg	UJ
					1,2-Dibromo-3-chloropropane (DBCP)	11 U	µg/Kg	UJ
Volatiles	W-42271-110205-WA-24	1,4-Dichlorobenzene-d4	36	50-200	1,4-Dichlorobenzene	6.8 U	µg/Kg	UJ
					1,2,4-Trichlorobenzene	6.8 U	µg/Kg	UJ
					1,3-Dichlorobenzene	6.8 U	µg/Kg	UJ
					1,2-Dichlorobenzene	6.8 U	µg/Kg	UJ
					1,2-Dibromo-3-chloropropane (DBCP)	14 U	µg/Kg	UJ

Notes:
J Estimated.
U Non-detect at associated value.
UJ The analyte was not detected above the sample quantitation limit. The reported quantitation limit is an estimated quantity.

PROPRIETARY DOCUMENT

TABLE 8

QUALIFIED SAMPLE RESULTS DUE TO OUTLYING SURROGATE RECOVERIES
SUPPLEMENTAL REMEDIAL INVESTIGATION

Parameter	*Surrogate*	*Surrogate Recovery (percent)*	*Control Limits (percent)*	*Sample ID*	*Analytes*	*Sample Results*	*Units*	*Qualifier*
PCBs	DCB	18	40 - 138	S-42271-102605-WA-02	Aroclor-1260 (PCB-1260)	14	µg/Kg	J
					Aroclor-1260 (PCB-1260)	42 U	µg/Kg	UJ
					Aroclor-1254 (PCB-1254)	42 U	µg/Kg	UJ
					Aroclor-1221 (PCB-1221)	42 U	µg/Kg	UJ
					Aroclor-1232 (PCB-1232)	37	µg/Kg	J
					Aroclor-1248 (PCB-1248)	42 U	µg/Kg	UJ
					Aroclor-1016 (PCB-1016)	42 U	µg/Kg	UJ
					Aroclor-1242 (PCB-1242)			
PCBs	DCB	175	40 - 138	S-42271-102605-WA-04	Aroclor-1260 (PCB-1260)	370 J	µg/Kg	J
					Aroclor-1248 (PCB-1248)	590	µg/Kg	J
PCBs	DCB	167	40 - 138	S-42271-102605-WA-09-D	Aroclor-1260 (PCB-1260)	55	µg/Kg	J
					Aroclor-1248 (PCB-1248)	120	µg/Kg	J
Pesticides	TCMX	37	39 - 130	W-42271-110405-WA-05	Heptachlor epoxide	0.050 U	µg/L	UJ
					Endosulfan sulfate	0.050 U	µg/L	UJ
					Aldrin	0.050 U	µg/L	UJ
					alpha-BHC	0.050 U	µg/L	UJ
					beta-BHC	0.050 U	µg/L	UJ
					delta-BHC	0.050 U	µg/L	UJ
					Endosulfan II	0.050 U	µg/L	UJ
					4,4'-DDT	0.050 U	µg/L	UJ

Notes:
DCB Decachlorobiphenyl.
J Estimated.
PCBs Polychlorinated Biphenyls.
[illegible]achloro-m-xylene.
U Non-detect at associated value.
UJ The analyte was not detected above the sample quantitation limit. The reported quantitation limit is an estimated quantity.

PROPRIETARY DOCUMENT

TABLE 9

QUALIFIED SAMPLE RESULTS DUE TO ANALYTE CONCENTRATIONS IN THE LABORATORY BLANKS
SUPPLEMENTAL REMEDIAL INVESTIGATION

Parameter	Analysis Date	Analyte	Blank Result [1]	Sample ID	Sample Result	Qualified Result	Units
Volatiles	11/07/05	1,2-Dichlorobenzene	0.30J	S-42271-102605-WA-06	0.51 J	5.3 U	µg/Kg
Volatiles	11/07/05	1,4-Dichlorobenzene	0.46J	S-42271-102605-WA-06	0.40 J	5.3 U	µg/Kg
Volatiles	11/08/05	Methylene chloride	3.0J	S-42271-102605-WA-04	5.5 J	6.6 U	µg/Kg
Volatiles	11/10/05	Acetone	110J	S-42271-102605-WA-07	170 J	1300 U	µg/Kg
Volatiles	11/10/05	1,4-Dichlorobenzene	12J	S-42271-102605-WA-07	41 J	320 U	µg/Kg
Volatiles	11/10/05	Methyl acetate	67J	S-42271-102705-WA-10-D	110 J	620 U	µg/Kg
				S-42271-102605-WA-07	100 J	640 U	µg/Kg
				S-42271-102705-WA-11	120 J	590 U	µg/Kg
Volatiles	11/10/05	Methylene chloride	170J	S-42271-102705-WA-10-D	230 J	310 U	µg/Kg
				S-42271-102605-WA-07	140 J	320 U	µg/Kg
				S-42271-102705-WA-11	190 J	300 U	µg/Kg
Volatiles	11/10/05	1,2,4-Trichlorobenzene	24J	S-42271-102705-WA-10-D	19 J	310 U	µg/Kg
				S-42271-102605-WA-07	36 J	320 U	µg/Kg
Volatiles	11/09/05	1,2-Dichlorobenzene	0.28J	S-42271-102705-WA-12	0.32 J	7.1 U	µg/Kg
Volatiles	11/09/05	1,4-Dichlorobenzene	0.40J	S-42271-102705-WA-10	0.82 J	6.2 U	µg/Kg
Volatiles	11/09/05	1,2,4-Trichlorobenzene	0.79J	S-42271-102705-WA-12	0.61 J	7.1 U	µg/Kg
Volatiles	11/10/05	Methylene chloride	1.9J	S-42271-103105-WA-17	2.4 J	5.9 U	µg/Kg
Volatiles	11/10/05	Carbon disulfide	0.31J	S-42271-110305-WA-025	1.5 J	7.5 U	µg/Kg
				S-42271-110305-WA-027	1.3 J	7.5 U	µg/Kg
				W-42271-110205-WA-22	1.3 J	5.1 U	µg/Kg
				S-42271-110305-WA-026	1.6 J	8.1 U	µg/Kg
Volatiles	11/10/05	Methylene chloride	3.3J	S-42271-110305-WA-025	4.0 J	7.5 U	µg/Kg
				S-42271-110305-WA-027	4.8 J	7.5 U	µg/Kg
				S-42271-110305-WA-026	4.6 J	8.1 U	µg/Kg
Volatiles	11/11/05	Carbon disulfide	0.27J	S-42271-110105-WA-19	0.32 J	5.5 U	µg/Kg
				S-42271-110205-WA-23	0.24 J	5.9 U	µg/Kg
				W-42271-110105-WA-20	0.28 J	6.1 U	µg/Kg
				W-42271-110205-WA-24	0.32 J	6.8 U	µg/Kg
Volatiles	11/11/05	Methylene chloride	4.4J	S-42271-110105-WA-19	1.9 J	5.5 U	µg/Kg
				S-42271-110205-WA-23	2.2 J	5.9 U	µg/Kg
				W-42271-110205-WA-24	2.4 J	6.8 U	µg/Kg

Notes:

[1] Results corrected for individual sample dilutions where applicable.

J Estimated.

U Non-detect at associated value.

PROPRIETARY DOCUMENT

TABLE 10

QUALIFIED SAMPLE RESULTS DUE TO OUTLYING LABORATORY CONTROL SAMPLE/LABORATORY CONTROL SAMPLE DUPLICATE RESULTS
SUPPLEMENTAL REMEDIAL INVESTIGATION

Parameter	*Compound*	*Preparation Date*	*LCS Percent Recovery*	*LCSD Percent Recovery*	*Control Limits (percent)*	*Associated Sample ID*	*Sample Results*	*Units*	*Qualifier*
VOCs in Air	1,2,4-Trichlorobenzene	11/10/05	41	48	70-130	A-42271-JC-001	0.50 U	ppbv	UJ
						A-42271-JC-002	0.50 U	ppbv	UJ
						A-42271-JC-003	1.5 U	ppbv	UJ
						A-42271-JC-004	2.5 U	ppbv	UJ
						A-42271-JC-005	1.5 U	ppbv	UJ
						A-42271-JC-006	0.50 U	ppbv	UJ
						A-42271-JC-007	0.50 U	ppbv	UJ
						A-42271-JC-008	5.0 U	ppbv	UJ
						A-42271-JC-009	5.0 U	ppbv	UJ
						A-42271-JC-010	0.50 U	ppbv	UJ
						A-42271-JC-011	0.50 U	ppbv	UJ
						A-42271-JC-012	5.0 U	ppbv	UJ
						A-42271-JC-013	2.5 U	ppbv	UJ
						A-42271-JC-014	0.50 U	ppbv	UJ
						A-42271-JC-015	1.5 U	ppbv	UJ
						A-42271-JC-017	5.0 U	ppbv	UJ
						A-42271-JC-018	1.1 U	ppbv	UJ
						A-42271-JC-019	0.50 U	ppbv	UJ
						A-42271-JC-020	0.50 U	ppbv	UJ
VOCs in Air	1,2,4-Trichlorobenzene	11/11/05	56	62	70-130	A-42271-JC-016	21 U	ppbv	UJ

Notes:
LCS Laboratory Control Sample.
LCSD Laboratory Control Sample Duplicate.
U Non-detect at associated value.
J The analyte was not detected above the sample quantitation limit. The reported quantitation limit is an estimated quantity.
VOCs Volatile Organic Compounds.

PROPRIETARY DOCUMENT

TABLE 11

QUALIFIED SAMPLE RESULTS DUE TO OUTLYING MATRIX SPIKE/MATRIX SPIKE DUPLICATE RECOVERIES
SUPPLEMENTAL REMEDIAL INVESTIGATION

Parameter	Analyte	MS Recovery (percent)	MSD Recovery (percent)	RPD	Control Limits Recovery (percent)	Control Limits RPD (percent)	Associated Sample ID	Sample Result	Units	Qualifier
Volatiles	Chlorobenzene	88	217	51	49-139	22	W-42271-110205-WA-22	50	µg/Kg	J
Metals	Lead	74	73	0.3	75-125	20	W-42271-110405-WA-08	1480	µg/L	J
							W-42271-110305-WA-01	40.7	µg/L	J
							W-42271-110305-WA-02	479	µg/L	J
							W-42271-110305-WA-03	102	µg/L	J
							W-42271-110405-WA-04	177	µg/L	J
							W-42271-110405-WA-05	1700	µg/L	J
							W-42271-110405-WA-06	28200	µg/L	J
							W-42271-110405-WA-07	26.2	µg/L	J
							W-42271-110405-WA-11	172	µg/L	J
							W-42271-110305-WA-03D	42.3	µg/L	J
Metals	Antimony	73	72	1.5	75-125	20	W-42271-110405-WA-08	6.6	µg/L	J
							W-42271-110305-WA-01	4.1 U	µg/L	UJ
							W-42271-110305-WA-02	6.7	µg/L	J
							W-42271-110305-WA-03	4.1 U	µg/L	UJ
							W-42271-110405-WA-04	4.1 U	µg/L	UJ
							W-42271-110405-WA-05	13.3	µg/L	J
							W-42271-110405-WA-06	197	µg/L	J
							W-42271-110405-WA-07	4.1 U	µg/L	UJ
							W-42271-110405-WA-11	7.5	µg/L	J
							W-42271-110305-WA-03D	4.1 U	µg/L	UJ
Metals	Calcium	71	73	0.61	75-125	20	W-42271-110405-WA-08	147000	µg/L	J
							W-42271-110305-WA-01	179000	µg/L	J
							W-42271-110305-WA-02	340000	µg/L	J
							W-42271-110405-WA-04	263000	µg/L	J

Notes:
J Estimated.
MS Matrix Spike.
MSD Matrix Spike Duplicate.
RPD Relative Percent Difference.
U Non-detect at associated value.
UJ The analyte was not detected above the sample quantitation limit. The reported quantitation limit is an estimated quantity.

PROPRIETARY DOCUMENT

TABLE 12

QUALIFIED SAMPLE RESULTS DUE TO OUTLYING ICP SERIAL DILUTION RESULTS
SUPPLEMENTAL REMEDIAL INVESTIGATION

Parameter	*Analyte*	*Serial Dilution Sample ID*	*%D*	*Associated Sample I.D.*	*Sample Results*	*Units*	*Qualifier*
Metals	Nickel	W-42271-110305-WA-03D	20.4	W-42271-110305-WA-03D	71.1	µg/L	J
	Chromium	W-42271-110305-WA-03D	11.8	W-42271-110305-WA-03D	68.4	µg/L	J
	Cobalt	W-42271-110305-WA-03D	11.8	W-42271-110305-WA-03D	31.2	µg/L	J
	Copper	W-42271-110305-WA-03D	10.3	W-42271-110305-WA-03D	71.9	µg/L	J
	Zinc	W-42271-110305-WA-03D	16.5	W-42271-110305-WA-03D	187	µg/L	J
Metals	Zinc	W-42271-102505-WA-01	20.6	W-42271-102505-WA-01	41.7	mg/Kg	J
				S-42271-102705-WA-09-D	170	mg/Kg	J
				S-42271-102705-WA-10-D	99.0	mg/Kg	J
				S-042271-102705-WA-09	92.1	mg/Kg	J
				S-42271-102605-WA-02	108	mg/Kg	J
				S-42271-102605-WA-03	465	mg/Kg	J
				S-42271-102605-WA-04	176	mg/Kg	J
				S-42271-102605-WA-06	66.0	mg/Kg	J
				S-42271-102605-WA-07	836	mg/Kg	J
				S-42271-102605-WA-08	145	mg/Kg	J
				S-42271-102705-WA-10	84.1	mg/Kg	J
				S-42271-102705-WA-11	138	mg/Kg	J

Notes:
%D Percent Difference.
J Estimated.

