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VOLUME 3 OF 3
FINAL REPORT
APPENDICES (CONTINUED)

REMEDIAL ACTION WORKPLAN ALBION-SHERIDAN TOWNSHIP LANDFILL CALHOUN COUNTY, MI

Prepared for
Cooper Industries
Houston, Texas

and

Corning, Inc.
Corning, New York

August, 1997

Woodward-Clyde

38777 West Six Mile Road
Suite 200
Livonia, Michigan 48152
6E13045

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List of Acronyms

A Acid Fraction (extractables)
AA Atomic Absorption
AFR Audit Finding Report
ARARs Applicable or Relevant and Appropriate Requirements
BN Base Neutral Fraction (extractables)
CCB Continuing Calibration Blank

CCC	Continuing Calibration Compounds
CCV	Continuing Calibration Verification
CERCLA	Comprehensive Environmental Responsibility Compensation and Liability Act
CVAA	Cold Vapor Atomic Absorption
DFTPP	Decafluorotriphenylphosphine
DL	Detection Limit
DQO	Data Quality Objectives
ECD	Electron Capture Detector
FID	Flame Ionization Detector
FSP	Field Sampling Plan
GC	Gas Chromatograph
GC/MS	Gas Chromatograph/Mass Spectrometer
GFAA	Graphite Furnace Atomic Absorption
ICP	Inductively Coupled Plasma Emission Spectrophotometer
LCS	Laboratory Control Sample
LD	Laboratory Duplicate
MCL	Maximum Concentration Level
MS/MSD	Matrix Spike/Matrix Spike Duplicate
MSA	Method of Standard Additions
ND	Not Detected
ORP	Oxidation/Reduction Potential
OVA	Organic Vapor Analyzer (Flame Ionization Detector)
PE	Performance Evaluation
PQAO	Project Quality Assurance Officer
QA	Quality Assurance
QC	Quality Control
QA/QC	Quality Assurance/Quality Control
QAPP	Quality Assurance Project Plan
QAU	Quality Assurance Unit
RD/RA	Remedial Design/Remedial Action
RI/FS	Remedial Investigation/Feasibility Study

ROD	Record of Decision
RPD	Relative Percent Difference
RPM	Remedial Project Manager
RRF	Relative Response Factors
SPC	Specific Conductivity Meter
SPCC	System Performance Calibration Compounds
SOP	Standard Operating Procedures
SVOC	Semi-Volatile Organic Compounds
SW846	"Test Methods for Evaluating Solid Waste, "Third Edition, September 1986 and approved updates.
U.S. EPA	United States Environmental Protection Agency
VOC	Volatile Organic Compounds
WP	Work Plan
%C	Percent Completeness
%D	Percent Difference
%R	Percent REcovery
%RSD	Percent Relative Standard Deviation

REMEDIAL ACTION (RA)
QUALITY ASSURANCE PROJECT PLAN (QAPP)
ALBION-SHERIDAN TOWNSHIP LANDFILL

CALHOUN COUNTY, MICHIGAN
PREPARED BY: WOODWARD-CLYDE CONSULTANTS

Approved by: _____ _____
Jon Peterson, Remedial Project Manager — Date
U.S. EPA - Region V

Approved by: _____ _____
Superfund Quality Assurance Reviewer — Date
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1.1 INTRODUCTION

The Albion-Sheridan Township Landfill Group ("Group") and Woodward-Clyde Consultants submit this Quality Assurance Project Plan (QAPP) to the United States Environmental Protection Agency (U.S. EPA), Region V, for the Remedial Action (RA) of the Albion-Sheridan Township Landfill (Site) located in Calhoun County, Michigan. The QAPP has been completed as part of the compliance requirements with the approved remedial action presented in the Record of Decision (ROD) and the Unilateral Administrative Order (UAO) for remedial design/remedial action (RD/RA), issued October 11, 1995 which took effect on December 11, 1995. The QAPP is to be used in conjunction with the following project documents:

- Operation And Maintenance Plan (O&M)
- Performance Monitoring Plan (PMP)
- Health and Safety Plan (HASP)

This QAPP describes protocols to be followed by personnel during field and laboratory sampling and analytical work. The objective of the QAPP is to provide procedures that document and ensure the precision, accuracy, completeness, and representativeness of data generated during field activities and laboratory analysis. This QAPP presents the organization, data quality objectives, functional activities and specific quality assurance (QA) and quality control (QC) activities associated with the RA activities for the Albion-Sheridan Landfill site in Calhoun County. This QAPP also describes the specific protocols which will be followed for sampling, sample handling, storage, chain of custody, and laboratory analyses.

The tasks described in this QAPP encompass all activities associated with the Operation and Maintenance (O&M) activities at the Albion-Sheridan Township Landfill Site.

1.1.1 Overall Project Objectives

The overall objective of remedial activities at the site is to implement the remedy presented in the ROD (U.S. EPA 1995). The ROD describes the remedy of the site as drum removal and construction of a cap over the landfill. The ROD states that this remedy is to reduce the risks associated with exposure to the contaminated materials on site, to eliminate or reduce migration of contaminants to the groundwater, and to reduce the risks associated with arsenic contamination in the groundwater. The ROD chose the remedial action in accordance with two threshold criteria, overall protection of human health and the environment, and compliance with the requirements of Federal and State Applicable or Relevant and Appropriate Requirements (ARARs). The ROD requires the design (RD) and implementation of the remedial action (RA) to meet the performance standards and specifications set forth in the ROD and the SOW. Performance standards shall include cleanup standards, standards of control, quality criteria and other substantive requirements, criteria or limitations including all ARARs set forth in the ROD, SOW and/or unilateral Administrative Order (UAO).

During O&M, an annual and quarterly groundwater monitoring program will be implemented as well as a landfill gas emission study to evaluate the effectiveness of the Site remedy. Six monitoring wells and seven drinking water wells will be sampled on a quarterly basis. The groundwater monitoring wells will be analyzed for field parameters, arsenic and ammonia. Field parameters include: groundwater depth/elevation before purging, temperature, pH conductivity, Eh, and dissolved oxygen. Analysis of the drinking water wells will include field parameters (less depth/elevation), Target Compound list (TCL) volatile Organic Compounds (VOCs) and 1,2-dibromo-3-chloroproprane, base / neutral and acid (BNA) extractable compounds, TAL Metals, Pesticides/PCBs, mercury, cyanide, chloride, sulfate, nitrate/nitrite and ammonia. On an annual basis, 17 monitoring wells will be sampled and submitted for analysis. The annual monitoring will be done in accordance with the SOW and consist of : 1) field parameters, and 2) chemicals of concern. Chemicals of concern will be 5 TAL chemicals (aluminum, arsenic; cobalt; manganese; and nickel), 2 TCL VOCs - benzene and vinyl chloride, and antimony, ammonia and 1,2-dibromo-3-chloropropane.

Seventeen designated monitoring wells will be sampled and analyzed for TCL organics, TAL inorganics and 1,2-dibromo-3-chloropropane to assist the EPA in meeting the requirements of Section 121(c) of CERCLA for the first five year review of the Site. Five-year review groundwater monitoring will occur approximately 50 to 52 months after approval of the Final Design.

After the groundwater analytical data from the initial year of groundwater sampling has been evaluated, analytes will be removed from the list if the provisions of the generic residential cleanup for the health based drinking water value for Public Act 307 amended, June 1995 Act 451 are met with the approval from the EPA and MDEQ. This list will be reevaluated each year upon the review of the full TCL and TAL laboratory results. A new compound may be added to the list for quarterly sampling parameters if it appears that the compound is originating from the landfill. A compound maybe dropped from the list if it is not observed during the next consecutive quarterly sampling events above the appropriate residential or industrial cleanup criteria. The quarterly and annual groundwater monitoring program are scheduled to commence following construction of the site cap (Table 1-1)

A landfill gas monitoring program will be conducted as part of the O&M monitoring activities. The objective of the gas monitoring program is to evaluate the concentrations of specific toxic pollutants under Michigan Public Act 348 and to verify that the total cancer risk level at the fence line does not exceed $1x\ 10^{-6}$. Ambient air at three selected locations (two gas vents at areas with the greatest apparent waste thickness and one downwind fenceline location) will be sampled once. These air samples will be analyzed in an off-site laboratory for a select group of VOCs. Additionally, the migration of combustible landfill gas, specifically methane, will be monitored on a quarterly basis as a percent of the Lower Explosive Limit (LEL). Direct readings of hydrogen sulfide and oxygen will also be monitored on a quarterly basis.

1.1.2 Project Status/Phase

The Group and U.S. EPA entered into a UAO for the completion of an RD/RA, which took effect on December 11, 1995. Preparation of the RD Work Plan and accompanying documents (QAPP, FSP and HASP) was the initial phase of this project. This QAPP has been primarily developed with respect to the O&M long-term groundwater and landfill gas emissions monitoring programs to assess the effectiveness of the remedial action.

This QAPP describes the O&M monitoring sampling and analyses that will be performed. As previously noted, monitoring activities during O&M will include:

- Quarterly groundwater sampling and analyses of six monitoring wells for arsenic and ammonia
- Quarterly groundwater sampling and analyses of seven drinking water wells for TCL VOCs and 1,2-dibromo-3-chloropropane, TCL BNAs, TCL pesticides/PCBs, mercury, cyanide, chloride, sulfate, nitrate/nitrite and ammonia
- Annual groundwater sampling and analysis of 12 monitoring wells for select metals (arsenic, aluminum, antimony, cobalt, manganese and nickel), select VOCs (benzene, 1,2-dibromo-3-chloropropane and vinyl chloride) and ammonia
- One time landfill gas emissions monitoring for select VOCs and quarterly monitoring for methane
- Five year review groundwater sampling and analysis of 17 monitoring wells for TCL organics and 1,2-dibromo-3-chloropropane and TAL inorganics

The results of the O&M Monitoring Program will be used to monitor the effectiveness of the remedial action and to minimize human exposure to landfill gas emissions during any phase of the remedial action.

Other additional activities that may be performed during the O&M include:

- Additional groundwater or air emissions sampling and analysis
- Refining the long term groundwater monitoring program

If these activities are added to the O&M tasks, additional addendum's to this QAPP will be submitted for approval by U.S. EPA.

1.1.3 QAPP Preparation Guidelines

The QAPP has been prepared in accordance with the "Region 5 Model Superfund Quality Assurance Project Plan", dated January 1996. Other documents which have been referenced for the Albion-Sheridan Township Landfill Site RA and referenced in this QAPP include the Operation and Maintenance (O&M) Plan, Performance Monitoring Plan (PMP) and the Health and Safety Plan (HASP).

1.2 SITE/FACILITY DESCRIPTION

1.2.1 Location

The Albion-Sheridan Township Landfill is an inactive landfill located at 29975 East Erie Road approximately one mile east of Albion, Michigan on the eastern edge of Calhoun County. The landfill is approximately 18 acres in area and its boundaries are shown in figure 1 the O&M Plan.

The study area for the O&M activities includes the Site property and off-site areas immediately surrounding the Site.

1.2.2 Facility/Size And Borders

This is addressed in Section 1.1 of the O&M Plan, which is herein incorporated through reference, and in the figures which have been submitted along with the O&M Plan.

1.2.3 Topography

See Sections 1.1 of the O&M Plan for information concerning the Site's general topography.

1.2.4 Local Hydrology And Hydrogeology

See sections 2.1 and 2.2 of the O&M Plan for information concerning the Site's geology and hydrogeology.

1.3 SITE FACILITY/HISTORY

1.3.1 General History

From 1966 to 1981, the landfill was privately owned and operated by Mr. Gordon Stevick. The landfills accepted municipal refuse and industrial wastes from households and industries in the City of Albion and nearby townships. In the early 1970's, the Michigan Department of Natural Resources (MDNR) approved the landfill to accept metal plating sludges. Other materials, such as paint wastes and thinners, oil and grease, and dust, sand, and dirt containing fly ash and casting sand were also disposed of at the site. In 1980, the MDNR collected and analyzed samples of non-containerized sludges that were being disposed at the site. The sludges contained heavy metals, including chromium (250,000 mg/kg), zinc (150,000 mg/kg), nickel (1,000 mg/kg) and lead (280 mg/kg). The sludges remain buried at the Site. The landfill ceased operation in 1981.

1.3.2 Past Data Collection Activities

Investigations and/or remedial actions conducted to date include:

- 1986 - A U.S. EPA Field Investigation Team (FIT) Contractor, performed a site screening inspection for scoring the site per the Hazard Ranking System (HRS). Based on the HRS, the Site was included on the National Priorities List (NPL) and designated as a Superfund Site.
- 1988 and 1989 - Site inspections conducted by a U.S. EPA Technical Assistance Team (TAT) resulted in a 1990 removal action of approximately forty-six (46) drums containing various RCRA hazardous waste. The removal action was conducted in accordance with a Unilateral Administrative Order (UAO, March 1990).
- 1992 through 1995 - U.S. EPA conducted a Remedial Investigation/Feasibility Study (RI/FS) for the Site, pursuant to CERCLA and the National Contingency Plan.
- The FS work culminated with the U.S. EPA ROD of March 1995, which described the selection of the remedial action to be implemented at the Site.
- 1996 - WCC conducted a Pre-Design Studies which included monitoring well installation, horizontal and vertical extent of waste verification and groundwater sampling and analysis.

1.3.3 Current Status

Based on reports and documents reviewed for the site, and a current assessment of all available information, the following summarizes the current status of conditions at the Albion-Sheridan Township Landfill.

The landfill is currently covered with 1 to 4 feet of silty sand with refuse scattered at the surface, including metal, plastic, concrete, asphalt, 55-gallon drums, wood, tires, a storage tank and a junk crane. Test pitting conducted by MDNR uncovered one area of concentrated drum disposal where an estimated 200 to 400 drums are present. Some of the drums contain liquid and solid wastes and suspected paint sludges, including up to 2.7 parts per million (ppm) arsenic, 730,000 ppm 1,2,4-trimethyl benzene, 40,000 ppm m&p xylenes, 6,500 ppm acetone and 2,400 ppm aluminum.

The landfill ranges from 16 to 35 feet in thickness and is producing landfill gasses in the form of volatile organic compounds (VOCs) in concentrations in excess of 10,000 ppm. The landfill waste contains numerous organic contaminants, including 10 VOCs, 19 semi-volatile compounds (SVOCs), 11 pesticides/PCBs, and inorganic contaminants including antimony, arsenic, chromium, copper, lead, mercury and zinc.

A leachate plume extends southwest of the landfill for approximately 900 feet and extends vertically to a depth of approximately 45 feet below the water table. The RI found landfill constituents in groundwater extending southwest of the landfill for approximately 900 ft and extending vertically to a depth of approximately 45 ft below the water table. The unconsolidated aquifer plume contained 1,2-dibromo-3-chloropropane and antimony at concentrations above their respective federal Maximum Contaminant Level (MCL). The bedrock aquifer plume

contained vinyl chloride at the MCL and arsenic above the MCL, at concentrations up to 126 µg/l.

The results of the Pre-Design Studies indicated that overall, shallow glacial monitoring well samples exhibited similar results as those obtained during the RI. The only organic compounds detected included vinyl chloride (MW03SG at 1.0 µg/l), chloroethane (MW07SG at 1.0 µg/l) and bis (2-Ethylhexyl) phthalate (MW05SG at 6.4 µg/l). Arsenic was detected in 2 wells, MW04SG and MW07SG, at concentrations of 7.9 µg/l and 13.2 µg/l, respectively. The results of the Pre-Design Studies also indicated that overall, bedrock monitoring well samples exhibited similar results as those obtained during the RI. There were no VOCs or SVOCs detected. The only inorganic analyte detected above the 50 µg/l MCL was Arsenic in MW06SB at 130 µg/l.

1.4 PROJECT OBJECTIVES

Data Quality Objectives are qualitative and quantitative statements which specify the quality of the data required to support decisions made during the O&M activities and are based on the end uses of the data collected. As such, different data uses may require different levels of data quality.

1.4.1 Specific Objectives And Associated Tasks - O&M Monitoring

Long-term groundwater monitoring will be used to evaluate the effectiveness of the cap integrity. The groundwater monitoring plan will provide pertinent background information and fulfill the requirements of the Michigan Solid Waste Rules under Act 641 and the Hazardous Waste Rules under Act 64.

The objective of the gas monitoring plan is to evaluate the concentrations of specific toxic pollutants that are regulated under Michigan Public Act 348 and to verify that the total cancer risk at the fence line does not exceed $1x10^{-6}$.

1.4.2 Project Target Parameters And Intended Data Usage - O&M Monitoring Program

Field Parameters

The following equipment will be used to obtain field parameter data:

Groundwater

- Water level meter for measuring groundwater depth/elevations
- Thermometer, conductivity meter, dissolved oxygen meter, oxidation-reduction meter, and pH meter for monitoring well development and sampling
- Bladder pump and dedicated tubing to be used for monitoring well sampling

Air Monitoring

Gas monitoring screening will be performed using specific monitors able to detect or quantify and methane.

Laboratory Parameters

The Project target limits (PTLs) are defined as those concentrations that laboratory analytical procedures should achieve to meet the project objectives. These PTLs should not be considered "cleanup" criteria at the site but rather laboratory performance criteria.

The Target Method Detection Limits (TMDLs) for groundwater to be used for laboratory analyses are in accordance with the TMDLs established by the Michigan Department of Natural Resources (MDNR) in MERA Operational Memorandum #6, Revision #4 dated September 13, 1995.

Groundwater

Groundwater samples from six monitoring wells for the O&M monitoring will be analyzed for arsenic and ammonia on a quarterly basis. Seven drinking water wells will be analyzed for TCL organics plus 1,2-dibromo-3-chloropropane, mercury, cyanide, chloride, sulfate, nitrate/nitrite and ammonia. Twelve monitoring wells will be sampled and analyzed on an annual basis for select metals (arsenic, aluminum, antimony, cobalt, manganese and nickel), select VOCs (benzene, 1,2-dibromo-3-chloropropane and vinyl chloride) and ammonia. Seventeen monitoring wells will be sampled as part of the five year review and will be analyzed for TCL organics and 1,2-dibromo-3-chloropropane and TAL inorganics. Detection limits are further discussed in Section 7.0 (see Tables 7-4 and 7-5).

Air Samples

Ambient air samples will be analyzed for select VOCs including: 1,2-dichloroethene, benzene, tetrachloroethene, chloroform, methylene chloride, vinyl chloride, 1,1-dichloroethene, trichlorethene, and carbon tetrachloride.

The results of the O&M Monitoring will be used to assess the effectiveness of the remedial action and to minimize exposure to landfill gas emissions.

1.4.3 Data Quality Objectives

EPA Guidance (U.S. EPA 1987) tailors the analytical methodology to watch the intended use of the data. In general, the five analytical levels are:

- Level I - field screening or analyses using portable instruments;
- Level II - field analyses using more sophisticated portable analytical instruments, possibly setup in a mobile laboratory;

- Level III - analyses performed at an off-site geotechnical or analytical laboratory but without the validation or documentation procedures required of the Contract Laboratory Program (CLP) Level IV analyses;
- Level IV - CLP (or CLP-like) routine analytical services; and
- Level V - analysis by non-standard methods;

Data validation procedures are provided in Section 9.0. To meet the objectives of the UAO, the following qualitative DQOs were identified:

Screening: The following measurements will be used under DQO Level I to collect and obtain basic site characteristics:

- Field Parameter Data: pH, temperature, specific conductance, oxidation-reduction potential, dissolved oxygen, and water levels/elevations
- Compile or acquire basic geologic and hydrogeologic information such as existing water table maps. These data will be used to further define migration pathways and background conditions in the area of the site.

The data acquired under DQO Level I will be used to detect changes in groundwater characteristics between sampling rounds, to describe basic physical properties of media investigated, and to verify adequate purging of monitoring wells. Water level elevations will be measured to map the water table and to calculate groundwater flow gradients by following standard contouring protocols.

Field Analysis: The following field analysis procedures will be used under DQO Level II. They will be used to generate data, if required, to evaluate the gas emissions from the landfill.

- Landfill gas samples: methane.
- DQO Level II data such as samples of landfill gas, will be used to assess the composition, relative quantity and location of gas production within the landfill area and to assess the presence of air emission constituents which are regulated under Michigan Public Act 348.

Off-site Laboratory Analyses Ambient Air Samples: This provides a level of data quality suitable for site characterization. Analyses may include mobile lab generated data and some analytical lab methods (e.g., laboratory data without DQO Level IV type quality control documentation).

Ambient air samples analyzed for chemicals of concerns (volatiles) will be required during the O&M Monitoring. The contract laboratory will use Method T0-14 for ambient air monitoring analyses.

Off-Site Laboratory Analyses Groundwater Samples: SW-846 analytical methods with an increased level of QA/QC will be used in place of CLP methodologies for groundwater sample analyses conducted during the O&M Monitoring. The data will be presented in CLP-type deliverables. Data validation procedures are performed according to U.S. EPA recognized

protocol. The methods are discussed in Section 7.0 and detection limits are discussed on Section 7.0.

Non-Standard Laboratory Analyses: No DQO Level V data are planned to be collected during the O&M Monitoring.

1.5 SAMPLE NETWORK DESIGN AND RATIONALE

The sample network design and rationale for sample locations is explained in detail in the PMP.

1.5.1 Laboratory Analysis Parameters and Sample Frequency

Sample matrices, analytical parameters and frequencies of sample collection is presented in Table 1-1.

1.5.2 Site Maps Of Sampling Locations

Maps showing intended ground water sampling locations are included as Figures in the O&M Plan, which is fully incorporated into this QAPP through reference. It is possible however, that depending on the nature of encountered field conditions some of these locations will be changed if approved by U.S. EPA. The person who shall be responsible for making such decisions will be the Site Field Manager whose responsibilities are described in Section 2.0 of this QAPP. Monitoring well screen depth are also indicated in the O&M Plan.

1.5.3 Rationale of Selected Sampling Locations

The rationale for why the selected sampling locations were chosen in conjunction with the area of concern is fully described in the O&M Plan and SOW.

A summary of the sampling and analysis plan for the O&M Monitoring is presented in Table 1-1 of this document. Table 1-1 will be revised by addenda if required, and prior to additional monitoring during subsequent phases of the O&M Monitoring Program.

1.6 PROJECT SCHEDULE

The initial quarterly groundwater sampling and analysis event will occur after cap construction is completed following EPA approval of the Final Construction Report. Thereafter, groundwater sampling and analysis will be conducted on a quarterly basis for the first five years of the monitoring program.

The sampling schedule may be modified in the future with the approval of U.S. EPA and consultation with MDEQ.

At the direction of the U.S. EPA's Remedial Project Manager, The Project Coordinator has overall responsibility for all phases of the RD/RA. The Project Coordinator assigned by Cooper Industries and Corning Corporation (Group) for this RD/RA project is Mr. John Seymour of Woodward-Clyde Consultants (WCC). The Project Coordinator will be responsible for the direction and supervision of work performed by the O&M Contractor pursuant to the UAO. The various quality assurance and management responsibilities of key project personnel are defined below.

2.1 PROJECT ORGANIZATION CHART

The lines of authority for the Remedial Action can be found in Figure 2-1. The chart includes all individuals discussed below.

2.2 MANAGEMENT RESPONSIBILITIES

2.2.1 U.S. EPA Remedial Project Manager

Mr. Jon Peterson has overall responsibility for all phases of the RD/RA. He will provide review and approval of work plans, QAPPs, reports, schedules, and specifications.

2.2.2 Group Authority and Responsibility

The Group will manage the overall project. The Group's Project Coordinator and the O&M Contractor's technical resources will be utilized as needed for specific areas of application and to accomplish specific tasks associated with the O&M Monitoring Program. The Group, Project Coordinator and the O&M Contractor will work together to assure that project resources are effectively utilized to meet schedules, budgets, and quality requirements.

The Group's responsibilities will include reporting to regulatory agencies, supervising and reviewing the Project Coordinator's and the O&M Contractor's work. This will assure that the work performed meets technical commitments, by evaluating permit condition compliance including scheduled commitments.

2.2.3 Project Coordinator

Mr. John Seymour of WCC will be the Project Coordinator for the Group during the O&M activities. The Project Coordinator will report directly to the Group.

2.2.4 O&M Contractor's Project Manager

The O&M Contractor's Project Manager has overall responsibility for ensuring that the project meets U.S. EPA's objectives and quality standards. The Project Manager will provide assistance to the Group in terms of writing and distribution of the QAPP to all those parties connected with

the project (including the laboratory). The Project Manager is responsible for technical quality control and project oversight. The Project Manager will report directly to the Group.

2.3 QUALITY ASSURANCE RESPONSIBILITIES

The Group's QA Manager

The Group's QA Manager will remain independent of direct job involvement and day-to-day operations. He will have direct access to corporate executive staff, necessary to resolve any QA dispute. He is responsible for oversight of the QA program in conformance with the demands of specific investigations, the O&M Contractor's policies, and U.S. EPA requirements. Specific functions and duties include:

- Providing QA oversight on various phases of the field operations;
- Reviewing and approving of QA plans and procedures;
- Providing QA technical assistance to project staff;
- Reporting on the adequacy, status, and effectiveness of the QA program on a regular basis to the remainder of the Group.

O&M Contractor's QA Manager

The O&M Contractor's QA Manager will report directly to the O&M Project Manager, and will be responsible for ensuring that all procedures for the O&M Monitoring Program are being followed. In addition, the QA Manager will be responsible for the data validation, verifying that sampling and analytical operations are carried out according to the Quality Assurance Project Plan. Audits of systems will also be conducted. The QA Manager or designee shall be responsible for performance and system audits of field, laboratory and data reduction/verification activities, and specifying corrective action as required. The QA Manager will review field QC test results, laboratory operations, and prepare QA reports.

U.S. EPA Region V Technical Support Section Quality Assurance Reviewer (RQAR)

The U.S. EPA RQAR has the responsibility to review and approve all Quality Assurance Project Plans (QAPPs). Additional EPA responsibilities for the project include:

- Conducting external Performance and System Audits of project laboratory(ies)
- Reviewing and evaluating analytical laboratory and field procedures

2.4 LABORATORY RESPONSIBILITIES

The Quanterra Environmental Services Laboratory in North Canton, Ohio, will perform analytical services during the O&M Monitoring Program. Specific analyses and matrices that

Quanterra laboratories will analyze and the protocols they will follow are described in other sections of this QAPP.

Quanterra Laboratories Project Manager - Ms. Alesia Danford

The Quanterra Laboratories Project Manager will report directly to the O&M Contractor's Project Manager. She will be responsible for the following:

- Ensuring all resources of the laboratory are available on an as-required basis; and
- Overviewing of final analytical reports.

Quanterra Laboratories Operations Manager - Mr. Chris Oprandi

The Quanterra Laboratories Operations Manager will report to the Quanterra Laboratories Project Manager and will be responsible for:

- Coordinating laboratory analyses Supervising in-house chain-of-custody
- Scheduling sample analyses
- Overseeing data review
- Overseeing preparation of analytical reports
- Approving final analytical reports prior to submission to the Group and the O&M Contractor

Quanterra Laboratories Quality Assurance Officer - Ms. Opal Davis-Johnson

Quanterra's Laboratory QA Officer has the overall responsibility for data after it leaves the laboratory. The QA Officer will be independent of the laboratory but will communicate data issues through the laboratory's Project Manager. In addition, the laboratory QA Officer will:

- Overview laboratory quality assurance
- Overview QA/QC documentation
- Conduct detailed data review
- Determine whether to implement laboratory corrective actions
- Define appropriate laboratory QA procedures
- Prepare laboratory Standard Operation Procedures
- Sign the title page of the QAPP

Quanterra Laboratories Sample Custodian - Ms. Lois Ezzo

The sample custodian will report to the laboratory Operations Manager. Responsibilities of the sample custodian will include:

- Receiving and inspecting the incoming sample containers
- Recording the condition of the incoming sample containers
- Signing appropriate documents
- Verifying chain-of-custody and its correctness
- Notifying laboratory manager and laboratory supervisor of sample receipt and inspection
- Assigning a unique identification number and customer number, and entering each into the sample receiving log
- Initiating transfer of the samples to the appropriate lab sections, with the help of the laboratory manager
- Controlling and monitoring access/storage of samples and extracts

Final responsibility for project quality rests with Quanterra's Project Manager. Independent quality assurance will be provided by the Quanterra's Project Manager and QA Officer prior to release of all data to the Group and the and the O&M Contractor.

Quanterra Laboratories Technical Staff

Quanterra Laboratories technical staff will be responsible for sample analysis and identification of corrective actions. The staff will report directly to the laboratory Operations Manager.

2.5 FIELD RESPONSIBILITIES

The Group will be supported by the O&M Contractor Field Manager. The Field Manager is responsible for leading and coordinating the day-to-day activities of the various resource specialists under his/her supervision. The Field Manager is an experienced environmental professional and will report directly to the O&M Contractor Project Manager. Specific Field Manager responsibilities include:

- Providing day-to-day coordination with his/her Project Manager on technical issues in specific areas of expertise;
- Developing and implementing field-related work plans, assurance of schedule compliance, and adherence to management-developed study requirements;
- Coordinating and managing field staff including sampling and drilling, and supervising field laboratory staff;
- Implementing QC for technical data provided by the field staff including field measurement data;
- Writing and approving text and graphics required for field team efforts;

- Coordinating and overseeing technical efforts of subcontractors assisting the field team;
- Identifying problems at the field team level, resolving difficulties in consultation with the Project Manager, implementing and documenting corrective action procedures, and providing communication between team and upper management; and
- Participating in data validation and in preparation of the final report.

2.6 CONTRACTORS

The Group anticipates contracting an O&M Manager (O&M Contractor), laboratory services, and related contractors for such services as drilling and surveying during the O&M Monitoring Program. The companies chosen will have contractual obligations to the Group but will work under the direction of the O&M Contractor. The Group will inform U.S. EPA when these services are contracted.

The overall QA objective is to develop and implement procedures for field sampling, chain-of-custody documentation, laboratory analysis, and reporting that will provide results that are of known quality and useable to meet project objectives. Specific procedures for calibration, laboratory analysis, reporting of data, internal quality control, audits, preventive maintenance of field equipment, and corrective action are described in other sections of this QAPP. This section addresses the specific objectives for completeness, representativeness, comparability, accuracy, and precision of analysis.

Data that are incidental to collecting samples for analytical testing or unrelated to sampling will be generated during many of the field activities. These activities include, but are not limited to:

- Documenting time and weather conditions
- Locating and measuring the elevation of sampling stations
- Determining depths in a well
- Static water level measurements
- Calculating well development and pre-sampling purge volumes
- Observing sample collection conditions

The general QA objective for such field data is to obtain reproducible and comparable measurements to a degree of accuracy consistent with the intended use of such data through the documented use of standard procedures.

3.1 PRECISION

3.1.1 Definition

Precision is defined as the reproducibility of the analysis under prescribed similar conditions. Any variability in the reported analysis is attributed to variability introduced by sampling, handling, or analytical procedures. Precision can be expressed as relative percent difference (RPD) between duplicate analyses or as percent relative standard deviation (%RSD) between multiple data points. Equations to calculate precision are given in Section 12.0.

3.1.2 Field Precision Objectives

- Precision goals for pH measurement for replicate samples are ± 0.2 standard pH units.
- Precision goals for the specific conductivity meter are consecutive readings with ten percent of each other. Precision will be assessed through replicate measurements.
- The precision of temperature readings will be assessed by performing replicate readings. These readings must be within one degree Celsius of the original readings.

- Precision of Oxidation/Reduction (Redox) Potential measurements will be assessed through replicate measurements. The replicate measurements must be within ± 5 millivolts of the original measurement.
- The precision of dissolved oxygen (DO) measurements will be accessed by performing replicate measurements. The replicate measurements must be within ± 0.2 mg/l of the original measurement.
- Precision goals for field screening of landfill gas emissions will be assessed by performing replicate readings.

3.1.3 Laboratory Precision Objectives

The precision of laboratory analyses will be measured by testing spiked samples and duplicates in accordance with the frequencies shown in Table 1-1. Matrix spikes and matrix spike duplicates will be analyzed for every 10 investigative samples. Precision criteria for the parameters to be tested are shown in Table 3-1.

Additionally, one duplicate sample will be collected in the field for every 10 investigative groundwater samples. It will be labeled as a completely separate sample with no notation as to which original sample it duplicates, and it will be submitted as a blind duplicate sample to the lab. The same set of analyses as the original sample will be performed. Since the samples will not be spiked, there will be less information due to non-detected compounds. However, an RPD can be calculated for duplicate sample data in the same way as duplicate spiked samples. Because of matrix effects, no criteria are set for the RPD, but this information will be used in estimating uncertainty in the aggregate sampling and analytical precision for this project.

3.2 ACCURACY

3.2.1 Definition

Accuracy is defined as a bias in the measurement, either low or high from the true value. The accuracy or bias of a laboratory analysis is evaluated by analyzing standards of known concentration both before and during sample analysis. Bias also is evaluated by spiking a sample with a known quantity of a chemical and measuring its actual, versus expected, recovery. Similarly, any bias introduced by laboratory contaminants are detected during blank analysis. Accuracy can be expressed as percent recovery (%R) of a spiked analyte. The formula to calculate accuracy is presented in Section 12.0 of this QAPP.

3.2.2 Field Accuracy Objectives

The accuracy of field measurements of pH will be assessed through pre-measurement calibrations and post-measurements verifications using at least three standard buffer solutions. The calibration measurement must be within ± 0.1 standard units for the buffer solution values.

Post-measurement verification will be accomplished using different containers of buffer solutions than the container used for pre-measurement calibration.

The accuracy of field measurements for specific conductivity will be assessed by performing pre-measurement calibration and post-measurement verifications. The calibration measurement must be within ± 20 micromhos/cm of the true value of the calibration solution. Post-measurement verification will be accomplished using a different container of standard calibration solution than the container used for pre-measurement calibration.

The accuracy of field measurements of Redox will be assessed through pre-measurement calibrations and post-measurement verifications using a standard reference solution.

The accuracy of temperature readings will be ensured by using thermometers certified by the National Institute of Standards and Technology.

The accuracy of field measurements of DO will be assessed through pre-measurement calibration to ambient air and post measurement evaluation of instrument drift using ambient air as the reference.

Field screening of landfill gas emissions will be performed for methane. Accuracy objectives will be in accordance with the manufacturer's recommendations.

The accuracy of conductivity measurements will not be assessed during the investigation. The survey yields apparent indicators of conductivity to identify changes in this property; absolute or true values are not important to the investigation.

3.2.3 Laboratory Accuracy Objectives

The accuracy of laboratory analyses will be measured by testing of spiked samples in accordance with the frequencies shown in Table 1-1. Matrix spikes and matrix spike duplicates will be analyzed for every 20 investigative samples. Method blanks and Laboratory Control Samples (LCS) will be analyzed one for every analytical batch. Surrogates will be analyzed for every sample and every blank, spike, and control sample. Accuracy criteria for the parameters to be tested are shown in Tables 3-1 and 3-2.

3.3 COMPLETENESS

3.3.1 Definition

Completeness is a measure of the amount of valid data obtained from a measurement system compared to the amount that was planned to be obtained or requested under normal conditions.

3.3.2 Field Completeness Objectives

Field completeness is a measure of the amount of valid measurements obtained from all the field measurements planned in the project. The equation for completeness is presented in Section 12.0 of this QAPP. Field completeness for this project will be greater than 90 percent.

3.3.3 Laboratory Completeness Objectives

Laboratory completeness is a measure of the amount of valid measurements obtained (including estimated values) from all the measurements planned in a project. The equation for completeness is presented in Section 12.0 of this QAPP. Laboratory completeness for this project will be greater than 90 percent.

3.4 REPRESENTATIVENESS

3.4.1 Definition

Representativeness expresses 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. Representativeness is a qualitative parameter which is dependent upon the proper design of the sampling program and proper laboratory protocol.