PROPRIETARY DOCUMENT

TABLE 13

QUALIFIED SAMPLE RESULTS DUE TO VARIABILITY IN FIELD DUPLICATE RESULTS
SUPPLEMENTAL REMEDIAL INVESTIGATION

Parameter	*Analyte*	*Original Sample ID*	*Original Result*	*Duplicate Sample ID*	*Duplicate Result*	RPD	Units	*Qualifier* [1]
Volatiles	1,2-Dichlorobenzene	S-42271-102705-WA-10	6.2 U	S-42271-102705-WA-10-D	27 J	*	µg/Kg	J
	1,4-Dichlorobenzene	S-42271-102705-WA-10	6.2 U	S-42271-102705-WA-10-D	200 J	*	µg/Kg	J
	2-Butanone (Methyl Ethyl Ketone)	S-42271-102705-WA-10	4.5 J	S-42271-102705-WA-10-D	1200 U	*	µg/Kg	J
	Acetone	S-42271-102705-WA-10	200	S-42271-102705-WA-10-D	1200 U	*	µg/Kg	J
	Benzene	S-42271-102705-WA-10	20	S-42271-102705-WA-10-D	1900	196	µg/Kg	J
	Carbon disulfide	S-42271-102705-WA-10	2.3 J	S-42271-102705-WA-10-D	310 U	*	µg/Kg	J
	Chlorobenzene	S-42271-102705-WA-10	1.3 J	S-42271-102705-WA-10-D	130 J	196	µg/Kg	J
	cis-1,2-Dichloroethene	S-42271-102705-WA-10	0.96 J	S-42271-102705-WA-10-D	64 J	194	µg/Kg	J
	Cyclohexane	S-42271-102705-WA-10	12 U	S-42271-102705-WA-10-D	98 J	*	µg/Kg	J
	Ethylbenzene	S-42271-102705-WA-10	2.1 J	S-42271-102705-WA-10-D	380	198	µg/Kg	J
	Isopropylbenzene	S-42271-102705-WA-10	4.5 J	S-42271-102705-WA-10-D	600	197	µg/Kg	J
	Methyl cyclohexane	S-42271-102705-WA-10	1.1 J	S-42271-102705-WA-10-D	260 J	198	µg/Kg	J
	Methylene chloride	S-42271-102705-WA-10	13	S-42271-102705-WA-10-D	310 U	*	µg/Kg	J
	Toluene	S-42271-102705-WA-10	2.1 J	S-42271-102705-WA-10-D	230 J	196	µg/Kg	J
	Trichloroethene	S-42271-102705-WA-10	6.2 U	S-42271-102705-WA-10-D	18 J	*	µg/Kg	J
	Xylene (total)	S-42271-102705-WA-10	17	S-42271-102705-WA-10-D	2900	198	µg/Kg	J
Metals	Aluminum	W-42271-110305-WA-03	104000	W-42271-110305-WA-03D	48700	72	ug/L	J
	Arsenic	W-42271-110305-WA-03	46.7	W-42271-110305-WA-03D	18.3	87	ug/L	J
	Calcium	W-42271-110305-WA-03	819000	W-42271-110305-WA-03D	304000	92	ug/L	J
	Chromium	W-42271-110305-WA-03	164	W-42271-110305-WA-03D	68.4	82	ug/L	J
	Cobalt	W-42271-110305-WA-03	77.9	W-42271-110305-WA-03D	31.2	86	ug/L	J
	Copper	W-42271-110305-WA-03	193	W-42271-110305-WA-03D	71.9	91	ug/L	J
	Iron	W-42271-110305-WA-03	193000	W-42271-110305-WA-03D	77600	85	ug/L	J
	Lead	W-42271-110305-WA-03	102	W-42271-110305-WA-03D	42.3	83	ug/L	J
	Magnesium	W-42271-110305-WA-03	200000	W-42271-110305-WA-03D	96600	70	ug/L	J
	Manganese	W-42271-110305-WA-03	5880	W-42271-110305-WA-03D	2310	87	ug/L	J
	Nickel	W-42271-110305-WA-03	178	W-42271-110305-WA-03D	71.1	86	ug/L	J
	Vanadium	W-42271-110305-WA-03	235	W-42271-110305-WA-03D	99.6	81	ug/L	J
	Zinc	W-42271-110305-WA-03	465	W-42271-110305-WA-03D	187	85	ug/L	J

Notes:

* Cannot be calculated due to non-detect value.

[1] Qualifier is associated with both the original and duplicate sample.

J Estimated.

RPD Relative Percent Difference.

U Non-detect at associated value.

PROPRIETARY DOCUMENT

TABLE 14

QUALIFIED SAMPLE RESULTS DUE TO ANALYTE CONCENTRATIONS IN THE RINSE BLANKS
SUPPLEMENTAL REMEDIAL INVESTIGATION

Parameter	*Rinse Blank Date*	*Analyte*	*Blank Result* [1]	*Sample ID*	*Sample Result*	*Qualified Sample Result*	*Units*
Volatiles	10/27/05	Acetone	3.6J	S-42271-102705-WA-09-D	31	31 U	µg/Kg
				S-42271-102705-WA-13	4.8 J	22 U	µg/Kg
Volatiles	11/03/05	Acetone	1.0J	W-42271-110305-WA-01	1.0 J	10 U	µg/L
				W-42271-110305-WA-02	2.1 J	10 U	µg/L
				W-42271-110305-WA-03	1.0 J	10 U	µg/L
General Chemistry	11/03/05	Cyanide	0.0028	SW-42271-110405-WA-09	0.0081 J	0.010 U	mg/L
				W-42271-110305-WA-01	0.0019 J	0.010 U	mg/L
				W-42271-110305-WA-02	0.0037 J	0.010 U	mg/L
				W-42271-110305-WA-03	0.0024 J	0.010 U	mg/L
				W-42271-110405-WA-04	0.0066 J	0.010 U	mg/L
				W-42271-110405-WA-06	0.006 J	0.010 U	mg/L
				W-42271-110405-WA-07	0.0053 J	0.010 U	mg/L
				W-42271-110405-WA-12	0.0028 J	0.010 U	mg/L
				W-42271-110305-WA-03D	0.0022 J	0.010 U	mg/L
Metals	10/27/05	Selenium	0.42	W-42271-102505-WA-01	1.7	1.7 U	mg/Kg
			0.48	W-42271-102805-WA-14	0.86	0.86 U	mg/Kg
			0.42	S-42271-102705-WA-09-D	1.3	1.3 U	mg/Kg
			0.38	S-42271-102705-WA-10-D	0.82	0.82 U	mg/Kg
			0.41	S-042271-102705-WA-09	0.54	0.54 U	mg/Kg
			0.38	S-42271-102605-WA-02	1.2	1.2 U	mg/Kg
			0.44	S-42271-102605-WA-03	0.91	0.91 U	mg/Kg
			0.38	S-42271-102605-WA-06	0.67	0.67 U	mg/Kg
			0.38	S-42271-102605-WA-07	0.76 J	1.3 U	mg/Kg
			0.38	S-42271-102705-WA-10	1.3	1.3 U	mg/Kg
			0.38	S-42271-103105-WA-16	1.2	1.2 U	mg/Kg

Notes:

[1] Blank results corrected for preparation factors and sample dilutions, where applicable.

J Estimated.

U Non-detect at associated value.

PROPRIETARY DOCUMENT

TABLE 15

QUALIFIED SAMPLE RESULTS DUE TO ANALYTE CONCENTRATIONS IN THE TRIP BLANK
SUPPLEMENTAL REMEDIAL INVESTIGATION

Parameter	*Blank Date*	*Analyte*	*Blank Result*	*Associated Sample ID*	*Sample Result*	*Sample Qualifier*	*Units*
Volatiles	10/27/05	Acetone	3.6J	S-42271-102705-WA-09-D	31	31 U	µg/Kg
				S-42271-102705-WA-13	4.8 J	22 U	µg/Kg
Volatiles	11/03/05	Acetone	0.97J	W-42271-110305-WA-01	1.0 J	10 U	µg/L
				W-42271-110305-WA-02	2.1 J	10 U	µg/L
				W-42271-110305-WA-03	1.0 J	10 U	µg/L

Notes:
J Estimated.
U Non-detect at associated value.

PROPRIETARY DOCUMENT

TABLE 16

QUALIFIED SAMPLE RESULTS DUE TO DIFFERENCES IN DUAL COLUMN RESULTS
SUPPLEMENTAL REMEDIAL INVESTIGATION

Parameter	*Compound*	*Associated Sample ID*	*%D*	*Sample Results*		*Units*	*Reported Results*
				Column 1	*Column 2*		
Pesticides	gamma-Chlordane	S-42271-102605-WA-03	58.9	42.5	78	µg/Kg	78J
Pesticides	gamma-Chlordane	S-42271-102605-WA-04	68.6	84	40.7	µg/Kg	84J
Pesticides	Methoxychlor	S-42271-102605-WA-08	43.9	1100	704	µg/Kg	1100J
Pesticides	Endrin ketone	S-42271-102605-WA-08	42.4	280	182	µg/Kg	280J

Notes:
%D Percent Difference.
J Estimated.

ANALYTICAL RESULTS SUMMARY - SOIL SAMPLING - TICs
SUPPLEMENTAL REMIEDIAL INVESTIGATION

	Sample Location:	MW-3-05	MW-3-05	MW-5-05	MW-7-05
	Sample ID:	S-42271-102605-WA-06	S-42271-102605-WA-07	S-42271-102605-WA-08	S-42271-110105-WA-21
	Sample Date	10/26/2005	10/26/2005	10/26/2005	11/1/2005
Parameter	*Units*				
Tentatively Identified Compounds (TICs) - Volatile					
1,2,3,4-Tetramethyl-benzene	µg/kg	--	--	--	--
1,2,3-Trimethylbenzene	µg/kg	12 NJ	--	--	--
1-ethyl-2,4-dimethylbenzene	µg/kg	--	--	--	--
1-Ethyl-2-methylbenzene	µg/kg	6.0 NJ	--	--	--
1-Ethyl-2-methyl-cyclohexane	µg/kg	--	--	--	--
1-Ethyl-3-methylbenzene	µg/kg	--	--	--	--
1-Methyl-2-prop-cyclohexane	µg/kg	--	17000 NJ	--	--
1-Propenylbenzene	µg/kg	--	--	--	--
4-Ethyl-1,2-dimethylbenzene	µg/kg	6.8 NJ	--	--	--
4-Ethyl-2,2,6,6-tetramethylheptane	µg/kg	--	--	--	--
4-Octene, 2,6-dimethyl-, [S	µg/kg	--	14000 NJ	--	--
Benzene, (1-methyl-1-propenyl)-, (E)-	µg/kg	--	--	--	--
Benzene, 1,2-diethyl-	µg/kg	9.3 NJ	--	--	--
Benzene, 1,3,5-trimethyl-	µg/kg	--	--	--	--
Benzene, 1-ethyl-3,5-dimethyl-	µg/kg	7.2 NJ	--	--	--
Benzene, 1-methyl-2-(1-methylethyl)-	µg/kg	7.8 NJ	--	--	--
Benzene, 1-methyl-3-(1-methylethyl)-	µg/kg	--	--	--	--
Benzene, 1-methylpropyl-	µg/kg	--	--	--	--
Benzene, 2-ethly-1,4-dimethy	µg/kg	--	--	--	--
Bicyclo[3.3.1]nonane	µg/kg	--	--	--	--