3.4.2 Measures to Ensure Representativeness of Field Data

Representiveness is dependent upon the proper design of the sampling program and will be satisfied by ensuring that the project standard operating procedures (SOPs) for field sampling (see Attachment A to the O&M Plan) are followed and that proper sampling techniques are used.

3.4.3 Measures to Ensure Representativeness of Laboratory Data

Representativeness in the laboratory is ensured by using the proper analytical procedures, meeting sample holding times and analyzing and assessing field duplicated samples. The sampling network was designed to provide data representative of facility conditions. During development of this network, consideration was given to past waste disposal practices, existing analytical data, physical setting and processes, and constraints inherent to the Superfund program. The rationale of the sampling network is discussed in detail in the PMP.

3.5 COMPARABILITY

3.5.1 Definition

Comparability is an expression of the confidence with which one data set can be compared with another.

3.5.2 Measures to Ensure Comparability of Field Data

Comparability is dependent upon the proper design of the sampling program and will be satisfied by ensuring the PMP is followed and that proper sampling techniques are used.

3.5.3 Measures to Ensure Comparability of Laboratory Data

Planned analytical data will be comparable when similar sampling and analytical methods are used and documented in the QAPP. Comparability is also dependent on similar QA objectives.

3.6 LEVEL OF QUALITY CONTROL EFFORT

Field duplicates, trip blanks, and matrix spikes/matrix spike duplicates (MS/MSD) samples will be collected and submitted to the analytical laboratory. Co-located field duplicate samples will be utilized to assess representativeness and sampling precision. The VOC trip blank samples will be analyzed to check for possible volatile organic compound (VOCs) contamination while VOC samples are in transit. The MS/MSD samples will be analyzed to measure long-term precision and accuracy of the analytical method and to demonstrate acceptable compound recovery by the laboratory at the time of sample analysis. One MS/MSD sample is designated or collected for both analyses.

For groundwater samples, the level of field QC effort will include one field duplicate sample for every 10 investigative samples, one trip blank for each shipping cooler, and one MS/MSD sample for every 20 investigative samples or one per sampling round if the number of investigative samples is less than 20. The trip blanks, to be provided by the laboratory, will be prepared with reagent grade dieonized ultra pure water. Field sampling personnel will need to collect triple volumes of sample for the VOC MS/MSD and double volumes for the remaining parameters.

For ambient air monitoring samples, the level of field QC effort will include one field duplicate sample for each sampling event (10 samples maximum) and one trip blank (provided by the laboratory) for each shipping cooler. The trip blank will consist of a SUMMA canister filled with an inert gas. The level of QC effort provided by the O&M Contractor for methane field analyses will be in accordance with the manufacturer's recommendations; minimally this will include duplicate analysis for methane. The specific level of field QC effort for the O&M Monitoring Plan is summarized in Table 1-1.

For groundwater analyses, the level of QC effort provided by Quanterra Laboratories will meet or exceed the level of QC effort specified under the Test Methods for Evaluating Solid Waste (SW-846) for the parameters identified in Table 1-1. For ambient air monitoring analyses, the level of QC effort will meet or exceed the level of effort specified in Method TO-14.

The QC level of effort for the field measurement of groundwater pH, dissolved oxygen, specific conductance, Redox and temperature are presented in detail in SOPs referenced in the O&M Plan (see Attachment A).

The procedures for sampling media and equipment decontamination are presented in standard operating procedures (SOPs) presented in Attachment A of the O&M Plan.

4.1 FIELD SAMPLING PROCEDURES

The sampling procedures used during the O&M activities will remain consistent for the duration of the Project. The detailed procedures for sampling various media and decontamination of equipment are presented in the Standard Operating Procedures (SOPs) included as Attachment A to the O&M Plan. The following SOPs are included.

SOP-01	Monitoring Well Installation In Bedrock Aquifer
SOP-02	Monitoring Well Development
SOP-03	Sample Custody Procedures And Field Documentation
SOP-04	Calibration And Maintenance Procedures
SOP-05	Quality Assurance/Quality Control Sampling
SOP-06	Water Level Measurements
SOP-07	Groundwater Sampling
SOP-08	Field Equipment Decontamination
SOP-09	Ambient Air Sampling
SOP-10	Sampling Gas Vents For Methane

4.2 FIELD QC SAMPLE PREPARATION PROCEDURES

Field QC samples will be collected at the frequency prescribed in the sample network summary (Table 1-1). Field duplicate and trip blank samples will be used to assess how sampling protocols, equipment and shipping conditions affect sample integrity. Protocols for collecting QC samples are described in Section 8.0 of this QAPP.

4.3 LABORATORY CONTAINER PREPARATION PROCEDURES

Quanterra will provide the proper containers and appropriate preservatives for the collection of samples. Laboratory SOPs are presented in Attachment A. In addition, the samples will be analyzed within a prescribed time frame for each parameter. The Laboratory Sample Preservation Summary (Table 4-1) details permissible sample containers, preservatives holding times, and minimum volume of sample needed. Appropriate chemical preservative will be added to each sample bottle by the laboratory prior to shipment to the field. Documentation of the preparation and addition of these reagents will be supplied by the lab along with the sample containers.

All samples will be packaged in ice (to 4°C ± 2°C) after collection. Insulated shipping coolers will be packed with additional ice and sealed by chain-of-custody labels. Coolers will be shipped by overnight courier to the laboratory in North Canton, Ohio.

4.4 SAMPLE IDENTIFICATION

Each bottle used for sampling will have a label attached. An example of a printed label is shown in SOP-01 which can be found in Attachment A of the O&M Plan. The project number, matrix and the unique sample code will be printed on the label.

EPA Region V follows the custody protocols described in "NEIC Policies and Procedures", EPA-330/9-78-DDI-R, Revised June 1985. Evidence of custody is recorded at three instances: sample collection, laboratory analysis, and final evidence files. Final evidence files, including all originals of laboratory reports and purge files, are maintained under document control by the O&M Contractor's Project Manager.

A sample or evidence file is under your custody if it is:

- in your possession
- in your view, after being in your possession
- in your possession and you place it in a secured location
- or is in a designated secure area

5.1 FIELD CUSTODY PROCEDURES

Chain-of-custody and sample bottle labels may be hand written or generated electronically using commercially available database software and word processing packages.

Sampling Team Members are responsible for contacting the Sampling Team Leader or designee to report media sampled, sample collection dates and times, and distribution of sample bottles in shipping coolers. The Sampling Team Leader or designee will be responsible for generating the chains-of-custody forms. Both the Sampling Team Leader and the Sampling Team Member reporting the sample collection information will review the chains-of-custody and make any corrections necessary. The review/correction process will be followed until no further corrections to the chains-of-custody are needed.

Procedures for the use of field logbooks, preparation of sample labels, sample and cooler custody and shipping, and a description of the sample numbering system is presented in detail in the SOPs referenced in the O&M Plan. Sample containers, preservation, and holding time requirements are presented in Table 4-1.

5.2 LABORATORY CUSTODY PROCEDURES

The sample custodian (Ms. Lois Ezzo or designee) will assign a unique number to each incoming sample for use in the laboratory. The unique number and customer number will then be entered into the sample receiving log. The laboratory date of receipt will also be noted. Laboratory custody procedures and document control for those samples received and analyzed by the laboratory will be carried out using the laboratory's standard operating procedure in Attachment A. Sample tags will be maintained in each laboratory's project file.

5.3 FINAL EVIDENCE FILES

The O&M Contractor's Project Manager will be the custodian of all the project files not in the possession of the Group. The Project Manager will be responsible for maintaining the contents of evidence files during any phase of the RA. This includes reports, personnel logs, field

notebooks, sample tags, pictures, subcontractor reports (including analytical data packages) and data reviews. The file will be stored in a secured, limited access area (such as the Project Managers office) and under custody of the Project Manager. The Group can request the return of all data from the O&M Contractor at the end of the project (The Group will define "the project").

The O&M Contractor's Project Manager or designee must be informed before documents are removed from the file. The title of material being checked out of the file, the name and affiliation of the person(s) removing the material from the file and the date and time the material was removed will be recorded on cardboard file insert pages (or equivalent). The card is to be inserted into the file from where the material was removed. When the material is returned, the date returned should be recorded on the card which is then removed from the file.

Evidence files will be maintained for at least ten (10) years after completion of all work pursuant to the UAO. The Group will notify U.S. EPA of its intent to destroy any files, and will give EPA 90-day written notice of this intent. EPA can take possession of the documents if it wishes.

All field and laboratory instruments will be calibrated prior to use. The calibration procedures will follow standard manufacturer's instructions and/or those instructions contained in the corresponding analytical method. This will ensure equipment is functioning within the tolerances established by the manufacturer or required by the analytical method. Instruments used for temperature, pH, oxidation-reduction potential, specific conductivity and dissolved oxygen will be calibrated in the field as described in the next section.

6.1 FIELD INSTRUMENT CALIBRATION

Thermometer - The sampling team will use precision thermometers certified by the National Institute of Standards and Technology. This will preclude the need for field calibration of thermometers. Thermometers will be inspected for separation in the mercury column. If it does not appear to be in good working order, it will be replaced (see O&M Plan, Attachment A, SOP-04).

pH Meter

The sampling team will calibrate a digital pH meter in the field according to the manufacturer's specifications. Field personnel will check instrument calibration at the beginning and end of each sampling day and log all calibration activities in the bound field log. The calibration procedure involves immersing the pH probe into a container of certified pH buffer solution and comparing the digital readout to the known value of the buffer solution. At least three ranges must be calibrated, and the accuracy of the pH meter must fall within 0.1 standard units of the pH, within the working temperature of 2C° to 40C°. Once calibrated, the response time of the pH meter must not exceed two minutes. After every ten uses, the calibration will be checked by immersing the probe in a standard solution different from the calibration fluid. The pH reading must be within 0.1 standard units; otherwise the meter must be re-calibrated or replaced (see O&M Plan, Attachment A, SOP-04).

Oxidation-Reduction Potential Meter

The sampling team will calibrate the oxidation-reduction (Redox) potential meter according to the manufacturer's specifications (see O&M Plan, Attachment A, SOP-04). Field personnel will check instrument calibration at the beginning and end of each sampling day, and log the calibration activities in the field notebook. The calibration procedure involves immersing the sensor into a factory supplied standard solution with a Redox potential of between 200 and 275 millivolts (mV). If the measured value is within the range of the standard, the Redox potential meter is properly calibrated. Calibration will be checked at least once for every 10 uses.

Specific Conductivity Meter

The sampling team will calibrate the specific conductivity (SPC) meter according to the manufacturer's specifications (see O&M Plan, Attachment A, SOP-04). Field personnel will check instrument calibration at the beginning and end of each sampling day, and log all

calibration activities in the field notebook. The calibration procedure involves immersing the sensor into a potassium chloride standard solution and comparing the reading with the known value of the standard solution. The calibration accuracy of the SPC meter must be within 20 micromhos/cm of the true value of the calibration fluid. Once calibrated, the response time of the SPC meter must not exceed two minutes.

Dissolved Oxygen Meter

The sampling team will calibrate the dissolved oxygen (DO) meter in the field according to the manufacturer's specifications (see O&M Plan, Attachment A, SOP-04). Field personnel will check the instrument calibration at the beginning and end of each sampling day, and log all calibration activities in the field notebook. The calibration procedure involves exposing the DO probe to air and then activating the automatic calibration circuitry on the DO meter. If after observing the measured value for one minute, no more than 0.2 units of instrument drift are observed, the DO meter is properly calibrated. Calibration will be checked at least once for every 10 uses.

6.2 LABORATORY INSTRUMENT CALIBRATION

Calibration for specific laboratory instruments will consist of initial calibration, initial calibration verification and continuing calibration verification. The SOPs in Attachment A present the specific calibration procedures for each method of analysis. In addition, Table 6-1 provides a summary of calibration frequencies and acceptance criteria for the methods that need to be calibrated.

7.1 FIELD ANALYTICAL PROCEDURES

Conducting quantitative chemical analysis under field conditions is not anticipated as part of this O&M Monitoring Program. However, field measurement data, associated with collecting samples for off-site analytical testing will be generated during many of the field activities. This field measurement data may be useful qualitatively for decision making purposes when the laboratory analytical data are evaluated. The field measurement activities may include, but are not limited to, the following:

- Documenting time and weather conditions
- Locating and measuring the elevation of sampling stations
- Measuring well depths
- Measuring static water levels
- Verifying well development and pre-sampling purge volumes
- Observing sample collection conditions
- Taking measurements for pH, temperature, specific conductance, dissolved oxygen and Redox
- Measuring relative concentrations of vapor-phase VOCs during water sampling activities.
- Screening for relative concentrations of typical landfill gas emissions (methane).

Field measurements will be performed according to the SOPs presented in the O&M Plan (Attachment A) and the operating procedures detailed in the respective equipment manuals. All field measurements will be documented in bound logbooks.

7.2 LABORATORY ANALYTICAL PROCEDURES

This section presents the laboratory procedures for sample preparation, cleanup, analytical testing, method validation, and QA/QC procedures. Procedures used for sample receipt in the laboratory are discussed in the SOPs in Attachment A.

Sample Preparation and Cleanup

All samples for analytical testing will be prepared in accordance with the methods outlined in Table 7-1 (Methods Summary for Sample Preparation/Sample Extraction) and Table 7-2 (Laboratory Analytical Methods Summary). The procedures used to clean laboratory glassware for use in organic, metals, and inorganic methods are outlined in Table 7-3 (Glassware Washing).

Analytical Methods

A summary of the laboratory analytical methods to be used during the Pre-Design Studies is outlined in Table 7-2 (Laboratory Analytical Methods Summary). For each analytical method, specific procedures and variances within the methods are detailed in the Analytical Methods SOPs (Attachment A). If during the duration of this project, the laboratory methods cited in Table 7-2 are changed, either by the issuing agency or through public notice in the Federal Register, the Quanterra method SOPs will be updated accordingly. The Analytical Methods SOPs are kept on file in the laboratory, available to the analysts at all times.

7.2.1 List of Project Target Compounds and Detection Limits

Summaries of laboratory method detection limits (MDLs) and Targeted Quantitation Limits to be used during this O&M Monitoring Program are outlined in Tables 7-4 through 7-6 (Laboratory Detection Limits and Quantitation Limits). The MDL is the lowest concentration that can be measured with 99% confidence that the analyte concentration is greater than zero. The MDL testing procedure is outlined in 40 CFR Part 136 Attachment B, and the MDL study SOP is included in Attachment A. Studies are performed by Quanterra on an annual basis or upon acquisition of new instrumentation. If there are changes resulting from detection limit studies, the changes will be updated and reported accordingly. Quanterra will use the Target Method Detection Limits (TMDLs) from MERA Memo No. 6, dated September 13, 1995 as Target Reporting Limits (TRLs) barring any dilutions required due to matrix effects or compound/analyte concentrations above the instrument linear calibration range.

Since the overall objective of the remedial action is to monitor the reduction of arsenic concentrations in the site groundwater, exceeding the TMDL requirements for parameters other than arsenic is acceptable.

8.1 FIELD QC CHECKS

Quality control procedures for field measurement of pH, temperature, Redox potential, specific conductivity, dissolved oxygen, and landfill gas emissions (methane), will be tailored to the qualitative nature of the DQOs for these data. The QC procedures for field equipment will include proper calibration of the instruments on a daily basis (refer to Section 6.0) and adhering to a preventive maintenance schedule during the O&M Monitoring Program (refer to Section 11.0). Calibration and maintenance procedures for each of the field instruments to be used during the O&M Monitoring Program are included in the O&M Plan as SOPs (see Attachment A).

Quality control procedures for assessing field sampling precision and bias will be adhered to during collection of investigatory samples submitted for quantitative laboratory analysis. These QC procedures are detailed in the following sections.

Field Duplicate Samples

Field duplicate samples will be used to assess overall representativeness. Aqueous field duplicates (QC samples) are taken from the same well volume and analyzed for the same constituents as the associated investigatory samples. Generally, analytical results greater than 5 times the quantitation limit should have RPDs less than 40. If either analytical result (i.e. the investigatory or duplicate) is less than or equal to 5 times the quantitation limit, the results should agree within two quantitation limits.

One set of field duplicate samples will be collected for every ten samples or once a day, whichever is more frequent (refer to Table 1-1).

Equipment Rinsate Samples

Rinsate samples will not be collected since all sampling equipment will be unique or disposable between each well.

During the O&M Monitoring Program, trip blank samples will be used to assess if samples for VOC analysis are cross-contaminated while being shipped to the laboratory. For groundwater samples, trip blank samples are reagent grade deionized distilled ultra pure water placed in VOA vials while at the laboratory. For Ambient air samples, trip blank samples consist of SUMMA canisters filled with an inert gas while at the laboratory. These samples are shipped from the laboratory with empty sample containers and stored on site with the containers. Trip blank samples will not be opened in the field. The trip blank will be analyzed for the same list of VOC analytes as the investigatory samples. Each shipping cooler containing VOC samples will contain a trip blank sample (refer to Table 1-1).

Matrix Spike/Spike Duplicate Samples (MS/MSDs)

During the O&M Monitoring Program, one MS/MSD will be collected and analyzed with each groundwater sampling round (maximum of one MS/MSD per 20 investigative samples) to maintain continuous surveillance of acceptable method performance (refer to Table 3-1). Percent recovery calculations (R) from these results are evaluated to provide a measure of the overall accuracy and precision of the method in addition to estimating extraction efficiencies and sample matrix effects (see QAPP Section 12.0). Aqueous MS/MSD samples will be collected from the same well volume as the associated investigatory sample. MS/MSD samples will not be collected for ambient air monitoring samples analyzed for VOCs.

8.2 LABORATORY QUALITY CONTROL CHECKS

Quanterra has QC programs to ensure the reliability and validity of the analyses performed at the laboratory. All analytical procedures are documented in writing as SOPs and each SOP includes a QC section which addresses the minimum QC requirements for the procedure. The internal quality control checks may vary slightly for each individual procedure but in general the QC requirements include the following:

i) Trip blanks

ii) Method blanks

iii) Reagent/preparation blanks (applicable to inorganic analyses)

iv) Instrument blanks

v) Matrix spikes/matrix spike duplicates

vi) Surrogate spikes

vii) Analytical spikes (furnace AA analyses)

viii) Laboratory control samples

ix) Internal standard areas for GC/MS analysis and control limits

x) Mass tuning for GC/MS analysis

xi) Endrin/DDT degradation checks for pesticides/PCB analyses

xii) Second, dissimilar column confirmation for GC analysis

A description of the specific QC requirements of this project and the frequency of QC samples analysis is provided in the SOPs. The QC acceptance criteria are also included in the SOPs and/or Tables 3-1 and 3-2.

All data obtained will be properly recorded. The data package will include a full deliverable package capable of allowing the recipient to reconstruct QC information and compare it to QC criteria. Any samples analyzed in non conformance with the QC criteria will be reanalyzed by

the laboratory, if sufficient volume is available. It is expected that sufficient volumes of samples will be collected for reanalysis when necessary.

9.1 DATA REDUCTION

9.1.1 Field Data Reduction Procedures

Field measurements are taken directly from instrument readings; therefore, no data calculations are involved. Field data reduction consists of transcribing and organizing these data into tables. This task will be performed by the Contractor's O&M Field Team and Field Manager.

9.1.2 Laboratory Data Reduction Procedures

Laboratory data reduction procedures will be followed according to the following protocol:

- Raw data produced and checked by the responsible analyst is turned over for independent review by another analyst
- The area supervisor or senior chemist reviews the data for attainment of quality control criteria established by the QAPP (see Tables 3-1, 3-2, and 4-1)
- Upon completion of all reviews and acceptance of the raw data by the laboratory area supervisor, a report will be generated and sent to the laboratory Project Manager
- The laboratory Project Manager will complete a thorough inspection of all reports
- The QA Officer and/or area supervisor will decide whether any sample reanalysis is required
- Upon acceptance of the preliminary reports by the QA Officer, final reports will be generated and signed by the Project Manager

Specific equations used for data reduction are contained in the SOPs in Attachment A.

9.2 DATA VALIDATION

Data validation procedures will be performed for both field and laboratory operations as described in the following subsections.

9.2.1 Procedures Used to Evaluate Field Data

Procedures to evaluate field data for this project primarily include checking for transcription errors and review of field logbooks, on the part of field sampling team. This task will be the responsibility of the Field Manager.

9.2.2 Procedures to Validate Laboratory Data

Validation of the analytical data will be performed by the O&M Contractor's QA Officer or designee based on the pertinent evaluation criteria outlined in "National Functional Guidelines

for Organic Data Review", February 1994 and "National Functional Guidelines for Inorganic Data Review", February 1994, on 100 percent of the data as described below:

The following deliverables will be evaluated in the data validation:

Organic Analyses

i) technical holding times

ii) GC/MS tuning/mass calibration

iii) initial and continuing calibration

iv) blanks

v) surrogate spikes

vi) MS/MSD results

vii) internal standard performance

viii) target compound identification and quantitation

ix) tentatively identified compounds

x) system performance

xi) GC/ECD instrument performance check (Pesticides/PCBs)

xii) pesticide cleanup checks, if performed (Pesticides/PCBs)

xiii) field duplicates

Inorganic Analyses

i) technical holding times

ii) calibration

iii) blanks

iv) interference check samples

v) laboratory control samples

vi) duplicate sample analysis

vii) matrix spike sample analysis

viii) furnace atomic absorption QC

ix) ICP serial dilution

x) sample result verification

xi) field duplicates

9.3 DATA REPORTING

Data reporting procedures will be carried out for field and laboratory operations as described in the following subsections.

9.3.1 Field Data Reporting

Field data reporting will be conducted principally through the transmission of report sheets containing tabulated results of all measurements made and documentation of all calibration activities.

9.3.2 Laboratory Data Reporting

The task of reporting laboratory data to the U.S. EPA begins after the validation activity has been concluded. The laboratory Project Manager will perform a final review of the report summaries and case narratives to determine whether the report meets the project requirements. In addition to the record of the chain-of-custody, the report format shall consist of the following:

1. Case Narrative
   - i) date of issuance
   - ii) laboratory analysis performed
   - iii) any deviations from intended analytical strategy
   - iv) laboratory batch number
   - v) number of samples and respective matrices
   - vi) quality control procedures utilized and also references to the acceptance criteria
   - vii) laboratory report contents
   - viii) project name and number
   - ix) condition of samples "as received"
   - x) discussion of whether or not sample holding times were met
   - xi) discussion of technical problems or other observations which may have created analytical difficulties
   - xii) discussion of any laboratory quality control checks which failed to meet project criteria
   - xiii) signature of laboratory QA Manager

2. Chemistry Data Package
   - i) case narrative for each analyzed batch of samples
   - ii) cross referencing of laboratory sample to project sample identification numbers
   - iii) description of data qualifiers to be used
   - iv) methods of sample preparation and analyses for samples
   - v) sample results
   - vi) raw data for sample results and laboratory quality control samples
   - vii) results of (dated) initial and continuing calibration checks and GC/MS tuning results
   - viii) matrix spike and matrix spike duplicate recoveries, laboratory duplicate analytical results, laboratory control samples, method blank results, calibrations check compounds and system performance check compound results
   - ix) labeled and dated chromatograms/spectra/instrument output of sample results and laboratory quality control checks
   - x) results of tentatively identified compounds

The data package submitted will be a "CLP-like" data package consisting of all the information presented in a CLP data package but not necessarily on CLP forms.

Performance and system audits conducted by the O&M Contractor shall be performed to:

- Verify that QA program is documented in accordance with specified requirements
- Verify documented program has been implemented
- Assess the Effectiveness of the QAPP
- Identify any non conformances
- Verify correction of identified deficiencies

This QA program operates independently of the overall project structure. The Audit Flowchart (Figure 10-1) summarizes the audit procedures established in this section. The O&M Contractor's Quality Assurance Officer (QAO) shall be responsible for initiating audits, selecting the audit team and overseeing the audit implementation. The QAO in consultation with the O&M Contractor's Project Manager, shall perform audits to coincide with appropriate activities on this project.

10.1 FIELD PERFORMANCE AND SYSTEMS AUDITS

Internal system audits on field work performance will be conducted by the O&M Contractor's QAO at least once yearly and as considered appropriate throughout the duration of the project. The Field Manager is responsible for supervising and checking that samples are collected and handled in accordance with the approved project plans and that documentation of field work is adequate and complete. The Project Manager is responsible for overseeing that the project performance satisfies the QA objectives, as set out in this QAPP. The O&M Contractor's QAO may also conduct unannounced field audits.

A field audit checklist (Figure 10-2) will be used to conduct field audits at the site during any phase of the RD/RA. Audits will examine adherence to protocol specified for items such as sample collection, sample handling, QA/QC sample collection, equipment calibration, equipment maintenance, field logbook documentation, and chain-of-custody preparation.

Follow-up audits may be performed to verify that any previously identified deficiencies were corrected. Corrective actions (Section 13.0) may be identified and recommended. An external audit may be conducted by U.S. EPA Region V personnel at any time.

10.2 LABORATORY PERFORMANCE AND SYSTEMS AUDITS

10.2.1 Internal Laboratory Audit Responsibilities

The internal laboratory audit will be conducted by the O&M Contractor's QAO.

10.2.2 Internal Laboratory Audit Frequency

The internal laboratory system audits will be performed on an annual basis while the internal laboratory performance audits will be conducted on a quarterly basis over the duration of O&M Monitoring Program any time laboratory analyses are required.

10.2.3 Internal Laboratory Audit Procedures

The internal laboratory system audits will include an examination of laboratory documentation on sample receiving, sample log-in, sample storage, chain-of-custody procedures, sample preparation and analysis, and instrument operating records. The performance audits will involve preparing blind QC samples and submitting them along with project samples to the laboratory for analysis throughout the project. The O&M Contractor's QAO will evaluate the analytical results of these blind performance samples to ensure the laboratory maintains acceptable QC performance.

Follow-up audits may be performed to verify that any previously identified deficiencies were corrected. Corrective actions (Section 13.0) may be identified and recommended.

10.2.4 External Laboratory Audit Frequency

An external laboratory audit will be conducted at least once prior to the initiation of the sampling and analysis activities. These audits may or may not be announced and are at the discretion of the U.S. EPA.

10.2.5 Overview of the External Laboratory Audit Process

External laboratory audits will include (but not be limited to) review of laboratory analytical procedures, laboratory on-site audits, and/or submission of performance evaluation samples to the laboratory for analysis.

11.1 FIELD INSTRUMENT PREVENTIVE MAINTENANCE

Standard Operating Procedures are presented in Attachment A of the O&M Plan. Table 11-1 provides the frequency of service for field instruments.

11.2 LABORATORY INSTRUMENT PREVENTIVE MAINTENANCE

As part of their QA/QC program, a routine preventive maintenance program is conducted by Quanterra 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 with the instrument manufacturer for the repair of) all instruments. All maintenance that is performed shall be documented in the laboratory's maintenance logbooks. All laboratory instruments are maintained in accordance with manufacturer's specifications.

Table 11-1 provides the frequency which components of key analytical instruments or equipment will be serviced.

12.1 CALCULATION OF DATA QUALITY INDICATORS

Quanterra uses specific routine procedures to assess the precision, accuracy, and completeness of its analytical data. The Laboratory's objective for precision and accuracy is to equal or exceed the stated performance in the method. These measures include the validation and internal quality control procedures discussed in Sections 7 and 8.

Precision, Accuracy and Completeness

Quantitation of precision and accuracy for field measurements are described in Section 3.0.

Specific procedures for assessing data accuracy and precision include calculation of percent recoveries for all laboratory check samples (LCS) and surrogates and relative percent differences (RPD) for all duplicate spike sample analyses. These calculations are summarized below.

a. Accuracy = Percent Recovery = $\frac{\text{(Amount in spiked sample - Amount in sample) x 100}}{\text{(Known amount added)}}$

(R%)

b. Precision = RPD = $\frac{\text{(Amount in Spike 1 - Amount in Spike 2) x 100}}{\text{0.5 (Amount in Spike 1 + Amount in Spike 2)}}$

c. Completeness = $\frac{\text{number of valid measurements obtained x 100}}{\text{number of measurements planned}}$

NOTE: Refer to the definitions of accuracy, precision, and completeness in Section 3.0.

Corrective actions may be required for two classes of problems: analytical and equipment problems and noncompliance problems. Analytical and equipment problems may occur during sampling, sample handling, sample preparation, laboratory instrumental analysis, and data review.

For noncompliance problems, formal corrective action will be determined and implemented at the time the problem is identified. The person who identifies the problem is responsible for notifying the O&M Contractor's Project Manager and Quality Assurance Officer (QAO) who will notify the U.S. EPA Remedial Project Manager and/or the U.S. EPA QAO. Implementation of corrective action will be confirmed in writing through the same channels.

Any non conformance with established quality control procedures in this QAPP will be identified and corrected in accordance with this QAPP. The O&M Contractor's QAO or designee will issue a Non conformance Report for each non conformance condition.

Corrective actions will be implemented and documented in the field record book. No staff member will initiate corrective action without prior communication of findings through the proper channels. If corrective actions are insufficient, work may be stopped by the Group, the O&M Contractor's Project Manager, or the U.S. EPA Remedial Project Manager.

13.1 FIELD CORRECTIVE ACTION

Technical staff and project personnel will be responsible for reporting all suspected technical or QA non conformance or suspected deficiencies of any activity or used document by reporting the situation to the Field Manager or designee. This manager will be responsible for assessing the suspected problems in consultation with the O&M Contractor's QAO and Project Manager and making a decision based on the potential for the situation to impact the quality of the data. If the situation warrants a corrective action, then a non conformance report will be initiated by the Field Manager.

The Field Manager will be responsible for ensuring that corrective action for non conformances are initiated by:

- evaluating all reported non conformances
- controlling additional work on non conforming items
- determining disposition or action to be taken
- maintaining a log of non conformances
- reviewing non conformance reports and corrective actions taken
- ensuring non conformance reports are included in the final site documentation in project files

If appropriate, the Field Manager will ensure that no additional work that is dependent on the non conformance activity is performed until the corrective actions are completed.

Corrective action for field measures may include:

- repeat the measurement to check the error
- check for all proper adjustments for ambient conditions such as temperature
- check the batteries
- re-calibration
- replace the instrument or measurement devices
- stop work (if necessary)

The Field Manager is responsible for all site activities. In this role, the Field Manager at times is required to adjust procedures to accommodate site-specific needs.

Any change in procedures will be documented and signed by the initiators and the Field Manager. Each document will be numbered serially as required, and attached to the field copy of the affected document.

The Field Manager is responsible for the controlling, tracking, and implementation of the identified field changes. Reports on all changes will be distributed to all affected parties including the U.S. EPA. The O&M Contractor and U.S. EPA Remedial Project Manager will be notified whenever program changes in the field are made.

13.2 LABORATORY CORRECTIVE ACTION

Corrective action in the laboratory may occur prior to, during, and after initial analyses. A number of conditions such as broken samples containers, multiple phases, low/high pH readings, and potentially high concentration samples may be identified during sample log-in or just prior to analysis. Following consultation with lab analysts and section leaders, it may be necessary for Quanterra's Quality Assurance Officer to approve the implementation of corrective action. The submitted SOPs specify some conditions during or after analysis that may automatically trigger corrective action or optional procedures. These conditions may include dilution of samples, additional sample extract cleanup, automatic reinjection/reanalysis when certain quality control criteria are not met, etc. A summary of method-specific corrective actions are found in this QAPP.

The bench chemist will identify the need for corrective action. The Quanterra QAO in consultation with the Quanterra supervisor and staff, will approve the required corrective action to be implemented by the laboratory staff. The Quanterra QA manager will ensure implementation and documentation of the corrective action. If the non conformance causes project objectives not to be achieved, it will be necessary to inform all levels of project management including the U.S. EPA Remedial Project Manager to concur with the corrective action.

These corrective actions are performed prior to release of the data from the laboratory. The corrective action will be documented in both the Quanterra's corrective action log (signed by analyst, section leader and quality control coordinator), and the narrative data report sent from

Quanterra to the O&M Contractor's QAO. If corrective action does not rectify the situation, Quanterra will contact the U.S. EPA Remedial Project Manager.

13.3 CORRECTIVE ACTION DURING DATA VALIDATION AND DATA ASSESSMENT

The O&M Contractor's QAO may identify the need for corrective action during either the data validation or data assessment. Potential types of corrective action may include resampling by the field team or reinjection/reanalysis of samples by the laboratory.

These actions are dependent upon the ability to mobilize the field team and whether the data to be collected are necessary to meet the required quality assurance objectives. When the O&M Contractor's QAO (or designee) identifies a corrective action situation, it is the Group who will be responsible for approving the implementation of corrective action, including resampling, during data assessment. All corrective actions of this type will be documented by the Group and O&M Contractor's QAO.

The deliverables associated with the tasks identified in the PMP and monthly progress reports will contain separate QA sections in which data quality information collected during the task is summarized. Those reports will be the responsibility of the Group and will include the Group and O&M Contractor's Quality Assurance Officer reports on the accuracy, precision, and completeness of the data as well as the results of the performance and system audits, and any corrective action needed or taken during the project.

14.1 CONTENTS OF PROJECT QA REPORTS

The QA reports will contain on a routine basis all results of field and laboratory audits, all information generated during the past month reflecting on the achievement of specific data quality objectives, and a summary of corrective action that was implemented, and its immediate results on the project. The status of the project with respect to the Project Schedule will be reported. Whenever necessary, updates on training provided, changes in key personnel, anticipated problems in the field or lab for the coming month that could bear on data quality along with proposed solutions, will be reported. Detailed references to QAPP modifications will be reported. All QA reports will be prepared in written, final format by the Group or designee.

In the event of an emergency, or in case it is essential to implement corrective action immediately, QA reports can be made by telephone to the appropriate individuals, as identified in the Project Organization or Corrective Action sections of this QAPP. However, these events, and their resolution will be addressed thoroughly in the next issue of the monthly QA report.

14.2 FREQUENCY OF QA REPORTS

The QA Reports will be prepared on a monthly basis and will be delivered to all recipients by the 10th day of each month. The reports will continue without interruption, until the project is completed. The frequency of any emergency reports that must be delivered verbally cannot be estimated at the present time.

14.3 INDIVIDUALS RECEIVING/REVIEWING QA REPORTS

The following individuals outside of the Group will receive copies of the monthly QA report:

U.S. EPA	-	Jon Peterson
Project Coordinator	-	J. Seymour, Woodward Clyde Consultants
O&M Contractor	-	***Insert Name***, Project Manager
	-	***Insert Name***, QA Officer
	-	***Insert Name***, Field Manager
MDEQ	-	Kim Sakowski
Quanterra	-	Alesia Danford

United States Environmental Protection Agency, 1995, Unilateral Administrative Order, U.S. EPA Docket No. V-W-96-C-316.

United States Environmental Protection Agency Region V, 1996, Region 5 Model QA Project Plan, January 1996.

MDNR, 1990, Michigan Environmental Response Act - 1982 Public Act 307, as amended Administrative Rules, Michigan Department of Natural Resources Environmental Response Division.

MDNR, 1995, Environmental Response Division Operational Memorandum #6, Revision #4, September 13, 1995.

United States Environmental Protection Agency, 1986, RCRA Ground-Water Monitoring Technical Enforcement Guidance Document, Washington D.C., September 1986, OSWER-9950.1.

United States Environmental Protection Agency, 1987a, Data Quality Objectives For Remedial Response Activities: Development Process, Washington D.C., March 1987, EPA 540/G-87/003.

United States Environmental Protection Agency, 1987b, Data Quality Objectives For Remedial Response Activities: Example Scenario RI/FS Activities at a Site With Contaminated Soil and Ground Water, Washington D.C., March 1987, EPA 540/G-87/004.