ANALYTICAL RESULTS SUMMARY - SOIL SAMPLING - TICs
SUPPLEMENTAL REMIEDIAL INVESTIGATION

	Sample Location:	MW-3-05	MW-3-05	MW-5-05	MW-7-05
	Sample ID:	S-42271-102605-WA-06	S-42271-102605-WA-07	S-42271-102605-WA-08	S-42271-110105-WA-21
	Sample Date	10/26/2005	10/26/2005	10/26/2005	11/1/2005
Parameter	*Units*				
Tentatively Identified Compounds (TICs) - Volatile (Cont'd.)					
Camphene	µg/kg	–	–	–	–
Cycloheptane, methyl-	µg/kg	–	–	–	–
Cyclohexane, 1-methyl-3-pro	µg/kg	–	–	–	–
Cyclohexane, 1-methyl-4-(1-	µg/kg	–	–	–	–
Cyclohexane, butyl-	µg/kg	–	14000 NJ	–	–
Cymene	µg/kg	6.4 NJ	–	–	–
Decahydro-naphthalene	µg/kg	–	–	–	–
Decane, 3-methyl-	µg/kg	–	–	–	–
Dimethyl sulfide	µg/kg	–	–	–	–
Heptane, 3,3,5-trimethyl-	µg/kg	–	8700 NJ	–	–
Isopropyltoluene	µg/kg	–	–	–	–
Naphthalene, decahydro-, trans-	µg/kg	–	–	–	–
Octane, 3,3-dimethyl-	µg/kg	–	–	–	–
Octane, 4-ethyl-	µg/kg	–	10000 NJ	–	–

ANALYTICAL RESULTS SUMMARY - SOIL SAMPLING - TICs
SUPPLEMENTAL REMIEDIAL INVESTIGATION

	Sample Location:	*MW-9-05*	*POND*	*Low lying area near RCR Yacht*
	Sample ID:	*S-42271-110105-WA-18*	*S-42271-110305-WA-027*	*S-42271-110305-WA-025*
	Sample Date	*11/1/2005*	*11/3/2005*	*11/3/2005*
Parameter	***Units***			
Tentatively Identified Compounds (TICs) - Volatile				
1,2,3,4-Tetramethyl-benzene	µg/kg	--	--	--
1,2,3-Trimethylbenzene	µg/kg	--	--	--
1-ethyl-2,4-dimethylbenzene	µg/kg	--	--	--
1-Ethyl-2-methylbenzene	µg/kg	--	--	--
1-Ethyl-2-methyl-cyclohexane	µg/kg	--	--	--
1-Ethyl-3-methylbenzene	µg/kg	--	--	--
1-Methyl-2-prop-cyclohexane	µg/kg	--	--	--
1-Propenylbenzene	µg/kg	--	--	--
4-Ethyl-1,2-dimethylbenzene	µg/kg	--	--	--
4-Ethyl-2,2,6,6-tetramethylheptane	µg/kg	--	--	--
4-Octene, 2,6-dimethyl-, [S	µg/kg	--	--	--
Benzene, (1-methyl-1-propenyl)-, (E)-	µg/kg	--	--	--
Benzene, 1,2-diethyl-	µg/kg	--	--	--
Benzene, 1,3,5-trimethyl-	µg/kg	--	--	--
Benzene, 1-ethyl-3,5-dimethyl-	µg/kg	--	--	--
Benzene, 1-methyl-2-(1-methylethyl)-	µg/kg	--	--	--
Benzene, 1-methyl-3-(1-methylethyl)-	µg/kg	--	--	--
Benzene, 1-methylpropyl-	µg/kg	--	--	--
Benzene, 2-ethly-1,4-dimethy	µg/kg	--	--	--
Bicyclo[3.3.1]nonane	µg/kg	--	--	--

ANALYTICAL RESULTS SUMMARY - SOIL SAMPLING - TICs
SUPPLEMENTAL REMEDIAL INVESTIGATION

	Sample Location:	MW-9-05	POND	Low lying area near RCR Yacht
	Sample ID:	S-42271-110105-WA-18	S-42271-110305-WA-027	S-42271-110305-WA-025
	Sample Date	11/1/2005	11/3/2005	11/3/2005
Parameter	Units			
Tentatively Identified Compounds (TICs) - Volatile (Cont'd.)				
Camphene	µg/kg	--	--	--
Cycloheptane, methyl-	µg/kg	--	--	--
Cyclohexane, 1-methyl-3-pro	µg/kg	--	--	--
Cyclohexane, 1-methyl-4-(1-	µg/kg	--	--	--
Cyclohexane, butyl-	µg/kg	--	--	--
Cymene	µg/kg	--	--	--
Decahydro-naphthalene	µg/kg	--	--	--
Decane, 3-methyl-	µg/kg	--	--	--
Dimethyl sulfide	µg/kg	--	8.3 NJ	--
Heptane, 3,3,5-trimethyl-	µg/kg	--	--	--
Isopropyltoluene	µg/kg	--	--	--
Naphthalene, decahydro-, trans-	µg/kg	--	--	--
Octane, 3,3-dimethyl-	µg/kg	--	--	--
Octane, 4-ethyl-	µg/kg	--	--	--

Notes:

- Not analyzed.
J Estimated.
N Tentatively Identified.
PAH Polynuclear Aromatic Hydrocarbon.

APPENDIX B-2

FULL DATA VALIDATION MEMO TEMPLATE

CONESTOGA-ROVERS & ASSOCIATES

2055 Niagara Falls Blvd., Suite #3
Niagara Falls, New York 14304
Telephone: (716) 297-6150 Fax: (716) 297-2265
www.CRAworld.com
PROPRIETARY DOCUMENT

MEMORANDUM

TO:

REF. NO.:

FROM:

DATE: February 12, 2008
E-Mail and Hard Copy if Requested

RE: Analytical Results and QA/QC Review
Groundwater and Soil Investigation

July - August 2007

The following details a quality assessment and validation of the analytical data resulting from the July and August 2007 collection of groundwater and soil samples from the _____ Site in _____. The sample summary detailing sample identification, sample location, quality control (QC) samples, and analytical parameters is presented in Table 1. Sample analysis was completed at _____Laboratories, in _____, in accordance with the methodologies presented in Table 2. Summaries of the analytical results are presented in Tables 3A and 3B.

The QC criteria used to assess the data were established by the methods and with the following guidance documents:

i) "USEPA Contract Laboratory Program National Functional Guidelines for Organic Data Review", United States Environmental Protection Agency (USEPA) 540/R-99/008, October 1999; and

ii) "USEPA Contract Laboratory Program National Functional Guidelines for Inorganic Review", USEPA 540/R-94/013, February 1994.

These guidelines are collectively referred to as "Guidelines" in this memorandum.

Sample Quantitation

The laboratory reported detected concentrations of organic compounds and metals below the laboratory's practical quantitation limit (PQL)/report limit (RL) but above the laboratory's method detection limit (MDL). The laboratory flagged these sample concentrations with a "J". These concentrations should be qualified as estimated (J) values unless qualified otherwise in this memorandum.

Sample Preservation and Holding Times

Sample holding time periods and preservation requirements are summarized in the analytical methods. All sample extractions and/or analyses were performed within the specified holding times.

All samples were properly preserved and cooled to 4°C(±2°C) after collection.

REGISTERED COMPANY FOR ISO 9001 ENGINEERING DESIGN

Gas Chromatography/Mass Spectrometer (GC/MS) - Tuning and Mass Calibration (Instrument Performance Check) - Volatile Organic Compounds (VOCs) and Semi-Volatile Organic Compounds (SVOCs)

To ensure adequate mass resolution, identification, and to some degree, sensitivity; the performance of each GC/MS instrument used for VOC and SVOC analyses was checked at the beginning of each 12-hour period using bromofluorobenzene (BFB) and decafluorotriphenylphosphine (DFTPP), respectively. The resulting spectra must meet the criteria cited in the "Guidelines" before initiating an analysis sequence.

Instrument performance check data were reviewed. These tuning compounds were analyzed at the required frequency throughout the VOC and SVOC analyses. The results of all instrument performance checks were within the acceptance criteria, indicating acceptable instrument performance.

GC/MS Initial Calibration - VOCs and SVOCs

Initial calibration data are used to demonstrate that each instrument is capable of generating acceptable quantitative data. A five point calibration curve containing all compounds of interest is analyzed to characterize instrument response for each over a specific concentration range.

Initial calibration criteria for organic analyses are evaluated against the following criteria:

i) must meet a minimum mean relative response factor (RRF) of 0.05; and

ii) the percent relative standard deviation (%RSD) values must not exceed 30.0 percent or a minimum coefficient of determination (R^2) of 0.99 if quadratic equation calibration curves are used.

Calibration standards were analyzed at the required frequency and the results met the above criteria for sensitivity. Some SVOC compounds exhibited a high standard deviation, therefore not meeting the linearity criteria. All associated results were qualified as estimated (see Table 4).

GC/MS Continuing Calibration - VOCs and SVOCs

To ensure that each instrument was capable of producing acceptable quantitative data over the analysis period, continuing calibration standards must be analyzed every 12 hours. The following criteria are employed to evaluate the continuing calibration data:

i) must meet a minimum mean RRF of 0.05;

ii) the percent difference (%D) between the mean initial calibration RRF and the continuing calibration RRF must not exceed 25 percent; and

iii) the percent drift between the true value and the continuing calibration value must not exceed 25 percent.

Calibration standards were analyzed at the required frequency and the results met the above criteria for instrument sensitivity and linearity of response for most analytes. Some VOCs and SVOCs exhibited variability between the initial and continuing response factors. All associated results were qualified as estimated (see Table 5).

GC Initial Calibration - Pesticides, Herbicides, and Polychlorinated Biphenyls (PCBs)

To quantify compounds of interest, calibration of the GC over a specific concentration range must be performed. Initially, five-point calibration curves are analyzed for all the pesticides and herbicides of interest. PCB calibration curves are analyzed for Aroclors 1016 and1260 only. A single point calibration is performed for the remaining Aroclors of interest.

Linearity of the calibration curves are acceptable if percent %RSD values are less than or equal to 20 percent or if the coefficient of determination (R^2) is greater than 0.99. Retention time (RT) windows are also calculated from the initial calibration analyses. These windows are then used to identify all compounds of interest in subsequent analyses.

Initial calibration standards were analyzed at the required frequencies. All RT and linearity criteria were satisfied.

GC Continuing Calibration - Pesticides, Herbicides and PCBs

To ensure that the calibration of the instrument is valid throughout the sample analysis period, continuing calibration standards are analyzed and evaluated on a regular basis. To evaluate the continued linearity of the calibration, %D values are calculated for each compound in all continuing standards and assessed against an acceptance criterion of 15 percent.

To ensure that compound RTs do not vary over the analysis period, all RTs must fall within the established RT windows.

Continuing calibration standards were analyzed at the required frequency, and all method criteria were met for analyte linearity with the exception of some pesticides and herbicides exhibiting a %D greater than 15. All associated sample results were qualified as estimated (see Table 5).

Initial Calibration - Inorganic Analyses

Initial calibration of the instruments ensures that they are capable of producing satisfactory quantitative data at the beginning of a series of analyses. For trace inductively coupled plasma (ICP) analysis, a calibration blank and at least one standard must be analyzed at each wavelength to establish the analytical curve. Mercury analysis by cold vapor atomic absorption spectroscopy (CVAA) requires the analysis of a calibration blank and a minimum of five standards to establish the calibration curve. The coefficient of variation for calibration curves must exceed 0.995.

Initial calibration is verified with an initial calibration verification (ICV) standard which must recover within 90 to 110 percent for metals by ICP and 80 to 120 percent for mercury by CVAA.

A review of the laboratory data showed that all inorganic initial calibration curves and ICVs were analyzed at the appropriate frequency and were within the acceptance criteria.

Continuing Calibration - Inorganic Analyses

Continuing calibration verification (CCV) standards are analyzed at method specified frequency (one every 10 samples). The CCVs must meet the percent recovery control limits specified above for the ICVs. Criteria for inorganic analyses are the same criteria as used for assessing the initial calibration data.

A review of the laboratory data showed that CCVs were analyzed at the appropriate frequency and the data were within the acceptance criteria.

Method Blank Samples

Method blank samples are prepared from a purified sample matrix and are processed concurrently with investigative samples to assess the presence and the magnitude of sample contamination introduced during sample analysis. Method blank samples are analyzed at a minimum frequency of one per analytical batch and target analytes should be non-detect.

Method blanks were analyzed at the recommended frequency and the results were non-detect for all analytes of interest with the exception of methylene chloride and various metals present at low level concentrations. All associated positive sample results with similar concentrations were qualified as non-detect (see Table 6).

Laboratory Blank Samples - Inorganic Analyses

Metals analyses include the analysis of initial calibration blanks (ICB) and continuing calibration blanks (CCB) to assess the presence and the magnitude of sample contamination introduced during sample analysis. The CCBs are analyzed at a minimum frequency of one every 10 samples and target analytes should be non-detect.

All ICBs and CCBs were non-detect with the exception of beryllium present on September 7, 2007. All associated positive sample results with similar concentrations were qualified as non-detect (see Table 6).

Surrogate Compounds - Organic Analyses

Individual sample performance for organic analyses was monitored by assessing the results of surrogate compound percent recoveries. Surrogate percent recoveries are reviewed against the laboratory developed control limits provided in the analytical report.

All surrogate recoveries met the method criteria, demonstrating acceptable analytical efficiency for these analyses with the exception of high SVOC surrogates for sample GW-37191-082107-RN-007. All associated positive sample results were qualified as estimated (see Table 7) and all non-detect results would not have been impacted by the implied high bias.

Matrix Spike/Matrix Spike Duplicate (MS/MSD) Analyses

To assess the long term accuracy and precision of the analytical methods on various matrices, MS/MSD percent recoveries and relative percent differences (RPD) of the concentrations were determined. The organic MS/MSD percent recovery and RPD control limits are established by the laboratory. The inorganic control limits are defined by the methods and the "Guidelines", which require recoveries between 75 to 125 percent with RPDs less than 20 percent.

All MS/MSD recoveries were acceptable with the following exceptions:

i) high aluminum and cyanide recoveries were observed. All associated positive results were qualified as estimated and all non-detect results would not have been impacted by the implied high bias;

ii) due to matrix interference, the 4,4'-dichlorodiphenyltrichloroethane (DDT) recoveries could not be calculated. The associated sample result was qualified as estimated; and

iii) high variability was observed between trichloroethene recoveries. The associated sample result was qualified as estimated.

A summary of the qualified dated is presented in Table 8.

Laboratory Control Sample (LCS)

The LCS analysis serves as a monitor of the overall performance in all steps of the sample analysis and are analyzed with each sample batch. The LCS percent recoveries were evaluated against method and laboratory established control limits. Some LCS analyses were performed in duplicate to monitor laboratory precision.

The LCS percent recoveries were all within the laboratory control limits indicating acceptable analytical accuracy and precision (where applicable).

Internal Standard (IS) Summaries - Organic Analyses

To correct for variability in the GC/MS response and sensitivity, IS compounds are added to all samples. All results are calculated as a ratio of the compound and associated IS response. Overall instrument stability and performance for VOC and SVOC analyses were monitored using IS peak area and RT data. The IS peak areas and RTs of the samples are required to meet the following criteria:

i) IS area counts must not vary by more than a factor of two (-50 percent to +100 percent) from the associated continuing calibration standard IS area counts; and

ii) the RT of the IS must not vary by more than plus or minus 30 seconds from the associated continuing calibration standard.

A review of the VOC and SVOC internal standard data showed that the IS area counts and RT data were within the acceptance criteria for all VOC and SVOC samples.

ICP ICS Analysis - Inorganic Analyses

To verify that proper inter-element and background correction factors had been established by the laboratory for metals analyses, the ICP ICS are analyzed. The ICSs are evaluated against recovery control limits of 80 to 120 percent.

The ICS analysis results were evaluated for all samples and were within the control limits.

Serial Dilution - Inorganic Analyses

The %D between a serial dilution of a sample for each matrix was monitored to determine physical or chemical interference. A minimum of one sample per 20 investigative samples is analyzed at a five-fold dilution. The serial dilution results must agree within 10 %D of the original results for samples with detected concentrations greater than 50 times the instrument detection limit.

The %D acceptance criteria was met for all metals.

Target Compound Identification

To minimize erroneous compound identification during organic analyses, qualitative criteria including compound RT and mass spectra (if applicable) were evaluated according to identification criteria established by the methods. The organic compounds reported adhered to the specified identification criteria.

Target Compound Quantitation

The reported quantitation results and detection limits were checked to ensure results reported were accurate. No discrepancies were found between the raw data and the sample results reported by the laboratory.

Field Quality Assurance/Quality Control (QA/QC)

The field QA/QC consisted of five field duplicate sample sets and a trip blank.

Overall precision for the sampling event and laboratory procedures was monitored using the results of the field duplicate sample sets. The RPDs associated with these duplicate samples must be less than 50 percent for water and 100 percent for soil/sediment. If the reported concentration in either the investigative sample or its duplicate is less than five times the RL, the evaluation criteria is one times the RL value for water or two times for soil/sediment.

Most field duplicate results were acceptable indicating good field and analytical precision. Some variability was observed between VOC and metals concentrations. The samples and the associated field duplicate were qualified as estimated to reflect the implied variability (see Table 9).

To monitor potential cross-contamination of VOC during aqueous sample transportation and storage, a trip blank was submitted to the laboratory for VOC analysis with each shipping cooler containing multiple samples.

All trip blank results were non-detect for the compounds of interest.

Dual Column Analysis

Pesticide analyses were performed using dual column analyses. In general, the pesticide results showed good correlation between the two columns. Variability was observed between some of the results (see Table 10). The associated data were qualified as estimated to reflect the implied variability.

System Performance

System performance between various quality control checks was evaluated to monitor for changes that may have caused the degradation of data quality. No technical problems or chromatographic anomalies were observed which would require qualification of the data.

Overall Assessment

The data were found to exhibit acceptable levels of accuracy and precision, based on the provided information, and may be used with the qualifications noted herein.

PROPRIETARY DOCUMENT

TABLE 1

SAMPLE COLLECTION AND ANALYSIS SUMMARY
GROUNDWATER AND SOIL INVESTIGATION
SITE
JULY - AUGUST 2007

						Analysis/Parameters									
Sample I.D.	*Location I.D.*	*Collection Date (mm/dd/yy)*	*Collection Time (hr:min)*	*Start Depth (ft bgs)*	*End Depth (ft bgs)*	*TCL VOCs*	*TCL SVOCs*	*Lead*	*TAL Metals + Cn*	*Pesticides*	*Herbicides*	*PCBs*	*Dissolved Metals*	*Diss. Lead*	*Comments*
SO-37191-072507-RN-SB-1	SB-1-07	07/25/07	10:11	2	4	X	X		X	X	X	X			
SO-37191-072507-RN-SB-05	SB-5-07	07/25/07	12:44	4	8	X	X		X	X	X	X			
SO-37191-072507-RN-SB-10	SB-10-07	07/25/07	13:24	3	8	X	X	X							
SO-37191-072507-RN-SB-9	SB-9-07	07/25/07	13:50	3	6	X	X	X							
SO-37191-072507-RN-SB-7	SB-7-07	07/25/07	14:21	3	6	X	X	X							
SO-37191-072507-RN-SB-8	SB-8-07	07/25/07	14:55	3.5	8	X	X		X	X	X	X			
SO-37191-072607-RN-SB-11	SB-11-07	07/26/07	8:53	2	6	X	X	X							
SO-37191-072607-RN-SB-15	SB-15-07	07/26/07	9:33	4	8	X	X	X							

Notes:

-	Not analyzed.
Cn	Cyanide.
PCBs	Polychlorinated Biphenyls.
SVOCs	Semi-Volatile Organic Compounds.
TAL	Target Analyte List.
TCL	Target Compound List.
VOCs	Volatile Organic Compounds.

PROPRIETARY DOCUMENT

TABLE 2

SUMMARY OF ANALYTICAL METHODS
GROUNDWATER AND SOIL SAMPLING
SITE
JULY - AUGUST 2007

Parameter	*Method* [1]
Soil	
TCL VOCs	SW-846 8260B
TCL SVOCs	SW-846 8270C
TCL Pesticides	SW-846 8081
Herbicides	SW-846 8151
Polychlorinated Biphenyls	SW-846 8082
TAL Metals	SW-846 6010/7000 Series
Cyanide	SW-846 9012
Groundwater	
TCL VOCs	SW-846 8260B
TCL SVOCs	SW-846 8270C
TCL Pesticides	SW-846 8081
Herbicides	SW-846 8151
Polychlorinated Biphenyls	SW-846 8082
TAL Metals (total and dissolved)	SW-846 6010/7000 Series
Cyanide (total and dissolved)	SW-846 9012

Notes:

[1] "Test Methods for Solid Waste/Physical Chemical Methods", SW-846, 3rd Edition, September 1986 (with all subsequent revisions).

SVOCs Semi-Volatile Organic Compounds.
TAL Target Analyte List.
TCL Target Compound List.
VOCs Volatile Organic Compounds.

TABLE 3A
ANALYTICAL RESULTS SUMMARY
GROUNDWATER AND SOIL INVESTIGATION
SITE
JULY-AUGUST 2007

		New York State Water Quality		Location ID:	MW-5/BH-5	MW-8/BH-15	MW-9/BH-1	MW-12
				Sample Name:	WG-37191-082107-RN-003	WG-37191-082107-RN-006	WG-37191-082107-RN-007	WG-37191-082107-RN-004
				Sample Date:	8/21/2007	8/21/2007	8/21/2007	8/21/2007
Parameters	*Units*	*Standards*	*Guidance Values*					
Volatile Organic Compounds								
1,1,1-Trichloroethane	ug/L	5	NC		12000 U	5.0 U	5.0 U	15000 U
1,1,2,2-Tetrachloroethane	ug/L	5	NC		12000 U	5.0 U	5.0 U	15000 U
1,1,2-Trichloroethane	ug/L	1	NC		9800 J	5.0 U	5.0 U	15000 U
1,1-Dichloroethane	ug/L	5	NC		12000 U	5.0 U	5.0 U	15000 U
1,1-Dichloroethene	ug/L	5	NC		12000 U	5.0 U	5.0 U	15000 U
1,2,4-Trichlorobenzene	ug/L	5	NC		12000 U	5.0 U	5.0 U	15000 U
1,2-Dibromo-3-chloropropane (DBCP)	ug/L	0.04	NC		12000 U	5.0 U	5.0 U	15000 U
1,2-Dibromoethane (Ethylene Dibromide)	ug/L	0.0006	NC		12000 U	5.0 U	5.0 U	15000 U
1,2-Dichlorobenzene	ug/L	3	NC		12000 U	5.0 U	5.0 U	15000 U
1,2-Dichloroethane	ug/L	0.6	NC		12000 U	5.0 U	5.0 U	15000 U
1,2-Dichloropropane	ug/L	1	NC		12000 U	5.0 U	5.0 U	15000 U
1,3-Dichlorobenzene	ug/L	3	NC		12000 U	5.0 U	5.0 U	15000 U
1,4-Dichlorobenzene	ug/L	3	NC		12000 U	5.0 U	5.0 U	15000 U
2-Butanone (Methyl Ethyl Ketone)	ug/L	50	50		12000 U	5.0 U	5.0 U	15000 U
2-Hexanone	ug/L	50	50		12000 U	5.0 U	5.0 U	15000 U
4-Methyl-2-Pentanone (Methyl Isobutyl Ketone)	ug/L	NC	NC		12000 U	5.0 U	5.0 U	15000 U
Acetone	ug/L	NC	50		50000 U	20 UJ	20 UJ	60000 UJ
Benzene	ug/L	1	NC		12000 U	5.0 U	5.0 U	15000 U
Bromodichloromethane	ug/L	50	50		12000 U	5.0 U	5.0 U	15000 U
Bromoform	ug/L	50	50		12000 U	5.0 U	5.0 U	15000 U
Bromomethane (Methyl Bromide)	ug/L	5	NC		12000 U	5.0 U	5.0 U	15000 U
Carbon disulfide	ug/L	NC	60		12000 U	5.0 U	5.0 U	15000 U
Carbon tetrachloride	ug/L	5	NC		12000 U	5.0 U	5.0 U	15000 U
Chlorobenzene	ug/L	5	NC		12000 U	5.0 U	5.0 U	15000 U
Chloroethane	ug/L	5	NC		12000 UJ	5.0 U	5.0 U	15000 U
Chloroform (Trichloromethane)	ug/L	7	NC		12000 U	5.0 U	5.0 U	15000 U
Chloromethane (Methyl Chloride)	ug/L	5	NC		12000 U	5.0 U	5.0 U	15000 U
cis-1,2-Dichloroethene	ug/L	5	NC		240000	1.0 J	5.0 U	65000 J
cis-1,3-Dichloropropene	ug/L	NC	NC		12000 U	5.0 U	5.0 U	15000 U
Cyclohexane	ug/L	NC	NC		12000 U	5.0 U	5.0 U	15000 U
Dibromochloromethane	ug/L	50	50		12000 U	5.0 U	5.0 U	15000 U
Dichlorodifluoromethane (CFC-12)	ug/L	5	NC		12000 U	5.0 UJ	5.0 UJ	15000 UJ
Ethylbenzene	ug/L	5	NC		12000 U	5.0 U	5.0 U	15000 U
Isopropylbenzene	ug/L	5	NC		12000 U	5.0 U	5.0 U	15000 U
Methyl acetate	ug/L	NC	NC		12000 U	5.0 U	5.0 U	15000 U
Methyl cyclohexane	ug/L	NC	NC		12000 U	5.0 U	5.0 U	15000 U
Methyl Tert Butyl Ether	ug/L	NC	10		12000 U	5.0 U	5.0 U	15000 U

TABLE 3A
ANALYTICAL RESULTS SUMMARY
GROUNDWATER AND SOIL INVESTIGATION
SITE
JULY-AUGUST 2007

Parameters	Units	New York State Water Quality Standards	New York State Water Quality Guidance Values	Location ID: MW-5/BH-5 Sample Name: WG-37191-082107-RN-003 Sample Date: 8/21/2007	Location ID: MW-8/BH-15 Sample Name: WG-37191-082107-RN-006 Sample Date: 8/21/2007	Location ID: MW-9/BH-1 Sample Name: WG-37191-082107-RN-007 Sample Date: 8/21/2007	Location ID: MW-12 Sample Name: WG-37191-082107-RN-004 Sample Date: 8/21/2007
PCBs							
Aroclor-1016 (PCB-1016)	ug/L	NC	NC	–	–	0.41 U	–
Aroclor-1221 (PCB-1221)	ug/L	NC	NC	–	–	0.41 U	–
Aroclor-1232 (PCB-1232)	ug/L	NC	NC	–	–	0.41 U	–
Aroclor-1242 (PCB-1242)	ug/L	NC	NC	–	–	0.41 U	–
Aroclor-1248 (PCB-1248)	ug/L	NC	NC	–	–	0.41 U	–
Aroclor-1254 (PCB-1254)	ug/L	NC	NC	–	–	0.41 U	–
Aroclor-1260 (PCB-1260)	ug/L	NC	NC	–	–	0.41 U	–
WetChemistry							
Cyanide (total)	ug/L	200	NC	–	–	2.4 J	–

Notes:

–	Not analyzed.
1.0	Exceeds Criteria.
B	Compound detected in an associated blank.
BHC	Benzene Hexachloride.
D	Reported from a diluted analysis.
E	Exceeds the linear range of the instrument.
GC	Gas Chromatograph
J	Estimated.
N	Tentatively identified.
NC	No Criteria.
P	Greater
PCBs	Polychlorinated Biphenyls.
U	Not detected.
UJ	Not detected, estimated reporting limit.