TABLES

TABLE 1-1
SUMMARY TABLE OF THE O&M SAMPLING AND ANALYSIS PROGRAM
ALBION-SHERIDAN TOWNSHIP LANDFILL

Matrix	Field Parameters	Laboratory Parameters[1]	Analytical Method	Total Investigative Samples	Total Field Duplicates[2]	Total Trip Blanks	Total MS/MSD[4]	Total Samples
Groundwater (Quarterly) Monitoring Wells	Groundwater depth/elevation pH, Specific Conductance, Temperature, Dissolved 0_2, Redox Potential	arsenic	SW-846-7060A	6	1	*NA*	--	7
		ammonia	EPA 350.3	6	1	*NA*	--	7
Groundwater (Quarterly) Drinking Water Wells	pH, Specific Conductance, Temperature, Dissolved 0_2, Redox Potential	TCL-VOCs + 1,2-dibromo-3-chloropropane	SW-846-8260	7	1	*(3)*	1/1	11
		TCL-BNAs	SW-846-8270	7	1	*NA*	1/1	10
		TCL-Pest/PCBs	SW-846-8080	7	1	*NA*	1/1	10
		TAL Metals	SW-846-6010/7000 series	7	1	*NA*	1/1	10
		total mercury	SW-846-7471A	7	1	*NA*	1/1	10
		cyanide	SW-846-9012	7	1	*NA*	1/1	10
		chloride	EPA 325.2	7	1	*NA*	1/1	10
		sulfate	EPA 374.4	7	1	*NA*	1/1	10
		nitrate/nitrite	EPA 353.2	7	1	*NA*	1/1	10
		ammonia	EPA 350.3	7	1	*NA*	1/1	10
Groundwater (Annual) Monitoring Wells	Groundwater depth/elevation pH, Specific Conductance, Temperature, Dissolved 0_2, Redox Potential	arsenic, aluminum, antimony, cobalt, manganese, nickel	SW-846-6010/7000 series	17	2	*NA*	1/1	21
		benzene, vinyl chloride, 1,2-dichloro-3-chloropropane	SW-846-8260	17	2	*(3)*	1/1	22
		ammonia	EPA 350.3	17	2	*NA*	1/1	21

TABLE 1-1
SUMMARY TABLE OF THE O&M SAMPLING AND ANALYSIS PROGRAM
ALBION-SHERIDAN TOWNSHIP LANDFILL

Matrix	Field Parameters	Laboratory Parameters[1]	Analytical Method	Total Investigative Samples	Total Field Duplicates[2]	Total Trip Blanks	Total MS/MSD[4]	Total Samples
Groundwater (Five Year Review) Monitoring Wells	Groundwater depth/elevation pH, Specific Conductance, Temperature, Dissolved 0_2, Redox Potential	TCL-VOCs + 1,2-dibromo-3-chloropropane	SW-846-8260	17	2	*(3)*	1/1	22
		TCL-BNAs	SW-846-8270	17	2	*NA*	1/1	21
		TCL - Pest/PCBs/	SW-846-8080	17	2	*NA*	1/1	21
		TAL Metals	SW-846-6010/ 7000 series	17	2	*NA*	1/1	21
		cyanide	SW-846-9012	17	2	*NA*	1/1	21
Landfill Gas Migration Monitoring Probes (Quarterly)	CH_3 O_2 H_2S % LEL	NA	NA	0	0	0	0	0
Landfill Gas Monitoring Event (one time event)		Select VOCs[5]	TO-14	3	1	*(3)*	0	5

Notes:
(1) Refer to QAPP Tables 7-1 and 7-2 for complete description of analytical methods.
(2) Field duplicates will be collected at a rate of one per 10 investigative samples.
(3) One trip blank set will be included with each shipping cooler containing samples for VOC analysis.
(4) Matrix spike/matrix spike duplicate sample for organics, matrix spike/laboratory duplicate for inorganics. These QC samples will be collected at a rate of one per 20 investigative samples. Triple the normal volume is required for VOCs and double sample volume is required for all other parameters.
(5) Select VOCs include: 1,2 dichloroethane, benzene, tetrachloroethylene, chloroform, methylene chloride, vinyl chloride, 1,1 dichloroethylene, trichloroethylene, carbon tetrachloride
NA - Not applicable
TCL - Target Compound List (Low Concentration)
TAL - Target Analyte List (Low Concentration)

TABLE 3-1
PRECISION AND ACCURACY CONTROL LIMITS
ALBION-SHERIDAN TOWNSHIP LANDFILL

ANALYSES	WATER CONTROL LIMITS RECOVERY LIMITS	RELATIVE PERCENT DIFFERENCE
VOC (8260A):		
1,1-dichloroethene	55-142	(19)
trichloroethene	77-124	(13)
benzene	83-123	(13)
toluene	82-122	(15)
chlorobenzene	85-120	(10)
BNA (8270B):		
1,2,4-trichlorobenzene	40-133	(35)
acenapthene	45-112	(28)
2,4-dinitrotoluene	37-124	(34)
pyrene	15-185	(45)
n-nitrosodi-n-propylamine	10-230	(30)
1,4-dichlorobenzene	33-90	(37)
pentachlorophenol	10-122	(71)
phenol	10-107	(35)
2-chlorophenol	10-134	(28)
4-chloro-3-methylphenol	21-120	(49)
4-nitrophenol	10-144	(100)
Pesticides/PCBs (8080):		
lindane	48-135	(51)
heptachlor	56-158	(36)
aldrin	54-120	(40)
dieldrin	54-143	(32)
endrin	64-142	(39)
4,4-DDT	48-154	(47)
ICP Metals (6010A):		
antimony	80-120	(20)
arsenic	80-120	(20)

TABLE 3-1
PRECISION AND ACCURACY CONTROL LIMITS
ALBION-SHERIDAN TOWNSHIP LANDFILL

ANALYSES	WATER CONTROL LIMITS RECOVERY LIMITS	WATER CONTROL LIMITS RELATIVE PERCENT DIFFERENCE
barium	80-120	(20)
ICP Metals (6010A): continued...		
beryllium	80-120	(20)
cadmium	80-120	(20)
chromium, total	80-120	(20)
cobalt	80-120	(20)
copper	80-120	(20)
lead	80-120	(20)
nickel	80-120	(20)
selenium	80-120	(20)
silver	80-120	(20)
thallium	80-120	(20)
zinc	80-120	(20)
vanadium	80-120	(20)
ICP Trace Metals (6010A):		
arsenic	80-120	(20)
cadmium	80-120	(20)
chromium, total	80-120	(20)
lead	80-120	(20)
selenium	80-120	(20)
silver	80-120	(20)
thallium	80-120	(20)
Furnace/Cold Vapor Metals:		
antimony (7041)	10-154	(20)
arsenic (7060)	44-140	(20)
cadmium	44-145	(20)
lead (7421)	54-123	(20)

TABLE 3-1
PRECISION AND ACCURACY CONTROL LIMITS
ALBION-SHERIDAN TOWNSHIP LANDFILL

	WATER CONTROL LIMITS	
ANALYSES	**RECOVERY LIMITS**	**RELATIVE PERCENT DIFFERENCE**
mercury (7470)	31-160	(20)
mercury (7471A)	NA	(20)
thallium (7841)	18-147	(20)
Inorganic Parameters:		
cyanide (9012A)	18-123	(68)
chloride (325.2)	90-110	(20)
sulfate (375.4)	90-110	(20)
nitrate/nitrite (353.2)	85-115	(20)
ammonia (350.3)	90-110	(20)

TABLE 3-2
CONTROL LIMITS FOR SURROGATE COMPOUNDS
ALBION-SHERIDAN TOWNSHIP LANDFILL

Analytical Method	Surrogate Compound	Water Recovery Limits(%)	
8260A	4-bromofluorobenzene	86	115
8260A	toluene-d_8	88	110
8260A	dibromofluoromethane	86	118
8080	dibutylchlorendate	10	155
8080	decachlorobiphenyl	60	150
8080	tetrachloro-meta-xylene	14	155
8270B	2-fluorobiphenyl	38	106
8270B	2-fluorophenol	17	106
8270B	2,4,6-tribromophenol	13	145
8270B	nitrobenzene-d_5	36	148
8270B	phenol-d_5	15	126
8270B	p-terphenyl-d_{14}	10	169
TO-14	4-bromofluorobenzene	70	130
TO-14	toluene-d_8	70	130
TO-14	1,2-dichloroethane-d_4	70	130

TABLE 4-1
SAMPLE PRESERVATION REQUIREMENTS
ALBION-SHERIDAN TOWNSHIP LANDFILL

Parameter	Container[1]	Preservative[2]	Recommended Holding Time[3]	Minimum Amount of Sample Required
Metals				
Metals, except Hg[4]	P	HNO_3 to pH <2	6 months	1 liter
Mercury	G	HNO_3 to pH <2	28 days	250 ml
Organics				
GC/MS Semi-Volatiles	G, TFE Lined Cap	Cool, 4°C	7 days until extraction, 40 days after extraction	2 liters
GC Semi-Volatiles (Pest/PCB)	G, TFE Lined Cap	Cool, 4°C	7 days until extraction, 40 days after extraction	2 liters
GC/MS Volatiles	G, TFE Lined Septum	Cool, 4°C HCl pH <2	14 days	3x40 ml
GC/MS Volatiles (Air Landfill gas)	SUMMA Canister	Cool, 4°C	14 days	fill canister

TABLE 4-1
SAMPLE PRESERVATION REQUIREMENTS
ALBION-SHERIDAN TOWNSHIP LANDFILL

Parameter	Container[1]	Preservative[2]	Recommended Holding Time[3]	Minimum Amount of Sample Required
Wet Chemistry				
Cyanide	P	Cool, 4°C NaOH to pH > 12	14 days	250 ml

1. Polyethylene (P) or Glass (G). Although polyethylene or glass may be appropriate for many of the samples, where there is a choice the Laboratory will ship polyethylene containers due to the reduced cost of the containers and shipping. The following containers are available upon request: 1 liter glass with TFE liner; 500 ml glass with TFE liner; 40 ml VOA with TFE septum; 250 ml glass with septum; 1 liter plastic; 250 ml plastic; 500 ml plastic; and 125 ml plastic.

2. Sample preservation should be performed immediately upon sample collection. For composite samples, each aliquot should be preserved at the time of collection. When use of an automated sampler makes it impossible to preserve each aliquot, the sample may be preserved by maintaining 4°C until compositing and sample splitting is completed.

3. Samples should be analyzed as soon as possible after collection. The times listed are the maximum times that samples may be held before analysis and still be considered valid. Samples may be held for longer periods of time only if the permittee, or monitoring laboratory, has data on file to show that the specific types of samples under study are stable for the longer time. Some samples may not be stable for the maximum time period listed in the table. A permittee, or monitoring laboratory, is obligated to hold the sample for a shorter time if knowledge exists to show this is necessary to maintain sample stability.

4. Samples should be filtered immediately on-site before adding preservative for dissolved metals if dissolved metals are requested.

METHOD	PARAMETER	CALIBRATION	FREQUENCY	ACCEPTANCE CRITERIA	CORRECTIVE ACTION
8080 (Gas Chromatography with an Electron Capture Detector)	Organochlorine Pesticides and PCBs	Multipoint calibration (minimum five points)	Initially and as required	$r \geq 0.995$	1) Evaluate system 2) Recalibrate
		Daily standard	Daily, before sample analysis	± 15% difference (± 20% for a maximum of 4 analytes) from multipoint calibration	1) Evaluate system 2) Repeat calibration standard 3) Recalibrate 4) Reanalyze affected samples
		Calibration Check standard	Every 10 samples	± 15% difference (± 20% for a maximum of 4 analytes) from multipoint calibration	1) Evaluate system 2) Repeat calibration check standard 3) Recalibrate 4) Reanalyze affected samples
		Terminal bracketing standard	At end of sample analysis	± 15% difference (± 20% for a maximum of 4 analytes) from multipoint calibration	1) Evaluate system 2) Assess impact on data 3) Reanalysis of samples and standards if significant impact is assessed.
8260 (GC/MS)	Volatile Organics	Check of mass spectral ion intensities using BFB	Every 12 hours	Refer to method narrative	1) Retune instrument 2) Repeat BFB analysis
		Multipoint calibration (minimum five points)	Initially and as required	% RSD for CCCs $\leq$ 30%; Avg. RF > 0.30 (0.25 for $CHBr_3$) for SPCCs	1) Evaluate system 2) Recalibrate

METHOD	PARAMETER	CALIBRATION	FREQUENCY	ACCEPTANCE CRITERIA	CORRECTIVE ACTION
8260 (GC/MS) continued	Volatile Organics	Continuing calibration check standard	Every 12 hours	RF $\geq$ 0.30 (0.25 for $CHBr_3$) for SPCC's; % Difference $\leq$ 25% for CCC's	1) Evaluate system 2) Repeat calibration check 3) Recalibrate 4) Reanalyze affected samples
8270B (Gas Chromatography with Mass Spectroscopy)	Semivolatile Organics	Check of instrument tuning criteria using DFTPP	Every 12 hours	Refer to method narrative	1) Retune instrument 2) Repeat DFTPP analysis
		Multipoint calibration (minimum five points)	Initially and as required	% RSD for CCCs < 30%; Avg. RF $\geq$ 0.050 for SPCCs	1) Evaluate system 2) Recalibrate
		Continuing calibration check standard	Every 12 hours	RF $\geq$ 0.050 for SPCCs; % Difference $\leq$ 25% for CCCs	1) Evaluate system 2) Repeat calibration check 3) Recalibrate 4) Reanalyze affected samples
6010A (Inductively Coupled Plasma)	Metals, Total	Laboratory mixed standard calibration	Daily prior to analyses	%REC ± 5%	Recalibrate
		Calibration blank	After ICAL verification (ICV) and after each continuing calibration verification (CCV)	±RL	1) Clean system 2) Recalibrate 3) Reanalyze affected samples

METHOD	PARAMETER	CALIBRATION	FREQUENCY	ACCEPTANCE CRITERIA	CORRECTIVE ACTION
6010A (Inductively Coupled Plasma) continued	Metals, Total	ICP interference check	Run at beginning of daily run, after 8 hours and/or end of run	80-120% of true value for EPA check sample elements.	1) Verify calibration 2) Verify IEC's and update as necessary 3) Recalibrate
		Initial calibration verification (ICV)	After calibration	± 10% expected response	1) Recalibrate
		Continuing calibration verification (CCV)	Every 10 samples and end of run sequence	± 10% expected response	1) Recalibrate 2) Reanalyze affected samples
7000 (Graphite Furnace Atomic Absorption) Includes: 7060, 7421, 7841	Metals, total	Calibration standard (minimum three points)	Daily prior to analyses required	$r \geq 0.995$	1) Evaluate system 2) Recalibrate
		Initial calibration verification (ICV)	After calibration	± 10% expected response	1) Recalibrate
		Continuing calibration verification (CCV)	Every 10 samples and end of run sequence	± 10% expected response	1) Recalibrate 2) Reanalyze affected samples
SW7470/7471A	Mercury, total	Six point calibration	Daily prior to analyses	$r \geq 0.995$	1) Recalibrate
		Initial calibration verification (ICV)	After calibration	± 20% for 7470/7471	1) Recalibrate 2) Reanalyze affected samples

METHOD	PARAMETER	CALIBRATION	FREQUENCY	ACCEPTANCE CRITERIA	CORRECTIVE ACTION
SW7470/7471A continued	Mercury, total	Calibration blank	After initial calibration and after each continuing calibration	± RL*	1) Clean system 2) Recalibrate 3) Rerun samples back to last clean blank
		Initial calibration verification (ICV)	After calibration	± 10% expected response	1) Recalibrate 2) Reanalyze affected samples
		Continuing calibration verification (CCV)	Every 10 samples and end of run sequence	± 10% expected response	1) Recalibrate 2) Reanalyze affected samples
9012A	Cyanide	Calibration standard (0.005, 0.01, 0.025, 0.05, 0.1 mg/L)	Daily, prior to analysis	$R \geq 0.995$	1) Evaluate system 2) Recalibrate
		CCV - Continuing calibration verification	After calibration, every 10 samples and end of run sequence	85-115%	1) Recalibrate 2) Reanalyze from last valid CCV
		CCB - Continuing calibration blank	After each CCV	< RL	1) Clean system 2) Recalibrate 3) Reanalyze from last valid CCB

TABLE 7-1
METHODS SUMMARY FOR SAMPLE PREPARATION/SAMPLE EXTRACTION
ALBION-SHERIDAN TOWNSHIP LANDFILL

Parameter	Matrix	Method[1]	Lab SOP Name
cyanide, Total	Water	9012	NC-WC-0032
Metals (ICP)	Water	3010A	CORP-IP-0003
Metals (GFAA)	Water	3020A	CORP-IP-0003
Semivolatiles[2]	Water	3520A	CORP-OP-0001
Volatiles	Water	5030	CORP-MS-0002
Volatiles	Air	TO-14	LP-ATL-0010

1. SW846 - Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, Third Edition, EPA, September 1986 and update II.
2. Includes Pesticides and PCBs.

ICP - Inductively Coupled Plasma GFAA - Graphite Furnace Atomic Adsorption

TABLE 7-2
LABORATORY ANALYTICAL METHODS SUMMARY
ALBION-SHERIDAN TOWNSHIP LANDFILL

Parameter	Methods[1,2]	
Metals	Groundwater	Laboratory SOP Name
aluminum	6010A	CORP-MT-0001
antimony	6010A	CORP-MT-0001
arsenic	7060A	CORP-MT-0003
barium	6010A	CORP-MT-0001
beryllium	6010A	CORP-MT-0001
cadmium	7131	CORP-MT-0003
calcium	6010A	CORP-MT-0001
chromium	6010A	CORP-MT-0001
cobalt	6010A	CORP-MT-0001
copper	6010A	CORP-MT-0001
iron	6010A	CORP-MT-0001
lead	7421/6010A	CORP-MT-0003/0001
magnesium	6010A	CORP-MT-0001
manganese	6010A	CORP-MT-0001
mercury	7471A/7470	CORP-MT-0005
nickel	6010A	CORP-MT-0001
potassium	6010A	CORP-MT-0001
selenium	6010A	CORP-MT-0001
silver	7761	CORP-MT-0003
sodium	6010A	CORP-MT-0001
thallium	7841	CORP-MT-0003
vanadium	6010A	CORP-MT-0001
zinc	6010A	CORP-MT-0001

TABLE 7-2
LABORATORY ANALYTICAL METHODS SUMMARY
ALBION-SHERIDAN TOWNSHIP LANDFILL

Parameter	Methods	
	Drinking Water/ Groundwater	Laboratory SOP Name
Organics		
TCL-BNAs	8270B[1]	CORP-MS-0001
TCL-Organochlorine Pesticides & PCBs	8080[1]	CORP-GC-0001
TCL-Volatile Organics (and 1,2-dibromo-3-chloropropane)	8260A[1]	CORP-MS-0002
Landfill Gas Volatiles	TO-14[2]	LP-ATL-0010
cyanide, Total	9012[1]	NC-WC-0031
chloride	325.2[3]	NC-WC-0013
sulfate	374.2[3]	NC-WC-0058
nitrate/nitrite	353.2[3]	NC-WC-0001
ammonia	350.3[3]	NC-WC-0038

1 SW-846 - Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, Third Edition, EPA, September 1986 and its Updates.

2 Compendium for the Analysis of Toxic Compounds in Ambient Air, EPA, 1984

3 Chemical Analysis of water and Wastewater, EPA, 1983

4 Quanterra will attempt to analyze for all appropriate metals by method 6010A first; however, if the lab has problems with instruments, samples will be analyzed by graphite furnace (7000 series).

GLASSWARE WASHING SOP			
	METALS	ORGANICS	WET CHEMISTRY
WASH:	Hot Water, Detergent Solution	Hot Water, Detergent Solution	Hot Water, Detergent Solution
RINSE:	3 Times Tap Water 1 Time 1:1 Nitric Acid 3 Times Type II Water	3 Times Tap Water 3 Times Type II Water	3 Times Tap Water 1 Time 1:2 Hydrochloric Acid 3 Times Type II Water
DRY:	Air	Muffle at 400°C for at least 2 hours	Air
STORAGE:	Designated Cabinets and Shelves	Designated Cabinets and Shelves	Designated Cabinets and Shelves

TABLE 7-4
TARGETED QUANTITATION LIMITS ORGANICS (AQUEOUS)
ALBION-SHERIDAN TOWNSHIP LANDFILL

	Targeted [1] Quantitation Limit	Method Detection Limit
TCL - Volatiles (8260A)	**Water µg/l**	**Water µg/l**
acetone	100	4.43
benzene	5	0.08
bromodichloromethane	1	0.12
bromoform	1	0.21
bromomethane	1	0.24
carbon disulfide	50	0.06
carbon tetrachloride	1	0.14
chlorobenzene	1	0.09
chloroethane	1	0.30
chloroform	1	0.14
chloromethane	1	0.19
chlorodibromomethane	1	0.13
1,2-dibromo-3-chloropropane	1	0.24
1,2-dichlorobenzene	1	0.13
1,3-dichlorobenzen	1	0.11
1,4-dichlorobenzene	1	0.10
1,1-dichloroethane	1	0.12
1,2-dichloroethane	1	0.13
1,1-dichloroethene	1	0.19
cis-1,2-dichloroethene	1	0.07
1,2-dichloropropane	1	0.09
cis-1,3-dichloropropene	1	0.11
trans-1,3-dichloropropene	1	0.09
ethylbenzene	1	0.11
2-hexanone	50	4.59
methylene chloride	1	0.37
trans-1,2-dichloroethene	1	0.13
methyl ethyl ketone	50	4.88
4-methyl-2-pentanone	10	3.03
styrene	1	0.08
1,1,2,2-tetrachloroethane	1	0.6
tetrachloroethene	1	0.07
toluene	1	0.07
1,1,1-trichloroethane	1	0.12
1,1,2-trichloroethane	1	0.20
trichloroethene	1	0.15
vinyl chloride	1	0.21
xylenes (total)	3	0.17

TABLE 7-4
TARGETED QUANTITATION LIMITS ORGANICS (AQUEOUS)
ALBION-SHERIDAN TOWNSHIP LANDFILL

TCL - Semi-Volatiles (8270B)	Targeted[1] Quantitation Limit Water µg/l	Method Detection Limit Water µg/l
acenaphthene	5	3.45
acenaphthalene	5	3.22
anthracene	5	3.56
benzo(a)anthracene	5	3.43
benzo(b)fluoranthene	5	4.02
benzo(k)fluoranthene	5	4.48
benzo(g,h,i)perylene	5	3.53
benzo(a)pyrene	5	3.74
bis(2-chloroethoxy)methane	5	2.99
bis(2-chloroethyl)ether	5	3.40
bis(2-chloroispropyl)ether	5	3.02
bis(2-ethylhexyl)phthalate	5	4.81
4-bromophenyl phenyl ether	5	3.66
butyl benzyl phthalate	5	4.03
4-chloroaniline	20	6.95
2-chloronaphthalene	5	2.83
4-chlorophenyl phenyl ether	5	2.95
chrysene	5	3.69
dibenz(a,h)anthracene	5	3.53
dibenzofuran	5	2.96
di-n-butyl phthalate	5	4.30
3,3'dichlorobenzidine	20	7.81
diethyl phthalate	5	3.28
dimethyl phthalate	5	2.99
2,4-dintrotoluene	5	3.58
2,6-dintrotoluene	5	3.81
di-n-octyl phthalate	5	4.43
fluoranthene	5	3.72
fluorene	5	3.22
hexachlorobenzene	5	3.82
hexachlorobutadiene	5	2.91
hexachlorocyclopentadiene	5	1.32
hexachloroethane	2	3.83
indeno(1,2,3-cd)pyrene	5	3.77
isophorone	5	3.29
2-methylnaphthalene	5	2.89
naphthalene	5	2.59
2-nitroaniline	20	3.13

TABLE 7-4
TARGETED QUANTITATION LIMITS ORGANICS (AQUEOUS)
ALBION-SHERIDAN TOWNSHIP LANDFILL

	Targeted[1] Quantitation Limit	Method Detection Limit
TCL - Semi-Volatiles (8270B)	**Water µg/l**	**Water µg/l**
3-nitroaniline	20	4.31
4-nitroaniline	20	6.23
nitrobenzene	5	2.82
n-nitrosodiphenylamine	5	3.99
n-nitrosodi-n-propylamine	5	3.23
phenanthrene	5	3.56
pyrene	5	4.15
1,2,4-trichlorobenzene	5	3.28
4-chloro-3-methylphenol	5	3.71
2-chlorophenol	5	3.29
2-methylphenol	5	3.52
4-methylphenol	5	8.05
2,4-dichlorophenol	5	3.55
2,4-dimethylphenol	5	5.33
4,6-dinitro-2-methylphenol	20	3.69
2,4-dinitrophenol	20	4.06
2-nitrophenol	5	2.56
4-nitrophenol	20	5.10
phenol	5	3.24
2,4,5-trichlorophenol	50	3.21
2,4,6-trichlorophenol	5	3.12
pentachlorophenol	20	4.29
carbazole	10	4.78

	Targeted[1] Quantitation Limit	Method Detection Limit
TCL - Pesticides/PCBs(8081)	**Water µg/l**	**Water µg/l**
alpha-BHC	0.01	0.0054
beta-BHC	0.01	0.0284
delta-BHC	0.01	0.0145
lindane	0.01	0.0073
heptachlor	0.01	0.0069
aldrin	0.01	0.0122
heptachlor epoxide	0.01	0.0133
endosulfan I	0.05	0.0075
dieldrin	0.02	0.0111
4,4'-DDE	0.02	0.0161

TABLE 7-4
TARGETED QUANTITATION LIMITS ORGANICS (AQUEOUS)
ALBION-SHERIDAN TOWNSHIP LANDFILL

	Targeted[1] Quantitation Limit	Method Detection Limit
TCL - Pesticides/PCBs(8080)	**Water µg/l**	**Water µg/l**
endrin	0.02	0.0350
endosulfan II	0.05	0.0140
4,4'-DDD	0.02	0.0143
endrin aldehyde	0.02	0.0197
endosulfan sulfate	0.05	0.0133
4,4'-DDT	0.02	0.0310
methoxychlor	0.5	0.0649
toxaphene	1	0.5180
endrin ketone	0.02	0.0125
alpha-chlordane	0.01	0.0095
gamma-chlordane	0.01	0.0088
Aroclor-1016	0.2	0.0374
Aroclor-1221	0.2	0.0725
Aroclor-1232	0.4	0.0668
Aroclor-1242	0.2	0.0811
Aroclor-1248	0.2	0.1183
Aroclor-1254	0.2	0.1054
Aroclor-1260	0.2	0.0984

Note:
(1)Targeted Quantitation Limits from MERA Operational Memorandum #6, Revision #4, September 13,1995.

TABLE 7-5
TARGETED QUANTITATION LIMITS INORGANICS (AQUEOUS)
ALBION-SHERIDAN TOWNSHIP LANDFILL

	Targeted [1] Quantitation Limit	Method Detection Limit
TAL - Inorganics (6010A/7000 series[2])	**Water**	**Water**
	µg/l	**µg/l**
aluminum	100	38.83
antimony	5	4.10
arsenic	5	2.26
barium	200	1.53
beryllium	1	1.53
cadmium	0.5	0.21
calcium	5,000	146.1
chromium	50	4.54
cobalt	10	6.72
copper	25	4.06
iron	100	43.46
lead	3	0.87
magnesium	30	51.27
manganese	20	2.38
mercury	0.2	0.0337
nickel	50	17.73
potassium	5,000	97.3
selenium	5	0.97
silver	0.5	0.168
sodium	1,000	211.81
thallium	2	0.923
vanadium	20	6.40
zinc	20	14.48
cyanide	5	0.003
Wet Chemistry Paramaters		
chloride	--	1,000
sulfate	--	5,000
nitrate/nitrite	--	40
ammonia	--	200

Note:
(1) Targeted Quantitation Limits from MERA Operational Memorandum #6, Revision #4, September 13,1995.
(2) For individual analytical methods, refer to Table 7-2.

TABLE 7-6
TARGETED QUANTITATION LIMITS LANDFILL GAS
ALBION-SHERIDAN TOWNSHIP LANDFILL

TCL - Volatiles (TO-14) Ambient Air Samples	**METHOD DETECTION LIMIT (ppb)**
benzene	0.61
carbon tetrachloride	0.32
chloroform	0.26
1,2-dichloroethane	0.84
1,1-dichloroethene	0.77
methylene chloride	0.68
tetrachloroethene	0.38
trichloroethene	0.25
vinyl chloride	0.26

FIELD PARAMETERS

methane	50 ppm
oxygen	Not Applicable
hydrogen sulfide	1 ppm

TABLE 11-1
PREVENTIVE MAINTENANCE PROCEDURES FOR FIELD INSTRUMENTS AND LABORATORY INSTRUMENTATION/EQUIPMENT
ALBION-SHERIDAN TOWNSHIP LANDFILL

INSTRUMENT	ACTIVITY	FREQUENCY
FIELD INSTRUMENTS:		
Redox Meter	Check Calibration	twice daily
	Clean electrode	each use
pH Meter	Check Calibration	Twice daily
	Immerse Probe in DI water	Each use
	Replace Batteries	As needed
Specific Conductance Meter	Check Calibration	Twice daily
	Clean Probe	Each use
	Replace Batteries	As needed
Thermometer	Inspect Instrument for change	Daily
	Replace Batteries (if digital)	As needed
Methane	Check calibration	Daily
Dissolved Oxygen Meter	Check Calibration	daily
	clean probe	Each use
	Replace Batteries	As needed

TABLE 11-1
PREVENTIVE MAINTENANCE PROCEDURES FOR FIELD INSTRUMENTS AND LABORATORY INSTRUMENTATION/EQUIPMENT
ALBION-SHERIDAN TOWNSHIP LANDFILL

INSTRUMENT	ACTIVITY	FREQUENCY
LABORATORY INSTRUMENTS:		
Gas Chromatography	Replace Septa	Daily
Mass Spectrometer	Clean Injection Port	Daily
	Clean Source	Weekly
	Change Pump Oil	Quarterly
	Clip Column Leader	Daily
	Check Gasses	Daily
	Check for Leaks	As Needed
	Check Autosampler Alignment	Daily
Gas Chromatography	Replace Septa	Weekly
	Clean Injection Port	Weekly
	Clip Column Leader	Weekly
	Check Reagents	Weekly
	Replace Nickel Tube	Monthly
	Clean Lamp (PID)	Monthly
	Clean and Refoil ECD	Annually
	Clean FID Jet	Monthly
	Check Gasses	Daily
	Check for Leaks	As Needed
	Check Autosampler Alignment	Daily
Purge and Trap	Replace Trap	Monthly
	Bake Lines	Monthly
	Clean Sample Vessels	Each Use
	Check Gasses	Daily
	Perform Leak Check	As Needed

TABLE 11-1
PREVENTIVE MAINTENANCE PROCEDURES FOR FIELD INSTRUMENTS AND LABORATORY INSTRUMENTATION/EQUIPMENT
ALBION-SHERIDAN TOWNSHIP LANDFILL

INSTRUMENT	ACTIVITY	FREQUENCY
Atomic Absorption FurnaceChange	Clean Windows	Weekly
	Graphite Tube	Daily
	Check Gasses	Daily
	Check Optics	Annually
	Check Autosampler Tubing	Daily
	Check Autosampler Alignment	Daily
	Check Rinse/Drain Bottles	Daily
	Change Graphite Contacts	Semi-Annually
	Flush Autosampler Tubing	Each Use
Inductively Coupled Plasma	Check Aspiration Tubing	Daily
	Clean Torch Assembly	Monthly
	Clean Spray Chamber	Monthly
	Check Gasses	Daily
	Clean/Lube Pump Rollers	As Needed
	Check O-Rings	Monthly
Mercury Cold Vapor Analyzer	Check Tubing	Daily
	Clean Sparger	After Each Sample
	Clean Windows	Monthly
	Change Source Lamp	As Needed
Autoanalyzer	Check Tubing	Daily
	Check for Bubbles	Each Use
	Check for Leaks	Each Use
	Check Pump	Daily
Laboratory Balances	Check Accuracy/Linearity	Daily
	Calibrate/Certify	Annually/As Needed
Laboratory Ovens	Temperature Monitoring	Daily
	Temperature Adjustments	As Needed

TABLE 11-1
PREVENTIVE MAINTENANCE PROCEDURES FOR FIELD INSTRUMENTS AND LABORATORY INSTRUMENTATION/EQUIPMENT
ALBION-SHERIDAN TOWNSHIP LANDFILL

INSTRUMENT	ACTIVITY	FREQUENCY
Laboratory Refrigerators	Temperature Monitoring	Twice a Day
	Temperature Adjustments	As Needed

FIGURES

FIGURE 2-1
PROJECT ORGANIZATION TEAM
ALBION-SHERIDAN TOWNSHIP LANDFILL
OPERATION AND MAINTENANCE

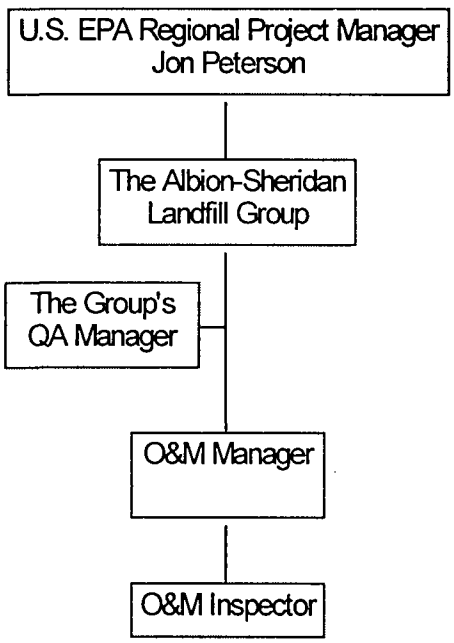
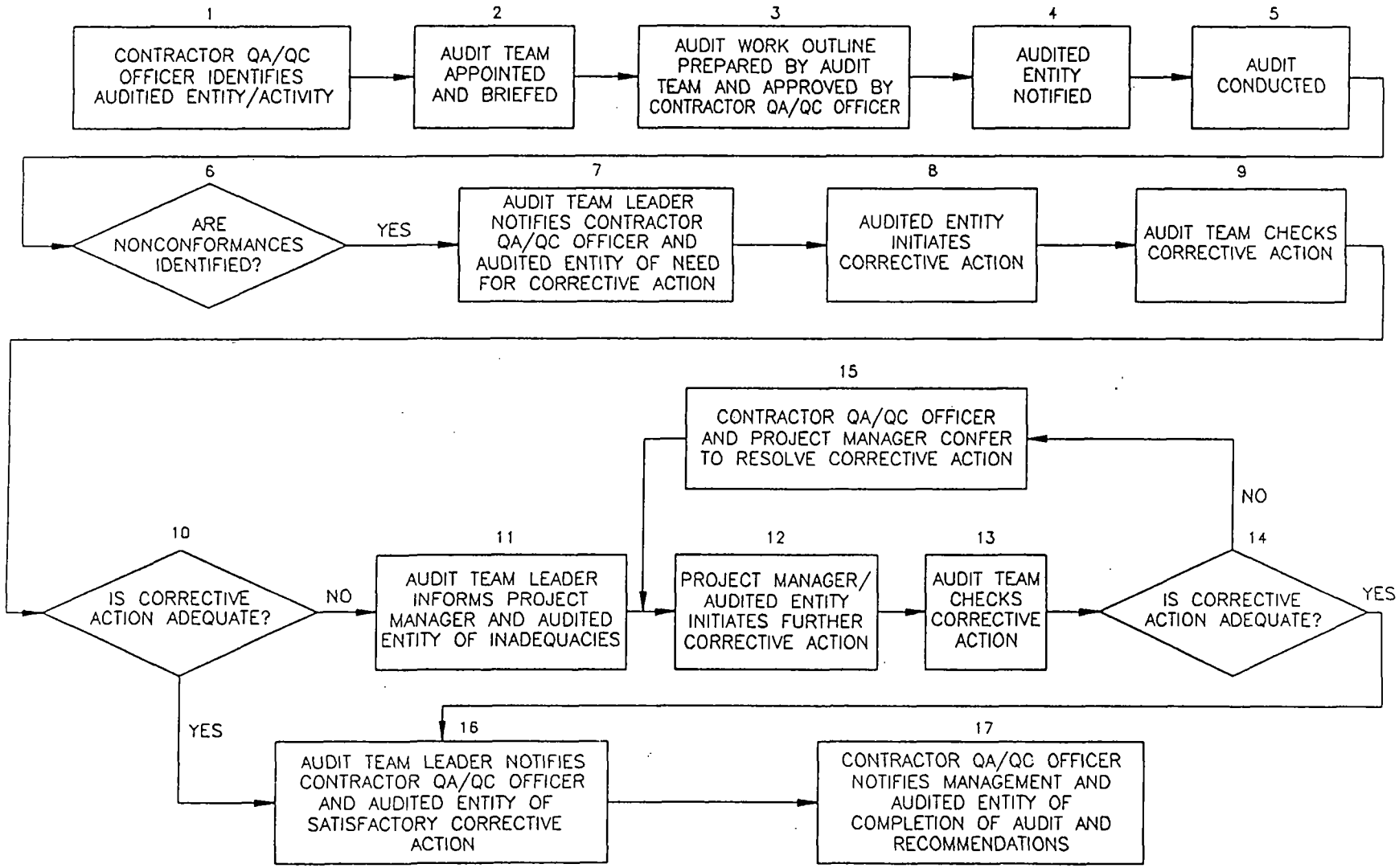