TABLE 3B

ANALYTICAL RESULTS SUMMARY
SOIL INVESTIGATION
SITE
JULY - AUGUST 2007

Parameters	Units [1]	6 NYCRR Part 375-6.8(b): Restricted Use Soil Cleanup Objectives Protection of Public Health - Industrial	Location ID: SB-1-07 Sample Name: SO-37191-072507-RN-SB-1 Sample Date: 7/25/2007 Depth: 2 - 4 ft	SB-2-07 SO-37191-072707-RN-SB-2 7/27/2007 6.5 - 8 ft	SB-2-07 SO-37191-072707-RN-SB-20 7/27/2007 6.5 - 8 ft Duplicate	SB-3-07 SO-37191-072707-RN-SB-3 7/27/2007 10 - 13 ft	SB-4-07 SO-37191-072707-RN-SB-4 7/27/2007 2 - 4 ft
Volatile Organic Compounds							
1,1,1-Trichloroethane	mg/kg	1000	0.0069 U	0.0062 U	0.0067 U	0.006 U	0.0062 U
1,1,2,2-Tetrachloroethane	mg/kg	NC	0.0069 U	0.0062 U	0.0067 U	0.006 U	0.0062 U
1,1,2-Trichloroethane	mg/kg	NC	0.0069 U	0.0062 U	0.0067 U	0.006 U	0.0062 U
1,1-Dichloroethane	mg/kg	480	0.0069 U	0.0062 U	0.0067 U	0.006 U	0.0062 U
1,1-Dichloroethene	mg/kg	1000	0.0069 U	0.0062 U	0.0067 U	0.006 U	0.0062 U
1,2,4-Trichlorobenzene	mg/kg	NC	0.0069 U	0.0062 U	0.0067 U	0.006 U	0.0062 U
1,2-Dibromo-3-chloropropane (DBCP)	mg/kg	NC	0.0069 U	0.0062 U	0.0067 U	0.006 U	0.0062 U
1,2-Dibromoethane (Ethylene Dibromide)	mg/kg	NC	0.0069 U	0.0062 U	0.0067 U	0.006 U	0.0062 U
1,2-Dichlorobenzene	mg/kg	1000	0.0069 U	0.0062 U	0.0067 U	0.006 U	0.0062 U
1,2-Dichloroethane	mg/kg	60	0.0069 U	0.0062 U	0.0067 U	0.006 U	0.0062 U
1,2-Dichloropropane	mg/kg	NC	0.0069 U	0.0062 U	0.0067 U	0.006 U	0.0062 U
1,3-Dichlorobenzene	mg/kg	560	0.0069 U	0.0062 U	0.0067 U	0.006 U	0.0062 U
1,4-Dichlorobenzene	mg/kg	250	0.0069 U	0.0062 U	0.0067 U	0.006 U	0.0062 U
2-Butanone (Methyl Ethyl Ketone)	mg/kg	1000	0.0069 U	0.0062 U	0.0067 U	0.006 U	0.0062 U
2-Hexanone	mg/kg	NC	0.0069 U	0.0062 U	0.0067 U	0.006 U	0.0062 U
4-Methyl-2-Pentanone (Methyl Isobutyl Ketone)	mg/kg	NC	0.0069 U	0.0062 U	0.0067 U	0.006 U	0.0062 U
Acetone	mg/kg	1000	0.028 U	0.025 UJ	0.023 J	0.024 UJ	0.025 U
Benzene	mg/kg	89	0.0069 U	0.0062 U	0.0067 U	0.006 U	0.0062 U
Bromodichloromethane	mg/kg	NC	0.0069 U	0.0062 U	0.0067 U	0.006 U	0.0062 U
Bromoform	mg/kg	NC	0.0069 UJ	0.0062 UJ	0.0067 UJ	0.006 UJ	0.0062 UJ
Bromomethane (Methyl Bromide)	mg/kg	NC	0.0069 UJ	0.0062 UJ	0.0067 UJ	0.006 UJ	0.0062 UJ
Carbon disulfide	mg/kg	NC	0.0069 U	0.0062 U	0.0067 U	0.006 U	0.0062 U
Carbon tetrachloride	mg/kg	44	0.0069 U	0.0062 U	0.0067 U	0.006 U	0.0062 U
Chlorobenzene	mg/kg	1000	0.0069 U	0.0062 U	0.0067 U	0.006 U	0.0062 U
Chloroethane	mg/kg	NC	0.0069 UJ	0.0062 UJ	0.0067 UJ	0.006 UJ	0.0062 UJ
Chloroform (Trichloromethane)	mg/kg	700	0.0069 U	0.0062 U	0.0067 U	0.006 U	0.0062 U
Chloromethane (Methyl Chloride)	mg/kg	NC	0.0069 U	0.0062 U	0.0067 U	0.006 U	0.0062 U
cis-1,2-Dichloroethene	mg/kg	1000	0.0069 U	0.0014 J	0.0067 U	0.006 U	0.0062 U
cis-1,3-Dichloropropene	mg/kg	NC	0.0069 U	0.0062 U	0.0067 U	0.006 U	0.0062 U
Cyclohexane	mg/kg	NC	0.0069 U	0.0062 U	0.0067 U	0.006 U	0.0062 U
Dibromochloromethane	mg/kg	NC	0.0069 U	0.0062 U	0.0067 U	0.006 U	0.0062 U
Dichlorodifluoromethane (CFC-12)	mg/kg	NC	0.0069 U	0.0062 U	0.0067 U	0.006 U	0.0062 U

ANALYTICAL RESULTS SUMMARY
SOIL INVESTIGATION
SITE
JULY - AUGUST 2007

Parameters	Units [1]	6 NYCRR Part 375-6.8(b): Restricted Use Soil Cleanup Objectives Protection of Public Health - Industrial	Location ID: SB-1-07 Sample Name: SO-37191-072507-RN-SB-1 Sample Date: 7/25/2007 Depth: 2 - 4 ft	SB-2-07 SO-37191-072707-RN-SB-2 7/27/2007 6.5 - 8 ft	SB-2-07 SO-37191-072707-RN-SB-20 7/27/2007 6.5 - 8 ft Duplicate	SB-3-07 SO-37191-072707-RN-SB-3 7/27/2007 10 - 13 ft	SB-4-07 SO-37191-072707-RN-SB-4 7/27/2007 2 - 4 ft
Ethylbenzene	mg/kg	780	0.0069 U	0.0062 U	0.0067 U	0.006 U	0.0062 U
Isopropylbenzene	mg/kg	NC	0.0069 U	0.0062 U	0.0067 U	0.006 U	0.0062 U
Methyl acetate	mg/kg	NC	0.0069 U	0.0062 U	0.0067 U	0.006 U	0.0062 U
Pesticides (Cont'd.)							
Methoxychlor	mg/kg	NC	0.0035 J	–	–	0.0039 U	–
Toxaphene	mg/kg	NC	0.093 U	–	–	0.079 U	–
PCBs							
Aroclor-1016 (PCB-1016)	mg/kg	25	0.023 U	–	–	0.02 U	–
Aroclor-1221 (PCB-1221)	mg/kg	25	0.023 U	–	–	0.02 U	–
Aroclor-1232 (PCB-1232)	mg/kg	25	0.023 U	–	–	0.02 U	–
Aroclor-1242 (PCB-1242)	mg/kg	25	0.023 U	–	–	0.02 U	–
Aroclor-1248 (PCB-1248)	mg/kg	25	0.023 U	–	–	0.02 U	–
Aroclor-1254 (PCB-1254)	mg/kg	25	0.03	–	–	0.02 U	–
Aroclor-1260 (PCB-1260)	mg/kg	25	0.018 J	–	–	0.02 U	–
Wet Chemistry							
Cyanide (total)	mg/kg	10000	0.29 J	–	–	0.60 U	–
Total Solids	%	NC	72.4	80.7	75.2	83.8	81

Notes:

[1] Reported results were converted from ug/kg (ppb) to mg/kg (ppm) for ease of comparison to criteria.

[2] The Soil Cleanup Objective (SCO) for this specific compound (or family of compounds) is considered to be met if the analysis for the total species of this contaminant is below the specific SCO. The most restrictive SCO for hexavalent Chromium was used for comparison to the total chromium results.

\- Not analyzed.

1.0 Exceeds Criteria.

B Compound detected in an associated blank.

BHC Benzene Hexachloride.

D Reported from a diluted analysis.

E Exceeds the linear range of the instrument.

GC Gas Chromatograph

J Estimated.

N Tentatively identified.

NC No Criteria.

P Greater than 25% difference between concentrations detected on the two GC columns.

PCBs Polychlorinated Biphenyls.

U *Not detected.*

UJ Not detected, estimated reporting limit.

PROPRIETARY DOCUMENT

TABLE 4

QUALIFIED SAMPLE RESULTS DUE TO OUTLYING INITIAL CALIBRATION RESULTS
GROUNDWATER AND SOIL SAMPLING
SITE
JULY - AUGUST 2007

Parameter	*Compound*	*Calibration Date*	*%RSD*	*Associated Sample ID*	*Sample Results*	*Units*	*Qualifier*
SVOCs	2,4-Dinitrophenol	09/11/07	41	WG-37191-082107-RN-001	53 U	ug/L	UJ
				WG-37191-082107-RN-002	52 U	ug/L	UJ
				WG-37191-082107-RN-007	50 U	ug/L	UJ
SVOCs	Hexachlorocyclopentadiene	09/11/07	38	WG-37191-082107-RN-001	11 U	ug/L	UJ
				WG-37191-082107-RN-002	10 U	ug/L	UJ
				WG-37191-082107-RN-007	9.9 U	ug/L	UJ
SVOCs	2,4-Dinitrophenol	08/03/07	34	SO-37191-072507-RN-SB-05	2000 U	ug/Kg	UJ
				SO-37191-072507-RN-SB-1	2300 U	ug/Kg	UJ
				SO-37191-072507-RN-SB-10	2000 U	ug/Kg	UJ
				SO-37191-072507-RN-SB-7	5300 U	ug/Kg	UJ
				SO-37191-072507-RN-SB-8	2100 U	ug/Kg	UJ
				SO-37191-072507-RN-SB-9	2000 U	ug/Kg	UJ
				SO-37191-072607-RN-SB-11	2200 U	ug/Kg	UJ
				SO-37191-072607-RN-SB-12	2100 U	ug/Kg	UJ
				SO-37191-072607-RN-SB-13	2000 U	ug/Kg	UJ
				SO-37191-072607-RN-SB-14	1900 U	ug/Kg	UJ
				SO-37191-072607-RN-SB-15	2000 U	ug/Kg	UJ
				SO-37191-072607-RN-SB-16	2200 U	ug/Kg	UJ
				SO-37191-072707-RN-SB-17	2400 U	ug/Kg	UJ
				SO-37191-072707-RN-SB-27	1900 U	ug/Kg	UJ
				SO-37191-072707-RN-SB-20	4400 U	ug/Kg	UJ
				SO-37191-072707-RN-SB-2	4100 U	ug/Kg	UJ
				SO-37191-072707-RN-SB-3	2000 U	ug/Kg	UJ
				SO-37191-072707-RN-SB-4	2100 U	ug/Kg	UJ
				SO-37191-073007-CB-SB6	1900 U	ug/Kg	UJ

Notes:
%RSD Percent Relative Standard Deviation.
SVOCs Semi-Volatile Organic Compounds.
U Not detected.
UJ Not detected, estimated reporting limit.