FIGURE 10-1

AUDIT FLOW CHART



PASAFC

FIGURE 10-2

EXAMPLE: FIELD AUDIT CHECKLIST

FIELD AUDIT CHECKLIST

Site Name _____

Location _____

Project Date(s) _____ Audit Date _____

Phone Number _____

Contractor/State Personnel _____

Address _____

Site Manager _____

Other Personnel and Affiliation _____

FIGURE 10-2 (Continued)
EXAMPLE: FIELD AUDIT CHECKLIST

Y, N, NA

PLANNING AND PREPARATION

1) What document(s) is(are) relevant to this audit? _____

_____

Date(s) Issued: _____

SAMPLE LOCATION

1) Do sample locations correspond to sampling plans? _____

2) Are sample locations noted in the field log? _____

SAMPLE COLLECTION

General Procedures

1) Were samples collected starting with the least likely contaminated and proceeding to the most likely contaminated? _____

Remarks _____

_____

2) Were new disposable rubber gloves worn during collection of samples? _____

Remarks _____

3) Was sampling equipment protected from possible contamination prior to sample collection? _____

If no, explain _____

_____

4) If equipment was cleaned in the field, were proper procedures used? _____

FIGURE 10-2 (Continued)
EXAMPLE: FIELD AUDIT CHECKLIST

Y, N, NA

5) What field instruments were used during this investigation? _____

_____

_____

_____

If no, explain _____

_____

Note: Y = Yes
N = Nonconformance
NA = Not Applicable

6) Were field instruments properly calibrated? _____
If no, explain _____

_____

7) Were calibration procedures documented in the field notes? _____
Remarks _____

_____

_____

8) Were the samples chemically preserved in the field? _____
If no, explain _____

9) Were the samples iced? _____

10) Were samples for selected parameters field filtered? _____
If yes, list parameters and describe procedures _____

_____

_____

FIGURE 10-2 (Continued)
EXAMPLE: FIELD AUDIT CHECKLIST

		Y, N, NA
11)	Do field staff have a copy of the Sampling and Analysis Plan?	_____
12)	Is the sampling equipment assembled according to the Sampling and Analysis Plan?	_____
13)	Do collection methods comply with the SAP?	_____
14)	Does field sampler have a sample cooler and proper forms, labels, tape, and ice?	_____
15)	Is sampling equipment decontaminated?	_____
16)	Is a bound notebook used to record all sampling activities?	_____
	Comment _____	

Surface Water Sampling

1)	What procedures and equipment were used to collect surface water samples?_____	_____
	_____	
	_____	
	Who collected samples? _____	
2)	Did the sampler insure that sediments were not collected along with water sample?	_____
3)	Note any deficiencies observed during the collection of the surface water samples _____	
	_____	
	_____	

FIGURE 10-2 (Continued)
EXAMPLE: FIELD AUDIT CHECKLIST

Soil/Sediment Sampling

1) What procedures, including equipment, were used to collect soil/sediment samples? _____

_____

2) Were the soil/sediment samples well mixed prior to placing the samples in the sample container? _____

3) Note any deficiencies observed during the collection of the soil/sediment samples _____

_____

_____

Biota Sampling

1) What procedures, including equipment, were used to collect the biota samples? _____

_____

_____

2) How were the samples preserved in the field? _____

_____

_____

3) Note any deficiencies observed during the collection of the biota samples. _____

_____

_____

FIGURE 10-2 (Continued)
EXAMPLE: FIELD AUDIT CHECKLIST

Other Sampling

1) What other types of samples were collected during this investigation?

_____

_____

_____

2) What procedures were used for collection of these samples?

_____

_____

_____

FIGURE 10-2 (Continued)
EXAMPLE: FIELD AUDIT CHECKLIST

Y, N, NA

QUALITY ASSURANCE/QUALITY CONTROL

(While all of these QA/QC procedures are not necessarily used, please identify the specific techniques which were employed by sampling personnel.)

1) Did the sampling personnel utilize any field blanks? _____

2) Were any equipment rinses collected? _____
If yes, list: _____
_____
_____

3) Were any duplicate samples collected? _____
If yes, list the types (parameter coverage, etc.); describe their collection: _____
_____
_____

4) Were any samples collected for matrix spike analysis?
If yes, list the types (parameter coverage, etc.); describe their handling: _____
_____
_____

FIGURE 10-2 (Continued)
EXAMPLE: FIELD AUDIT CHECKLIST

Y, N, NA

FIELD DOCUMENTATION AND CHAIN-OF-CUSTODY

1) Were split samples offered to the site owner or facility representative? _____

2) Was a receipt for samples given to the site owner or facility representative prior to leaving the site? _____

3) Were chain-of-custody records completed for all samples? _____

4) Were all samples properly sealed at the time of collection? _____

5) Were samples kept in a secure place after collection? _____

6) Were all sample labels and chain-of-custody forms signed by sample collector(s)? _____

7) Were sampling locations adequately documented? _____
If no, explain _____
_____
_____

8) Was sampling documented with photographs? _____
If yes, was a photolog maintained? _____

9) Were the samples shipped to a contract laboratory? _____

If yes:
Were the traffic report forms filed out properly? _____
Were the samples properly packed for shipment? _____

ATTACHMENTS

A

ATTACHMENT A
STANDARD OPERATING PROCEDURES FOR LABORATORY TASKS

SOP NC-SC-0001	SAMPLE CONTROL SOP
SOP NC-SC-0005	SAMPLE RECEIVING
SOP NC-QA-0002	BOTTLE BLANK SOP
SOP CORP-MS-0002	DETERMINATION OF VOLATILE ORGANICS BY GC/MS BASED ON METHODS 8240B AND 8260A
SOP CORP-OP-0001	EXTRACTION AND CLEANUP OF ORGANIC COMPOUNDS FROM WATERS AND SOILS, BASED ON SW-846 3500 SERIES, 3600 SERIES, 8150, 8151 AND 600 SERIES METHODS
SOP CORP-MS-0001	GC/MS ANALYSIS BASED ON METHOD 8270B, SW-846
SOP CORP-GC-0001	GAS CHROMATOGRAPHIC ANALYSIS BASED ON METHOD 8000A, 8010B, 8020A, 8021A, 8080A, 8081, 8150B AND 8151, SW-846
SOP CORP-IP-0003	ACID DIGESTION OF AQUEOUS SAMPLES BY SW846 AND MCAWW 200 SERIES METHODS
SOP CORP-MT-0005	PREPARATION AND ANALYSIS OF MERCURY IN AQUEOUS SAMPLES BY COLD VAPOR ATOMIC ABSORPTION, SW846 7470A AND MCAWW 245.1
SOP CORP-MT-0001	INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROSCOPY, SPECTROMETRIC METHOD FOR TRACE ELEMENT ANALYSIS, METHOD 6010A AND METHOD 200.7
SOP CORP-MT-0003	GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROSCOPY, SW-846 METHOD 7000A AND MCAWW 200 SERIES METHODS
SOP NC-WC-0032	CYANIDE DISTILLATION METHOD

SOP NC-WC-0031	CYANIDE AUTOMATED, PYRIDINE-BARBITURIC ACID METHOD
SOP NC-WC-0013	CHLORIDE-AUTOMATED FERRICYANIDE
SOP NC-WC-0001	NITRATE (NO2), NITRATE/NITRITE (NO3, NO2) AND NITRATE (NO3) AUTOMATED
SOP NC-WC-0038	AMMONIA (ISE)
SOP NC-WC-0058	SULFATE (TURBIDIMETRIC)
SOP-LP-ATL-0010	EPA METHOD TO-14 THE DETERMINATION OF VOLATILE ORGANICS (VOCS) IN AMBIENT AIR BY GC/MS-SCAN MODE

3.4. Exposure to chemicals must be maintained **as low as reasonable 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.

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

3.6. All work must be stopped in the event of a known or potential compromise to the health and safety of a Quanterra associate. The situation must be reported **immediately** to a laboratory supervisor.

3.7. Definitions{VITON gloves may be worn when halogenated solvents are used for extraction or sample preparation, nitrile gloves may be used when other solvents are handled. [Note: VITON is readily degraded by acetone; all solvents will readily pass through disposable latex rubber gloves.]}

4. PROCEDURE

4.1. 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.

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

4.3. Samples are requested by an analyst through the AS400 data base program PSR02401 designated by analyst sign on name and password. Options to request bottle(s) are method code, workorder number, prep code, QC batch number, lot I.D., and method group. This program is requested by MNLAB1 option 27 in AS400 data system.

4.4. Once the analyst requests bottles and the analyst exits out of the request program a requisition prints in the custodian area. This requisition contains Requested by: name Method: parameter. These requisitions are filled by the sample custodian. Once filled, the sample custodian enters the removal sample program. In the AS400 the custodian indicates which bottle number was removed for the specific test. The bottle is then signed out into the possession of the analyst requesting the bottle by name and date (See Fig. 4.1).

4.5. Each bottle has a lot number, sample workorder number, and a bottle suffix number (See Fig. 4.2).

4.6. Samples are signed out based on analyst users name and password and also date of transition and returned by the same means in the custody of the sample custodian.

4.7. Once the bottle is returned by the analyst, the sample custodian enters into the return maintenance program by the control number and reenters the custody of the bottle into the sample control area.

4.8. This program attaches the custodians name and date to the return of a specific bottle by control number (See Fig. 4.1). Control numbers are random numerical numbers. Control numbers are used only one time if the same bottle is requested again for the same or different parameters the bottle is given a different control number.

5. DEFINITIONS

5.1. Sample Receiving Inventory- Shows activity on a given workorder/bottle containing removal and return.

5.2. Open Removal Request Maintenance- If a bottle is requested twice or a bottle was not removed. Maintenance can be performed to delete the non used control numbers.

5.3. Sample Summary Removal/Inquiry/Maintenance- Driven by work order number then bottle number. Shows activity on each bottle by work order number. This is a internal chain of custody.

5.4. Work order number- Given to each sample designated to have a suffix for each individual test.

5.5. Bottle control number- Random number assigned to each bottle by test and by test requester.

5.6. Bottle number- Each sample number is suffixed with bottle numbers for each corresponding bottle

6. APPENDICES

QUANTERRA STANDARD OPERATING PROCEDURE

TITLE: SAMPLE CONTROL SOP

(SUPERSEDES: ENSECO SOP # LP-WALN-8100)

Prepared by: _____

Reviewed by: _____
Technology Specialist

Approved by: _____
Quality Assurance Manager

Approved by: _____
Environmental Health and Safety Coordinator

Approved by: _____
Laboratory Director

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1. PURPOSE

1.1. The intent of the sample custodian maintenance program is to show custody of individual bottles based on workorder number as well as bottle control numbers. This program is designed to act as an internal chain of custody.

2. RESPONSIBILITIES

2.1. Analyst - It is the analysts responsibility to provide the correct request(s) for bottles to the sample custodian via the PSR02401 Program, and return all bottles to the custodian.

2.2. Sample Custodian -

2.2.1. The sample custodian shall fill all bottle requests in a timely fashion, and document the transfers in the AS400.

2.2.2. The custodian must correctly document the bottle information as required.

2.2.3. The custodian is responsible for checking that each outgoing bottle has a lot number, workorder number, and a bottle suffix number.

2.2.4. The custodian is responsible for re-entering the returned bottles to the system.

2.3. Quality Assurance/Management - It is the responsibility of QA and Management to provide the analysts with training to perform the procedures described herein, and to make sure that the system protocols are being followed by all analysts.

3. SAFETY

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

3.2. Eye protection that satisfied ANSI Z87.1 (as per the Chemical Hygiene Plan), 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.

3.3. The health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the Material Safety Data Sheets (MSDS) maintained in the laboratory.

FIGURE 4.1

[illegible] 6/15/94 [illegible] SAMPLE [illegible] REMOVAL REQUEST PAGE [illegible]

REQUESTED BY: KARDOS

METHOD: DB Petro.Hydrocarbons, Total Rec. (TRPH) by IR

STORAGE LOCATION	WORK ORDER #	PICKED CNTR#	CONTROL #	CLIENT #	ANALYSIS	LOTID	SMP#	SFX	MATRIX DESCRIPTION	QTY RCVD	QTY REQD
IN TRANSIT	N9444-1-11		10018	074704	I-10-DB	A4F080045	032		WATER SURFACE/GROUND	10	1
	N9444-1-12		10019	074704	I-10-DB	A4F080045	032	S	WATER SURFACE/GROUND	10	1
	N9444-1-13		10020	074704	I-10-DB	A4F080045	032	D	WATER SURFACE/GROUND	10	1
IN TRANSIT	N9485-1-11		10022	074704	I-10-DB	A4F080054	022		WATER SURFACE/GROUND	8	1
IN TRANSIT	N9488-1-11		10023	074704	I-10-DB	A4F080054	023		WATER SURFACE/GROUND	8	1
IN TRANSIT	N9495-1-11		10024	074704	I-10-DB	A4F080054	025		WATER SURFACE/GROUND	9	1
CC/GC	00324-1-01		[illegible]	007561	I-09-DB	A4F100016	001		WATER SURFACE/GROUND	4	1
CD/GC	00326-1-01		10029	007561	I-09-DB	A4F100016	003		WATER SURFACE/GROUND	4	1
CD/GC	00327-1-01		[illegible]	007561	I-09-DB	A4F100016	004		WATER SURFACE/GROUND	4	1
CD/MS	00325-1-01		[illegible]	007561	I-09-DB	A4F100016	002		WATER SURFACE/GROUND	4	1
GG	00780-1-01		10032	074704	I-10-DB	A4F110007	026		WATER SURFACE/GROUND	4	1
GE/537/MS	00784-1-12		10033	074704	I-10-DB	A4F110007	027		WATER SURFACE/GROUND	9	1
GE/537/MS	00786-1-12		[illegible]	074704	I-10-DB	A4F110007	028		WATER SURFACE/GROUND	9	1
KK/MS/GCS	01249-1-09		10035	007561	I-10-DB	A4F130046	001		WATER SURFACE/GROUND	7	1
N/540/MS	00045-1-11		10025	074704	I-10-DB	A4F090034	050		WATER SURFACE/GROUND	10	1
N/540/MS	00066-1-11		[illegible]	074704	I-10-DB	A4F090034	057		WATER SURFACE/GROUND	[illegible]	1
NN/537/MS	01591-1-11		10036	074704	I-10-DB	A4F140029	001		WATER SURFACE/GROUND	8	1
NN/537/MS	01592-1-11		[illegible]	074704	I-10-DB	A4F140029	002		WATER SURFACE/GROUND	8	1
NN/537/MS	01607-1-11		[illegible]	074704	I-10-DB	A4F140029	014		WATER SURFACE/GROUND	[illegible]	1
NN/537/MS	01610-1-11		10039	074704	I-10-DB	A4F140029	016		WATER SURFACE/GROUND	10	1
NN/537/MS	01612-1-11		10040	074704	I-10-DB	A4F140029	017		WATER SURFACE/GROUND	10	1
[illegible]	00485-1-01		10031	074704	I-10-DB	A4F100029	016		WATER SURFACE/GROUND	5	1
95/VF W D E	N9481-1-11		10021	074704	I-10-DB	A4F080054	021		WATER SURFACE/GROUND	8	1

RECEIVED BY: _____ DATE: __/__/__

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

FIGURE 4.2

001
A35GT 063036
2X40ML VIAL RECDATE: 030495
TB-0303
EMS REQUIRED, CLIE A-5C040010-001
Nor MS

FIGURE 4.3

[illegible] SAMPLE RECEIVING INVENTORY [illegible]
[illegible] NORTH CANTON

CLIENT: 005637 PPG INDUSTRIES, INC. WORK ORDER: A2X7P
CONTACT: Duane Nielsen LAB ID: A-50220005-001
[illegible] COLLECTION DATE: 2/21/95
TO: LIME LAKE #5 1ST QUARTER 1995 SAMPLING DATE: 2/21/95
AMOUNT RECVD: 1X1GAL/6X1L/500/4X40ML ANALYTICAL DUE DATE: 3/06/95
STORAGE LOC: W-63/S44/MS DISPOSAL DATE: 0/00/00
MATRIX: WATER SURFACE/GROUND
[illegible] 2-21-95
COMMENTS
REPORT QC, METDISS ARE FILT & PRES.