PROPRIETARY DOCUMENT

TABLE 5

QUALIFIED SAMPLE RESULTS DUE TO OUTLYING CONTINUING CALIBRATION RESULTS
GROUNDWATER AND SOIL SAMPLING
SITE
JULY - AUGUST 2007

Parameter	Calibration Date	Compound	%D	Associated Sample ID	Sample Results	Units	Qualifier
VOCs	08/27/07	Acetone	41	WG-37191-082107-RN-001	600 U	ug/L	UJ
				WG-37191-082107-RN-004	60000 U	ug/L	UJ
				WG-37191-082107-RN-006	20 U	ug/L	UJ
				WG-37191-082107-RN-007	20 U	ug/L	UJ
VOCs	08/28/07	Chloroethane	74	WG-37191-082107-RN-002	100 U	ug/L	UJ
VOCs	08/30/07	Chloroethane	84	WG-37191-082107-RN-005	1200 U	ug/L	UJ
VOCs	09/02/07	Chloroethane	39	WG-37191-082107-RN-003	12000 U	ug/L	UJ
VOCs	08/27/07	Dichlorodifluoromethane (CFC-12)	39	WG-37191-082107-RN-001	150 U	ug/L	UJ
				WG-37191-082107-RN-004	15000 U	ug/L	UJ
				WG-37191-082107-RN-006	5.0 U	ug/L	UJ
				WG-37191-082107-RN-007	5.0 U	ug/L	UJ
VOCs	09/02/07	Trichlorofluoromethane (CFC-11)	49	WG-37191-082107-RN-003	12000 U	ug/L	UJ
				SO-37191-072707-RN-SB-3	0.98 J	ug/Kg	J

Notes:

%D	Percent Difference.
J	Estimated.
SVOCs	Semi-Volatile Organic Compounds.
U	Not detected.
UJ	Not detected, estimated reporting limit.
VOCs	Volatile Organic Compounds.

TABLE 6

QUALIFIED SAMPLE RESULTS DUE TO ANALYTE CONCENTRATIONS IN THE METHOD BLANKS
GROUNDWATER AND SOIL SAMPLING
SITE
JULY - AUGUST 2007

Parameter	*Analysis Date*	*Analyte*	*Blank Result*	*Sample ID*	*Sample Result*	*Qualified Result*
VOCs	08/01/07	Methylene chloride	2.1	SO-37191-072507-RN-SB-05	3.5 J	6.0 U
				SO-37191-072507-RN-SB-1	3.9 J	6.9 U
				SO-37191-072507-RN-SB-10	3.2 J	5.9 U
				SO-37191-072507-RN-SB-9	6.1	6.1 U
				SO-37191-072607-RN-SB-11	3.3 J	6.7 U
				SO-37191-072607-RN-SB-12	4.0 J	6.2 U
				SO-37191-072607-RN-SB-15	3.1 J	6.1 U
				SO-37191-072707-RN-SB-17	4.0 J	7.2 U
				SO-37191-072707-RN-SB-4	3.1 J	6.2 U
				SO-37191-072707-RN-SB-20	5.3 J	6.7 U
				SO-37191-072707-RN-SB-27	2.6 J	5.7 U
VOCs	08/01/07	Methylene chloride	56	SO-37191-072507-RN-SB-7	130 J	400 U
				SO-37191-072607-RN-SB-13	190 J	310 U
VOCs	08/01/07	Methylene chloride	1.2	SO-37191-072507-RN-SB-8	1.7 J	6.1 U
				SO-37191-072607-RN-SB-14	1.4 J	5.7 U
				SO-37191-072607-RN-SB-16	1.3 J	6.7 U
				SO-37191-072707-RN-SB-3	1.5 J	6.0 U
VOCs	08/02/07	Methylene chloride	1.5	SO-37191-073007-CB-SB18	1.6 J	5.2 U
VOCs	08/03/07	Methylene chloride	100	SO-37191-073007-CB-SB6	380 J	380 U
				SO-37191-073007-CB-SB19	210 J	280 U
Metals	9/7/07-ICB	Beryllium	1.0	WG-37191-082107-RN-001	0.48	4.0 U
				WG-37191-082107-RN-002	0.82	4.0 U
				WG-37191-082107-RN-007	1.2	4.0 U
Metals	08/30/07	Aluminum (Dissolved)	18.4	WG-37191-082107-RN-001	53.3	200 U
				WG-37191-082107-RN-002	65.3	200 U
				WG-37191-082107-RN-007	37.1	200 U
Metals	08/30/07	Beryllium (Dissolved)	0.65	WG-37191-082107-RN-001	0.58	4.0 U
				WG-37191-082107-RN-002	0.60	4.0 U
				WG-37191-082107-RN-007	0.64	4.0 U
Metals	8/30/07	Cadmium	0.33	WG-37191-082107-RN-001	0.71	5.0 U
				WG-37191-082107-RN-002	0.44	5.0 U

Notes:
J Estimated.
U Not detected.
VOCs Volatile Organic Compounds.

TABLE 7

QUALIFIED SAMPLE DATA DUE TO QUALIFYING SURROGATE RECOVERIES
GROUNDWATER AND SOIL SAMPLING
SITE
JULY - AUGUST 2007

Parameter	*Surrogate*	*Surrogate Recovery (percent)*	*Control Limits (percent)*	*Sample ID*	*Analytes*	*Sample Results*	*Units*	*Qualifier*
SVOCs	2-Fluorobiphenyl	99	34-97	WG-37191-082107-RN-007	bis(2-Ethylhexyl)phthalate	2.4 J	ug/L	J
	Nitrobenzene-d5	111	38-97		2-Methylnaphthalene	0.62 J	ug/L	J

Notes:
J Estimated.
SVOCs Semi-Volatile Organic Compounds.

PROPRIETARY DOCUMENT

TABLE 8

QUALIFIED SAMPLE RESULTS DUE TO OUTLYING MATRIX SPIKE/MATRIX SPIKE DUPLICATE RECOVERIES
GROUNDWATER AND SOIL SAMPLING
SITE
JULY - AUGUST 2007

Parameter	*Analyte*	*Associated Sample ID*	*MS Recovery (percent)*	*MSD Recovery (percent)*	*RPD*	*Control Limits*		*Sample Result*	*Units*	*Qualifier*
						Recovery (percent)	*RPD (percent)*			
Metals	Aluminum	WG-37191-082107-RN-001	183	168	9	75-125	30	5110	ug/L	J
		WG-37191-082107-RN-002						4190	ug/L	J
		WG-37191-082107-RN-007						8250	ug/L	J
Pesticides	4,4'-DDT	SO-37191-072507-RN-SB-1	MI	MI	-	70-130	20	1.7 J	ug/kg	J
General Chemistry	Cyanide (total)	SO-37191-072507-RN-SB-1	131	130	1	75-125	20	0.29	mg/kg	J
		SO-37191-072507-RN-SB-8						0.23	mg/kg	J
VOCs	Trichloroethene	SO-37191-072707-RN-SB-17	28	127	128	46-141	20	140	ug/kg	J

Notes:
- Not applicable.
J Estimated.
MI Matrix interference. Recoveries were not calculated.
MS Matrix Spike.
MSD Matrix Spike Duplicate.
RPD Relative Percent Difference.
VOCs Volatile Organic Compounds.

TABLE 9

QUALIFIED SAMPLE RESULTS DUE TO VARIABILITY IN FIELD DUPLICATE RESULTS
GROUNDWATER AND SOIL SAMPLING
SITE
JULY - AUGUST 2007

Parameter	*Analyte*	*Original Sample ID*	*Original Result*	*Duplicate Sample ID*	*Duplicate Result*	*RPD*	*Units*	*Qualifier* [1]
VOCs	cis-1,2-Dichloroethene	WG-37191-082107-RN-001	2200	WG-37191-082107-RN-002	1100	67	ug/L	J
VOCs	Trichloroethene	WG-37191-082107-RN-001	2000	WG-37191-082107-RN-002	1000	67	ug/L	J
VOCs	cis-1,2-Dichloroethene	WG-37191-082107-RN-004	65000	WG-37191-082107-RN-005	25000	89	ug/L	J
VOCs	Trichloroethene	WG-37191-082107-RN-004	190000	WG-37191-082107-RN-005	26000	152	ug/L	J
Metals	Lead	WG-37191-082107-RN-001	56.8	WG-37191-082107-RN-002	30.0	52	ug/L	J
Metals	Lead	SO-37191-072707-RN-SB-17	155	SO-37191-072707-RN-SB-27	13.4	200	mg/Kg	J

Notes:
[1] Qualifier is associated with both original and duplicate result.
J Estimated.
RPD Relative Percent Difference.
VOCs Volatile Organic Compounds.

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TABLE 10

QUALIFIED SAMPLE RESULTS DUE TO DIFFERENCES IN DUAL COLUMN RESULTS
GROUNDWATER AND SOIL SAMPLING
SITE
JULY - AUGUST 2007

Parameter	*Compound*	*Associated Sample ID*	*%D*	*Sample Results*		*Units*	*Reported Results*
				Column 1	*Column 2*		
Pesticides	delta-BHC	WG-37191-082107-RN-007	131	0.081	0.017 J	ug/L	0.081 U
	Endrin aldehyde	WG-37191-082107-RN-007	82	0.036 J	0.015 J	ug/L	0.051 U

Notes:

%D	Percent Difference.
BHC	Benzene Hexachloride.
J	Estimated.
U	Not detected.

APPENDIX B-3

REDUCED DATA VALIDATION REPORT TEMPLATE

CONESTOGA-ROVERS & ASSOCIATES

2055 Niagara Falls Blvd., Suite #3
Niagara Falls, New York 14304
Telephone: (716) 297-6150 Fax: (716) 297-2265
www.CRAworld.com
PROPRIETARY DOCUMENT

MEMORANDUM

TO:

REF. NO.:

FROM:

DATE:

E-Mail and Hard Copy if Requested

C.C.:

RE: **Analytical Results and QA/QC Review**

Semi-Annual Groundwater Sampling Program

INTRODUCTION

Thirteen groundwater samples including one field duplicate were collected in support of the Semi-Annual Sampling Monitoring Program at the _____ Site during _____. Samples were submitted to ____ Labs, located in _____. A sample key is presented in Table 1 and the analytical parameter list, methodologies, and holding time criteria are presented in Table 2. The analytical results are summarized in Table 3. Copies of the Chain of Custody are attached.

The final results and supporting quality assurance/quality control (QA/QC) data were reviewed. Evaluation of the data was based on information obtained from the Chain of Custody forms, finished report forms, blank data, and recovery data for matrix and surrogate spikes. The QA/QC criteria by which the data have been assessed are outlined in the respective methods and the following documents:

i) "USEPA Contract Laboratory Program National Functional Guidelines for Organic Data Review," October 1999, United States Environmental Protection Agency (USEPA) 540/R-99/008; and

ii) "USEPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review," February 1994, USEPA 540/R-94/013.

QA/QC REVIEW

Sample holding times were assessed against the criteria outlined in Table 2. All holding time criteria were met, and all samples were properly preserved and maintained at 4°C (±2°C).

Method blanks were analyzed with the investigative samples for all parameters. All method blank results were non-detect for the compounds of interest.

All samples and blanks were spiked with surrogate compounds prior to sample extraction and/or analysis in accordance with the organic methods. All surrogate spike recoveries met the associated method criteria

indicating adequate analytical efficiency with the exception of a high recovery for diesel range organics. All associated positive sample results were qualified as estimated based on the implied high bias (see Table 4).

A blank spike and/or blank spike duplicate (BS and/or BSD) was analyzed for all parameters. All recoveries were within the laboratory control limits indicating good analytical accuracy and/or precision.

A matrix spike/matrix spike duplicate (MS/MSD) was analyzed for dissolved iron, ferrous iron, nitrate, sulfate, and total alkalinity. All recoveries were within the laboratory control limits indicating good analytical accuracy and precision, with the exception of low recoveries for sulfate. All associated sample results were qualified as estimated based on the implied low bias (see Table 5).

Trip blanks were collected and analyzed with the investigative samples for gasoline range organics. All trip blank results were non-detect for the compounds of interest.

A field duplicate sample was collected and analyzed as shown in Table 1. All results showed good precision.

CONCLUSION

Based on this QA/QC review, the data summarized in Table 3 were judged to be acceptable with the qualifications noted.

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TABLE 1

SAMPLING AND ANALYSIS SUMMARY
SEMI-ANNUAL GROUNDWATER SAMPLING PROGRAM

				Analysis/Parameters								
Sample ID	*Location ID*	*Collection Date (mm/dd/yy)*	*Collection Time (hr:min)*	*TPHg (BTEX, Gasoline)*	*TPHd (Motor Oil, Diesel)*	*Dissolved Iron*	*Ferrous Iron*	*Total Alkalinity*	*Nitrate*	*Sulfate*	*Carbon Dioxide, Methane*	*Comments*
GW020807JSMW110	MW-110	02/08/07	11:00:00	X	X	X	X	X	X	X	X	
GW020807JSMW106	MW-106	02/08/07	12:50:00	X	X	X	X	X	X	X	X	
GW020807JSMW109	MW-109	02/08/07	15:40:00	X	X	X	X	X	X	X	X	
GW020807JSMW108	MW-108	02/08/07	17:10:00	X	X	X	X	X	X	X	X	
GW021107JSMW107	MW-107	02/12/07	9:55:00	X	X	X	X	X	X	X	X	
GW021107JSMW105	MW-105	02/12/07	10:40:00	X	X	X	X	X	X	X	X	
GW021107JSMW103	MW-103	02/12/07	13:22:00	X	X	X	X	X	X	X	X	
GW021107JSMW102	MW-102	02/12/07	14:59:00	X	X	X	X	X	X	X	X	
GW021307JSMW104	MW-104	02/13/07	12:23:00	X	X	X	X	X	X	X	X	
GW021307JSMW904	MW-104	02/13/07	14:32:00	X	X	X	X	X	X	X	X	Field duplicate of GW021307JSMW104
GW021307JSMW104-26	MW-104 @ 26 feet	02/13/07	10:23:00	X								
GW021307JSMW104-30	MW-104 @ 30 feet	02/13/07	10:27:00	X								
GW021307JSMW104-34	MW-104 @ 34 feet	02/13/07	10:39:00	X								

Notes:
BTEX Benzene, Toluene, Ethylbenzene, and Xylene.
TPH Total Petroleum Hydrocarbons.

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TABLE 2

ANALYTE PARAMETER LIST
SEMI-ANNUAL GROUNDWATER SAMPLING PROGRAM

Analytical Parameter	*Method Number*	*Holding Time Criteria*
DRO - Diesel/Motor Oil	USEPA 8015B/3501C [1]	7 days from collection to extraction 40 days from extraction to analysis (preserved with HCl pH<2)
GRO/BTEX	USEPA 8015B/5030B [1]	14 days from collection to analysis (preserved with HCl pH<2)
Dissolved Iron	USEPA 6020 [1]	180 days from collection to analysis (preserved with HNO_3 pH<2)
Ferrous Iron	SM 3500 Fe D [2]	Analyze in the field or immediately upon receipt in the laboratory
Alkalinity (as CaCO3)	SM 2320B [2]	14 days from collection to analysis
Nitrate	USEPA 353.2 [3]	48 hours from collection to analysis
Sulfate	USEPA 300.0 [3]	28 hours from collection to analysis
Carbon Dioxide	RSK-175 [4]	14 days from collection to analysis
Methane	RSK-175 [4]	14 days from collection to analysis

Notes:

(1) "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods," 3rd Edition, November, 1986 (with all subsequent revisions).

(2) revisions).

(3) "Methods for Chemical Analysis of Water and Wastes," USEPA 600/4-79-020, March 1983.

(4) USEPA Internal Standard Operating Procedure dated August 11, 1994 by Bryan Newell at the R. S. Kerr Laboratory in Oklahoma.

BTEX Benzene, Toluene, Ethylbenzene, and Xylene.

DRO Diesel Range Organics.

GRO Gasoline Range Organics.

USEPA United States Environmental Protection Agency.

PROPRIETARY DOCUMENT

TABLE 3

ANALYTICAL RESULTS SUMMARY
SEMI-ANNUAL GROUNDWATER SAMPLING PROGRAM

Parameters	Units	Sample Location:	MW-102	MW-103	MW-104	MW-104	MW-104	MW-104	MW-104
		Sample ID:	GW021207JSMW102	GW021207JSMW103	GW021307JSMW104	GW021307JSMW904	GW021307JSMW104-26	GW021307JSMW104-30	GW021307JSMW104-34
		Sample Date:	2/12/2007	2/12/2007	2/13/2007	2/13/2007 Duplicate	2/13/2007	2/13/2007	2/13/2007
Petroleum Products									
Benzene	µg/L		36	0.5 U	530	510	53	1400	460
Ethylbenzene	µg/L		0.5 U	0.5 U	11	11	0.5 U	5.9	8.2
Toluene	µg/L		0.5 U	0.5 U	0.5 U	0.5 U	0.5 U	0.5 U	0.5 U
Xylene (total)	µg/L		0.5 U	0.5 U	0.5 U	0.5 U	0.5 U	0.5 U	0.5 U
Diesel Fuel	µg/L		330	330	390 J	410 J	-	-	-
Gasoline	µg/L		140	20 U	1200	1200	130	3100	1000
TPH-Motor Oil	µg/L		250 U	310	250 U	250 U	-	-	-
Metals									
Iron (Dissolved)	µg/L		820	236	6410	6520	-	-	-
Ferrous Iron	mg/L		1.0	1.0 U	10.7	10.8	-	-	-
Gas									
Carbon dioxide	µg/mL		200	120	240	240	-	-	-
Methane	µg/mL		0.36	0.036	0.02	0.021	-	-	-
General Chemistry									
Alkalinity, Total (as CaCO3)	mg/L		998	398	1400	1400	-	-	-
Nitrate (as N)	mg/L		0.43	0.45	0.60	0.52	-	-	-
Sulfate	mg/L		7590 J	1270 J	10600 J	10400 J	-	-	-

Parameters	Units	Sample Location:	MW-105	MW-106	MW-107	MW-108	MW-109	MW-110
		Sample ID:	GW021207JSMW105	GW020807JSMW106	GW021207JSMW107	GW020807JSMW108	GW020807JSMW109	GW020807JSMW110
		Sample Date:	2/12/2007	2/8/2007	2/12/2007	2/8/2007	2/8/2007	2/8/2007
Petroleum Products								
Benzene	µg/L		0.5 U	0.5 U	0.5 U	0.5 U	0.5 U	0.5 U
Ethylbenzene	µg/L		0.5 U	0.5 U	0.5 U	0.5 U	0.5 U	0.5 U
Toluene	µg/L		0.5 U	0.5 U	0.5 U	0.5 U	0.5 U	0.5 U
Xylene (total)	µg/L		0.5 U	0.5 U	0.5 U	0.5 U	0.5 U	0.5 U
Diesel Fuel	µg/L		50 U	590	480	50 U	50 U	50 U
Gasoline	µg/L		20 U	20 U	20 U	20 U	20 U	20 U
TPH-Motor Oil	µg/L		250 U	250 U	250 U	250 U	250 U	250 U
Metals								
Iron (Dissolved)	µg/L		4260	50 U	228	50 U	132	1570
Ferrous Iron	mg/L		7.7	1.0 U	1.0 U	1.0 U	1.0 U	0.89J
Gas								
Carbon dioxide	µg/mL		67.0	59.0	60.0	58.0	16.0	110
Methane	µg/mL		0.010 U	0.010 U	0.010 U	0.010 U	0.34	0.010 U
General Chemistry								
Alkalinity, Total (as CaCO3)	mg/L		388	179	386	345	464	815
Nitrate (as N)	mg/L		2.0	3.9	1.4	4.5	3.5	2.3
Sulfate	mg/L		15900 J	24.5 J	2390 J	532 J	2310 J	1240 J

Notes:
- Not analyzed.
J Estimated.
TPH Total Petroleum Hydrocarbon.
U Non-detect at associated value.

TABLE 4

QUALIFIED SAMPLE RESULTS DUE TO OUTLYING SURROGATE RECOVERIES
SEMI-ANNUAL GROUNDWATER SAMPLING PROGRAM

Parameter	*Surrogate*	*Surrogate Recovery (percent)*	*Control Limits (percent)*	*Sample ID*	*Analyte*	*Sample Results*	*Units*	*Qualifier*
TPH	Octacosane	145	28-142	GW021307JSMW104	Diesel Fuel	390	µg/L	J
				GW021307JSMW904		410	µg/L	J

Notes:
J Estimated.
TPH Total Petroleum Hydrocarbons.

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TABLE 5

QUALIFIED SAMPLE RESULTS DUE TO OUTLYING MATRIX SPIKE/MATRIX SPIKE DUPLICATE RECOVERIES
SEMI-ANNUAL GROUNDWATER SAMPLING PROGRAM

Parameter	*Associated Sample ID*	*Analyte*	*MS Recovery (percent)*	*MSD Recovery (percent)*	*RPD*	*Control Limits*		*Sample Result*	*Units*	*Qualifier*
						Recovery (percent)	*RPD (percent)*			
General Chemistry	GW020807JSMW110	Sulfate	75	74	0.3	90-110	20	1240	mg/L	J
	GW020807JSMW106							24.5	mg/L	J
	GW020807JSMW108							532	mg/L	J
	GW020807JSMW109							2310	mg/L	J
General Chemistry	GW021207JSMW107	Sulfate	60	60	0.0	90-110	20	2390	mg/L	J
	GW021207JSMW102							7590	mg/L	J
	GW021207JSMW103							1270	mg/L	J
	GW021207JSMW105							15900	mg/L	J
General Chemistry	GW021307JSMW104	Sulfate	67	68	0.43	90-110	20	10600	mg/L	J
	GW021307JSMW904							10400	mg/L	J

Notes:
J Estimated.
MS Matrix Spike.
MSD Matrix Spike Duplicate.
RPD Relative Percent Difference.

CONESTOGA-ROVERS
& ASSOCIATES

651 Colby Drive, Waterloo, Ontario, Canada N2V 1C2
Telephone: 519-884-0510 Facsimile: 519-884-0525
www.CRAworld.com

September 8, 2008 Reference No. 039611

Mr. Rosauro del Rosario
EPA Project Manager/Coordinator
United States Environmental Protection Agency
Region 5
77 West Jackson Boulevard
Chicago, IL 60604

Dear Mr. del Rosario:

Re: Response to Comments on Remedial Design Work Plan
Himco Site, Elkhart, Indiana (Site)

Conestoga-Rovers & Associates (CRA) prepared this response to comments on behalf of the Himco Site Trust (the Trust) in response to your letter dated July 8, 2008. The responses to your comments in this letter reflect the July 24, 2008 teleconference discussions with the Trust, CRA, the Indiana Department of Environmental Management (IDEM), the United States Army Corps of Engineers (USACE) and the United States Environmental Protection Agency (USEPA), and subsequent email and telephone correspondence. As requested, we have also attached the revised pages, tables, and figures from Remedial Design Work Plan (RD Work Plan) and appendices, which we have amended to address your comments. The changes to the documents are shown in redline/strikeout format for ease of review.

For clarity, your comments have been reproduced verbatim from your July 8, 2008 correspondence, and are shown in italics, followed by CRA's response.

WORK PLAN COMMENTS

General Comments:

General Comment #1

The basis for using MCLs exclusively to screen groundwater data is still problematic. Although the site is officially in the remedial design phase of the project, it has not been completely characterized in regard to delineation of contaminants. It is recommended that groundwater data collected as part of the VAS be screened using concentrations based on risk. For those contaminants with MCL concentrations that represent a target cancer risk equal to or in excess of 1 × 10-4 risk (arsenic, TCE, vinyl chloride), an alternate risk-based concentration is recommended.

In regard to soil screening, it is recommended that the actual values from IDEM's Residential Default Closure Levels be presented. This will ensure that the laboratory methods have adequate sensitivity to meet the objectives, that field decisions are based on a single standard that is apparent to all, and it could prevent confusion should the state revise the standards before the remedial action is complete.

Response #1

As agreed during a teleconference on August 27, 2008, CRA will use the Targeted Quantitation Limits (TQLs) presented in Table 3.2 of the EPA-approved Quality Assurance Project Plan (QAPP) as screening values for evaluating concentrations of trichloroethylene (TCE), vinyl chloride and arsenic in groundwater samples to be collected during groundwater monitoring activities outlined in the Remedial Design (RD) Work Plan. Data reporting will include analytes detected in soil and groundwater samples at estimated concentrations greater than or equal to their respective method detection limit (MDL) but less than their respective TQLs. The concentrations of organic and inorganic analytes detected between the MDL and TQL will be flagged by the laboratory with the "J" qualifier and the "B" qualifier, respectively. Summary tables of validated data prepared by CRA also will include estimated concentrations, but the data validation "J" qualifier will be used to identify estimated concentrations for both organic and inorganic analytes.

The TQLs and the laboratory's current MDLs for TCE, vinyl chloride and arsenic in groundwater follow.

TCE: TQL = 1.0 µg/L; MDL = 0.17 µg/L
Vinyl chloride: TQL = 1.0 µg/L; MDL = 0.22 µg/L
Arsenic: TQL = 1.0 µg/L; MDL = 0.40 µg/L

As discussed, a note will be included in tables summarizing groundwater monitoring data that provides the 10^{-5} cancer risk concentration for these three analytes.

As agreed during the July 24, 2008 teleconference, soil collected from residential properties will be screened using the IDEM's Residential Default Closure Levels and soils collected outside of residential properties will be screened using the IDEM's Industrial Default Closure Levels. The soil screening criteria are presented in Table 4.4 of the revised RD Work Plan.

Specific Comments:

Specific Comment #2.1

One sample per two acres is still somewhat sparse; however, this may be acceptable as the author has indicated it intends to collect additional samples in areas of stressed vegetation that are outside the grid.

Response #2.1

No response required.

Specific Comment #2.4

In section 4.1, the text indicates elevation will be surveyed at 50-foot intervals. It may be possible to lay that grid on top of the 100-foot boring grid to guarantee all boring locations are surveyed as well.

Response #2.4

Noted. This may be possible in many cases except where the surveyor will bias the topographic survey towards surface features rather than a grid pattern.

Specific Comment #3

This may be adequate, but we are interested in determining the author's definition of "cover". The Consent Decree (CD) anticipates 18-24 inches of soil cover will be necessary, not the 18-24 inches of calcium sulfate cover. This definition should be discussed to determine if both the regulatory agencies and the author agree on this definition.

Response #3

As discussed in the teleconference on July 24, 2008, the definition of cover soils does not include the thickness of existing calcium sulfate. The purpose of the evaluation is to determine areas of the existing soil cover that can be used as a portion of the thickness of the final soil cover.

Specific Comment #5

Since the author has acknowledged there are no permanent GMPs at the site, maintaining the current strategy under the Work Plan seems like a waste of effort and will only delay field work. CRA should proceed with submitting an addendum to the Work Plan to U.S. EPA for review and approval.

Response #5

As requested by USEPA/IDEM, CRA has amended Section 4.3 of the RD Work Plan and Section 2.2 of the Field Sample Plan (FSP) assuming that gas monitoring probes (GMPs) do not exist at the Site. If GMPs are found at the Site during the investigation, CRA will re-evaluate the remedial design and submit an addendum to the Work Plan, as appropriate.

Specific Comment #6

Construction of the 0.5-inch gas monitoring probes (GMPs) is acceptable. The 2-inch monitoring/extraction GMPs are not discussed in the response specifically, but the response seems to indicate the three 2-inch probes will be replaced with two 0.5-inch GMPs located, if possible, outside the limit of the waste. This is acceptable.

Response #6

Confirmed.

Specific Comment #8

The appropriate soil gas attenuation factor is 0.01, but if additional soil gas sampling is required, U.S. EPA guidance states that 0.1 should be used for soil gas less than five feet from the foundation. In addition, it may appropriate to refer to U.S. EPA guidance for evaluation soil gas from closed/abandoned landfills, as it may provide a more logical framework from addressing residential soil gas sampling if necessary.

Response #8

Concur.

Specific Comment #10

It appears the author meant to say "multiplied", rather than "divided" in this response.

Response #10

As detailed in the USEPA OSWER Draft Guidance for Evaluating the Vapor Intrusion to indoor Air Pathway from Groundwater and Soils (Subsurface Vapor Intrusion Guidance), Appendix F, Empirical Attenuation Factors and Reliability Assessment (Page F-1) "the attenuation factor represents the ratio of the indoor air concentration measured in a residence to the vapor concentration measured in the subsurface materials underlying or adjacent to the residence." Therefore, the soil gas target concentration is the indoor air target concentration divided by the attenuation factor.

As discussed in the teleconference on July 24, 2008, the equation that CRA will use to determine the Site specific soil gas criteria is:

$$C_{sg} = \frac{C_{air}}{\alpha}$$

Where:

- C_{air} - USEPA's target indoor air concentration for a residential exposure scenario based on a risk level of 1×10^{-5} and hazard index of 1.0 [micrograms per cubic meter ($\mu g/m^3$)];
- C_{sg} - the allowable Site-specific soil gas criteria that would not result in an indoor air concentration greater than C_{air} ($\mu g/m^3$); and
- α - the Site-specific calculated soil gas attenuation factor which relates the indoor air concentration to the concentration in soil gas based on the heuristic model developed by Johnson and Ettinger (1991; Equation 21) and accounts for the advective-diffusive migration of contaminants in soil gas through the unsaturated zone soil and building foundation, followed by the mixing of the intruding vapors with building indoor air.

Specific Comment #12

The statement "Additionally, gas generation is continuing in its progressive decline both for the VOCs and products of organic decomposition." is not supported by data and may be inaccurate. There has been no gas samples collected for at least 6 years. In addition, the

Statement of Work requires the installation of a gas collection/mitigation system that not only addresses risk from inhalation of indoor air, but also prevents the future migration of hydrogen sulfide and methane gases beyond the facility boundary. It would be more appropriate to determine the level of required control at the area of highest gas generation, such as the southeast corner. (Note: CRA's response to Comment # 12 is also contradictory to its response to Comment #16 and needs to be resolved).

Response #12

As discussed during the teleconference on July 24, 2008, CRA agrees that the response in our May 16, 2008 Response to Comments letter should have read, "Additionally, gas generation is likely continuing in its progressive decline both for the VOCs and products of organic decomposition". Further, as agreed during the July 24, 2008 teleconference, CRA has incorporated six additional SGPs along the southern boundary of the Site to better characterize soil gas concentrations along the southern perimeter of the landfill. The new SGP locations are pictured in Figure 4.4 of the RD Work Plan and in Figure 2.4 of the FSP.

Specific Comment #14

CRA should indicate that any site-specific attenuation calculations will be included in the Work Plan addendum and only default values will be used under the current plan (i.e., 0.01).

Response #14

Concur. Section 4.3.5 of the RD Work Plan has been modified as requested.

Specific Comment #16

See note in Response to Comment # 12 above. Also, CRA has not demonstrated that the Phase 1 soil gas probe spacing along the eastern side of the site will adequately capture the area where chlorinated ethenes had migrated offsite to the east. Consequently, the installation of additional probes along this side is recommended.

Response #16

As agreed during the teleconference on July 24, 2008, the spacing for SGPs along the east property boundary is appropriate to monitor potential gas migration to the east. The work plan has been changed to include SGPs at 200 foot intervals along the southern Site boundary. As

mentioned in Response #12, the new SGP locations are pictured in Figure 4.4 of the RD Work Plan and in Figure 2.4 of the FSP.

Specific Comment #20

This method may be risky for an old landfill. The highly soluble ions sodium, chloride, and bromide may have leached away, while metals continue to be released. While turbidity may be a confounding problem in its own, turbidity should be monitored, metals analyses run, and the results compared to the turbidity numbers to determine how closely the two parameters are associated.

Response #20

The RD Work Plan has been revised to include metals analyses at all groundwater locations during Phase I of the groundwater investigation. CRA will review the analytical results upon completion of the Phase I vertical aquifer sampling (VAS) and determine if metals analysis is appropriate in future phases.

Specific Comment #21

Shallow groundwater results cannot be used to direct deeper groundwater sampling, or make decisions regarding the necessity. The initial Phase 1 Vertical Aquifer Sampling (VAS) needs to include sampling at all levels of the aquifer.

Response #21

As discussed during the July 24, 2008 call, CRA has revised Section 4.4 of the RD Work Plan to specify that the first phase of the VAS sampling will be focused on the southeast portion of the Site and will be limited to 150 feet in depth. Subsequent phases of investigation will further delineate the vertical or horizontal extent of contaminant plumes emanating from the Site.

FIELD SAMPLING PLAN (FSP) COMMENTS

General Comment #1

The SOW requires the settling defendants to adequately address the future migration of hydrogen sulfide and methane from the landfill. It would be appropriate to further characterize concentrations along the southern perimeter of the landfill, based on this objective.

Response #1

See Response to Comment #16 on the RD Work Plan.

General Comment #2

See Response to Specific Comment # 20 on the Work Plan above. Stabilization parameters are perfectly appropriate for VAS when using an exposed screen sampler as described in Section 2.3.1.1 of the FSP; the device should be purged and monitored until parameters stabilize. See ASTM Standard D6001: Direct-Push Water Sampling for Geoenvironmental Investigations.

Response #2

The Geoprobe SP16 is a direct push groundwater sampling device that consists of a well screen inside a steel sheath that is driven to depth and then deployed by retracting the steel sheath and exposing the well screen directly to the formation. As discussed in the July 24, 2008 conference call, it is not an exposed screen sampler. CRA has clarified this with more detail in the VAS by Geoprobe procedure located in Section 2.3.1.1 of the FSP.

Field measurements of turbidity will be collected at approximate 5-minute intervals. No other stabilization parameters will be measured. Purging will continue until the turbidity of the purge water is equal to or less than 5 nephelometric turbidity units (NTUs). In the event that turbidity values of less than 5 NTUs cannot be achieved, purging may also be considered complete if a minimum of 10 screen point well volumes have been purged or three successive turbidity readings are within 10 percent of their average value.

Specific Comment #2 & #4

The response indicates that soil samples for VOC analysis will be collected if headspace readings using a PID indicate the presence of VOCs. However, the FSP, Section 2.1.2 and supporting tables have not been revised to include this approach. Although historical sampling of soil did not demonstrate VOCs, the presence of these constituents in soil gas and some groundwater samples indicates the potential for a source that has not been found.

Response #2 & #4

The headspace analysis will be used primarily to determine the appropriate level of personal protective equipment. However, if the PID readings of headspace exceed 10 ppm above

background, the soil sample will be analyzed for VOCs. Section 2.1.2.2 of the FSP has been revised to add this detail.

General Comment #6

The quantity and quality of soil gas will likely be affected if the probe extends below the waste. If borings penetrate the layer below the waste, grout the penetrated interval and install the gas probe within the waste as recommended by EPA and IDEM.

Response #6

Concur. Section 2.2.1 of the FSP has been amended to incorporate this requirement.

General Comment #7 & #9

Page 11 of the revised FSP states that dead volumes will be calculated solely on casing/tubing volume. Sand pack or gravel pack porosity must be used to calculate dead volume for this material, and the total dead volume is the sum of the casing and sand pack dead volumes. (Note: Also, see Response to Comment # 21 of the Work Plan above).

Response #7 & #9

Appendix II, Soil Gas Sampling Procedures (page II-3), of IDEM Guidance notes that the "dead volume" is "the internal volume of the sampling apparatus, including the implant screen, and the tubing, but excluding the sample container volume and the sand pack volume." As such, CRA interprets the "dead volume" to exclude the sand pack volumes. As discussed during the July 24, 2008 conference call and as indicated in Section 2.2.1 of the FSP, the volume of soil gas initially purged during installation of the GMPs will be calculated using the dead volume plus the sand pack volume, but the volume purged prior to sampling will be calculated using the dead volume, excluding the sand pack volume.

General Comment #13

See Response to Specific Comment # 20 for the Work Plan above.

Response #13

No further response required.

General Comment #19

Monitoring wells installed more than five feet away from a logged boring must themselves be logged. IDNR rules (312 IAC 13-2-6, 13-8-3) state that all wells must be logged; the 5-foot criterion offered is the maximum deviation allowed from this rule.

Response #19

IDNR Rule 312 IAC 13-2-6 lists requirements for well records. 312 IAC 13-2-6 (11) states the well record must include:

> *(11) The type and thickness formations or materials encountered, including color, hardness and a geologic description.*

IDNR Rule 312 IAC 13-2-6 does not describe how this information is obtained and does not include any discussion of how the geologic material is sampled or at what frequency. IDNR Rule 312 IAC 13-8-3 describes requirements specific to monitoring well materials and installation procedures and it does not include any requirements for soil sampling.

CRA will provide a stratigraphic log for each VAS borehole installed during the investigation. CRA will confirm that any monitoring wells installed in the vicinity of each VAS location are screened in the target formation by collecting a soil sample from the well screen interval prior to installing the well. CRA will provide a separate instrumentation log for each monitoring well. The log will conform to the requirements outlined in Rule 312 IAC 13-2-6 and will provide information on the well materials, screen depth and other construction details specific to each individual monitoring well.

General Comment #22

ASTM Standard D5521 for well development in granular aquifers (Fig. 5 and Note 1) recommends pumping both out of and into the well (presumably the latter is the "backwashing" "the contractor refers to). Surging per se (with a surge block) is not mandatory in the ASTM procedure, but may be warranted in this case. It is also recommended that ASTM D5521 be added to Attachment C of the FSP and that the contractor plan to use bidirectional flow during well development in conformity with this standard.

Response #22

CRA recognizes that achieving the well development criterion of 5 NTU typically involves some degree of bidirectional flow during well development. The procedures outlined in Section 2.3.3 of the revised FSP provide for bidirectional flow (mild surging) during well development and are consistent with ASTM Standard D5521. If mild surging is not successful, CRA will employ reasonable efforts to achieve the 5 NTU criteria. CRA has amended Section 2.3.3 of the FSP to include more detail with regard to methods that can be used to achieve the 5 NTU criteria.

General Comment #25

The investigation-derived waste should be containerized until the landfill cover is actually replaced, rather than disposed of in an uncontrolled fashion. The fence by itself does not constitute proper control.

Response #25

As discussed during the July 24, 2008 conference call, Section 7.0 of the FSP has been revised to state that investigation-derived waste will be contained and stored on Site or shipped off Site for disposal.

Should you have any questions on the above, please do not hesitate to contact us.

Yours truly,

CONESTOGA-ROVERS & ASSOCIATES

Alan Van Norman

BB/ca/7

c.c.: John Fagiolo, USEPA
Jessica Fliss, IDEM
Gary Toczylowski, Bayer HealthCare
Tom Lenz, Bayer HealthCare
Bryce Barker, CRA