CNTR#	STAT	WORK #	CTRL #	CODES	<----REQUESTED----> REMOVED DATE	USER ID	<---- RETURNED ----> DATE	USER ID
		METHOD DESCRIPTION						
1	OUT	A2X7P	102060	I-15-DN	2/22/95	[illegible]		
		Volatile Organics, 30/MS (624)			2/22/95		2/22/95	
2	OUT	A2X7P	102060	I-15-DN	2/22/95	[illegible]		
		Volatile Organics, 30/MS (624)			2/22/95		2/22/95	
3	OUT	A2X7P	102060	I-15-DN	2/22/95	[illegible]		
		Volatile Organics, 30/MS (624)			2/22/95		2/22/95	
4	OUT	A2X7P	102060	I-15-DN	2/22/95	[illegible]		
		Volatile Organics, 30/MS (624)			2/22/95		2/22/95	
5	INSPD	A2X7P	102427	I-49-DP	2/22/95	[illegible]		
		Base/Neutrals and Acids (625)			2/22/95		2/22/95	STEPHENT
6	AVAIL							
		NO ACTIVITY ON THIS CONTAINER						
7	AVAIL	A2X7P	105661	I-88-VC	3/06/95	CDXC		
		Alkalinity, Total			3/06/95		3/06/95	STEPHENT
8	AVAIL	A2X7P	105757	I-88-DM	3/06/95	BELVIN		
		Chloride, Manual Titration			3/06/95	STEPHENT	3/06/95	STEPHENT
9	AVAIL	A2X7P	102120	I-88-VD	2/22/95	GREGORY		
		Nitrate			2/22/95		2/22/95	STEPHENT
10	AVAIL	A2X7P	102122	I-88-VE	2/22/95	GREGORY		
		Nitrite			2/22/95	STEPHENT	2/22/95	STEPHENT
11	AVAIL	A2X7P	103561	I-88-AX	2/27/95	KUHLEN		
		Solids, Filterable (TDS)			2/27/95	STEPHENT	2/27/95	STEPHENT
12	AVAIL							
		NO ACTIVITY ON THIS CONTAINER						
13	AVAIL							
		NO ACTIVITY ON THIS CONTAINER						
14	AVAIL							
		NO ACTIVITY ON THIS CONTAINER						
15	OUT	A2X7P	105854	I-88-CW	3/06/95	HARDGREE		
		Chemical Oxygen Demand, Titrim			3/06/95		3/06/95	STEPHENT
16	OUT	A2X7P	106255	I-88-CI	3/07/95	HARTS		
		Nitrogen, Ammonia			3/07/95	STEPHENT	[illegible]	

End of Report

QUANTERRA STANDARD OPERATING PROCEDURE

TITLE: SAMPLE RECEIVING

(SUPERSEDES: QES NC-SC-0005 (REVISION 0))

Prepared by: Lois Esso

Reviewed by: Doris Verver
Technology Specialist

Approved by:
Quality Assurance Manager

Approved by:
Environmental Health and Safety Coordinator

Approved by: for Robert George
Laboratory Director

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1. PURPOSE

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

1.2. 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.

2. RESPONSIBILITIES

2.1. It is the responsibility of the analyst to perform the analysis described herein in full compliance with this SOP.

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

3. SAFETY

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

3.2. Eye protection that satisfies ANSI Z87.1 (as per the Chemical Hygiene Plan), 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.

3.3. The health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the Material Safety Data Sheets (MSDS) maintained in the laboratory

3.4. 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. Solvent and waste containers will be kept closed unless transfers are being made.

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

3.6. All work must be stopped in the event of a known or potential compromise to the health and safety of a Quanterra associate. The situation must be reported **immediately** to a laboratory supervisor.

4. PROCEDURES

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

4.2. The Sample Control person will open and examine the shipping container, remove the enclosed sample documents, and record the following information on the Cooler Receipt Form.

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

4.2.2. Presence of the custody papers inside the cooler

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

4.2.4. The custody papers were signed in the appropriate place

4.2.5. Presence of the shippers packing slip

4.2.6. Presence of packing material information, if yes, type of packing material

4.2.7. Conditions of samples at receipt (chilled, ect.). If temp vial is present, it is used to take the temperature. Otherwise temperature is taken along side of the bottle containers. It is recorded which way the temperature was taken.

4.2.8. Bottles sealed in separate plastic bags

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

4.2.10. Complete bottle labels (date, signed, analysis, preservations)

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

4.2.12. Correct bottles used for the tests indicated

4.2.13. VOA bottles were checked for the presence of air bubbles

4.2.14. Sufficient amount of sample sent in each bottle

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

4.2.16. pH's are taken, on all preserved samples less volatiles, 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.

4.3. 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 to 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.

4.4. 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 not discrepancy between documents and ensure that all documents are properly completed and signed.

4.5. If any problems or discrepancies are noted during the sample receiving process, such as improper paperwork, broken, leaking samples, immediately notify the Project Manager. They in turn will contact the client contact in an attempt to rectify the situation.

4.6. 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.

4.7. The Sample Control person will assign each sample a laboratory identification number as determined by the laboratory computer, designating a unique lot number for each project received with each lot delegating specific sample numbers for each client identification.

4.7.1. Lot Numbers: The lot number is nine characters. Lot number A5J010121 is described as follows:

A - The alpha character indicates the Quanterra location where the samples were received.

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

4 - The numeric character indicates the last digit of the year (i.e. 1995).

J - The alpha character indicates the 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.

01 - The next 2 numeric characters identify the system under which the lot has been logged (01 = QuantIMS, 00 = Legacy. This is a temporary identification allowing for easy identification of the system in use while the QuantIMS system is phased in and the Legacy system is phased out.

21 - The next 2 numeric characters are the sequential assignment of numbers specific to each lot received. Each day the first lot logged in receives the number "01", the second lot receives the number "02", etc..

For example:

If four bottles were submitted under Client ID numbers AB100-AB103 and the laboratory identification number generated by the computer is A2K100001, 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	A2K100001-001
AB 101	A2K100001-002
AB 102	A2K100001-003
AB 103	A2K100001-004

4.7.2. 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 A5J010121-001 and A5J010121-002.

4.7.3. 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: A5J010121-001X is a sample duplicate for sample A5J010121-001.

4.7.4. Work Order Numbers: Each test requested by the client for an individual sample receives an individual 8 digit work order number assigned by the LIMS system. 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).

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 sequental, 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.

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

4.8.1. Organic extractable samples (Semivolatiles, Pesticides/PCBs) are to be placed into the walk-in refrigerators located in Sample Receiving. (Between Sample Log-In and Sample Custodian)

4.8.2. Volatile samples are to be stored in the two two-doored refrigerators located in the Sample Custodian area. One refrigerator is for MS Volatile samples and the second is for GC Volatiles samples.

4.8.3. Inorganic samples are to be placed into the walk-in refrigerators located in Sample Receiving. (Between Sample Log-In and Sample Custodian)

4.8.4. Metals samples are placed in a non-refrigerated room located in the Sample Custodian area.

5. DEFINITIONS

5.1. Refer to the glossary in the Quality Assurance Management Plan (QAMP)

6. APPENDICES

6.1. Comments

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

6.1.2. 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.

QUANTERRA STANDARD OPERATING PROCEDURE

TITLE: BOTTLE BLANK SOP

(SUPERSEDES: QUANTERRA SOP #NC-QA-0002 (REVISION #0))

Prepared by: _____

Reviewed by: _____
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1. PURPOSE

1.1. This SOP details the protocols followed by Quanterra Laboratories in verifying that sampling bottles are free of contaminants. The methods used for this SOP are all EPA-approved methods and meet the requirements in *Specifications and Guidance for Contaminant-Free Sample Containers,* EPA 540/R-93/051.

1.2. Quanterra Laboratories uses precleaned sampling bottles for aqueous volatile organic compounds and total Organic Halogen samples. These bottles are verified to be free of contamination by the manufacturer.

1.3. Quanterra Laboratories will purchase certified, precleaned sampling bottles whenever requested for a site-specific project.

1.4. All other sampling bottles used by Quanterra Laboratories are included in a bottle blank program.

1.5. 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.

2. RESPONSIBILITIES

2.1. It is the responsibility of the employee to perform the procedure described herein in full compliance with this SOP.

2.2. It is the responsibility of the Laboratory Director, QA Manager, and departmental Supervisor of this facility to assure that the analysis described is performed in full compliance wit this SOP. It is also their responsibility to supply adequate training, materials, and equipment to enable the employee to perform this SOP correctly.

2.3. The Shipping Supervisor is responsible for ordering bottles, notifying QA of the need to start a bottle blank project, releasing lots as approved by QA, and keeping the bottle blank data on file.

2.4. The QA Manager is responsible for establishing a bottle blank work order in the database, review of the analytical data and approval of the lot(s).

2.5. The laboratory staff will analyze the bottle blanks as per any routine samples, as per the cited prep/analytical methods, and compliant to all Quanterra policies.

2.6. Quanterra Laboratories uses precleaned sampling bottles for aqueous volatile organic compounds and Total Organic Halogen samples. These bottles are verified to be free of contamination by the manufacturer.

2.7. Quanterra Laboratories will purchase certified, preclean sampling bottles whenever requested for a site-specific project.

2.8. All other sampling bottles used by Quanterra Laboratories are included in a bottle blank program.

2.9. It is the responsibility of Shipping to order and make sure the bottles are tested for the proper analysis described herein in full compliance with this SOP.

3. SAFETY

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

3.2. Eye protection that satisfies ANSI Z87.1 (as per the Chemical Hygiene Plan), 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.

3.3. The health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the Material Safety Data Sheets (MSDS) maintained in the laboratory. The following specific hazards are known:

3.4. 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. Solvent and waste containers will be kept closed unless transfers are being made.

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

3.6. All work must be stopped in the event of a known or potential compromise to the health and safety of a Quanterra associate. The situation must be reported **immediately** to a laboratory supervisor.

3.7. Definitions {VITON gloves may be worn when halogentated solvents are used for extraction or sample preparation, nitrile gloves may be used when other solvents are handled. [Note: VITON is readily degraded by acetone; all solvents will readily pass through disposable latex rubber gloves.]}

4. PROCEDURES

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

4.2. 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.

4.3. Quanterra Laboratories purchases several different types of sampling bottles directly from the manufacturer. These bottles include the following types:

TABLE 1 BOTTLE SIZES AND TYPES

SIZE	TYPE
1 liter	Glass[3]
1 liter	Plastic[1]
*40 mL	Glass[1]
*250 mL	Glass[1]
250 mL	Plastic[2]
500 mL	Plastic[2]
60 mL	Widemouth Glass[1]
120 mL	Widemouth Glass[1]
500 mL	**Widemouth Glass[1]

[1]Shipment is 400 cases of bottles. [2]Shipment is 20 cases of bottles. [3]Shipment is 800 cases of bottles.

4.4. Each bottle type is purchased in designated quantities. Each shipment received at the laboratory is labeled with a designated lot number for tracking purposes.

*Note: 40 mL vials with HCl, 40 mL vials with no preservative, and total organic halogen bottles, will have certification of analysis from the manufacturer. The certification will be stored with the bottle blank program reports.

**Note: 500 mL widemouth will have manufacturer's certification

4.5. Upon placing an order for bottles, the Shipping department will notify the Quality Assurance Manager or their designee, that a bottle blank project is needed.

4.6. The QAM or designee will establish a project in the AS400 database for the bottles to be tested.

4.7. Three cases are randomly selected from each lot number of bottles. Several bottles are randomly chosen from the three cases selected and are prepared and analyzed for each analytical parameter. Table 2 lists those parameters tested in the bottle blank program.

TABLE 2 BOTTLE BLANK PROGRAM

No. of Bottles	Bottle Size	Bottle Type	Preservative	Parameter	Method
Water					
*	40 mL	Glass	Hydrochloric Acid	GC VOC 502.2	502.2
1	1 liter	Glass	NP	BNA	8270
1	1 liter	Glass	NP	Pest/PCB	8080
1	1 liter	Glass	Hydrochloric Acid	TRPH by IR	418.1
1	1 liter	Plastic	Nitric Acid	TAL metals	6010/7000
1	1 liter	Glass	Sulfuric Acid	Oil & Grease	413.1
*	250 mL	Glass	Sulfuric Acid	Total Organic Halogen	9020
1	250 mL	Plastic	NP	Conductivity	9050
1	500 mL	Plastic	Sulfuric Acid	Ammonia Nitrogen	350.3
Solid					
1	60 mL	Widemouth	NP	GC VOC 502.2	502.2

4	60 mL	Widemouth	NP	TAL Metals	6010/7000
9	120 mL	Widemouth	NP	BNA	8270
9	120 mL	Widemouth	NA	Pest/PCB	8080
1	120 mL	Widemouth	Freon	TRPH by IR	418.1

NP - No preservative required

*Note: 40 mL vials with HCl, 40 mL vials with no preservative, and total organic halogen bottles, will have certification of analysis from the manufacturer. The certification will be stored with the bottle blank program.

4.8. Each bottle selected for analysis is filled with purged, reagent water and submitted to the laboratory for analysis, for total recoverable petroleum hydrocarbons (TRPH), Freon is used in place of purged, reagent water.

4.9. Upon completion of the analysis the lab will provide a report to the QAM of the analytical results.

4.10. The QAM will review the analysis and approve the lot for release to the laboratory. This approval will be communicated to the Shipping department and the report given to the Shipping department for filing.

4.11. Results of the analyses for each bottle type are complied and verified against quality control chart criteria prior to using any of the sampling bottles in the field. Results are kept in Shipping in a secure file.

4.12. Each bottle blank is required to contain less than the laboratory reporting quantitation limit for the parameter tested.

4.13. If a bottle is found to contain greater than the reporting quantitation limit, then another identical bottle type from that lot is chosen and analyzed for that specific parameter. (Repeat Section 4.3)

5. DEFINITIONS

5.1. Refer to the glossary in the Quality Assurance Management Plan (QAMP)

6. APPENDICES

6.1. Not Applicable

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QUANTERRA STANDARD OPERATING PROCEDURE

TITLE: DETERMINATION OF VOLATILE ORGANICS BY GC/MS BASED ON METHODS 8240B AND 8260A

(SUPERSEDES: REVISION 0)

Prepared by: Richard Burrows

Reviewed by: _____
Technology Standardization Committee

Approved by: _____
Director, Quality Assurance

Approved by: _____
Director, Environmental Health and Safety

Approved by: _____
Management

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APPLICATION OF METHOD 8260A TO THE DRINKING WATER ANALYTE LIST 49

QUANTERRA STANDARD OPERATING PROCEDURE

TITLE: **EXTRACTION AND CLEANUP OF ORGANIC COMPOUNDS FROM WATERS AND SOILS, BASED ON SW-846 3500 SERIES, 3600 SERIES, 8150, 8151 AND 600 SERIES METHODS.**

(SUPERSEDES: Revision 1)

Prepared by: Richard Burrows

Reviewed by: _____
Technology Standardization Committee

Approved by: _____
Director, Quality Assurance

Approved by: _____
Director, Health and Safety

Approved by: _____
Management

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1. SCOPE AND APPLICATION

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

1.2. This SOP is applicable to methods 8240B (capillary column) and 8260A.

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. Directions are provided for analysis based on methods 8240B and 8260A. The approximate working range is 5 to 200 µg/L for 5 mL waters, 1 to 60 µg/L for 25 mL purge waters, 5 to 200 µg/kg for low-level soils, and 630 to 25,000 µg/kg for medium-level soils. Reporting limits are listed in Tables 1, 3 and 14.

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

2. SUMMARY OF METHOD

2.1. The differences between method 8240B and 8260A as performed at Quanterra are summarized here.

2.1.1. Method 8240 was written as a packed column method; however, Quanterra has modified the method to use capillary columns for improved performance. Accordingly, when the surrogates and internal standards listed in this SOP are used, methods 8240B and 8260A are similar except for the minimum response factors listed in Table 11. ***Both*** methods may use 5 or 25 mL purge volumes, depending on the detection limits required, and both methods have the same calibration criteria.

2.1.2. When a method 8260A analysis is requested, a target compound list based on that contained in method 524.2 is frequently requested. One of the target compounds, bromochloromethane, is a method 8240B internal standard, so alternative surrogates and internal standards must be used. Quanterra's standard analyte list, surrogates and internal standards for method 8260A (drinking water analyte list) are listed in Appendix A, Tables 14, 15, and 16.

2.2. The 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.

2.3. If the above sample introduction techniques are not applicable, a portion of the sample is dispersed in methanol to dissolve the volatile organic constituents. A portion of the methanolic solution is combined with water in a purging chamber. It is then analyzed by purge and trap.

2.4. In the purge and trap process, an inert gas is bubbled through the solution at ambient temperature (40°C for 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.

2.5. 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. 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. If no changes to instrumental parameters are made, a batch may extend for a maximum of 24 hours. 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. In some cases, at client request, the MS/MSD may be replaced with a matrix spike and sample duplicate. Refer to the Quanterra QC Program document (QA-003) for further details of the batch definition.

3.2. Method Blank

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)

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

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)

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)

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)

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 an antifoaming agent (e.g., J.T. Baker's Antifoam B silicone emulsion) can be used. A blank spiked with this agent must be analyzed with the sample because of the non-target interferences associated with the agent.

5. SAFETY

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

5.2. The Chemical Hygiene Plan (CHP) gives details about the specific health and safety practices which are to be followed in the laboratory area. Personnel must receive training in the CHP, including the written Hazard Communication plan, prior to working in the laboratory. Consult the CHP, the Quanterra Health and Safety Policies and Procedures Manual, and available Material Safety Data Sheets (MSDS) prior to using the chemicals in the method.

5.3. Consult the Quanterra Health and Safety Policies and Procedures Manual for information on Personal Protective Equipment. Eye protection that satisfies ANSI Z87.1 (as per the Chemical Hygiene Plan) and a laboratory coat must be worn in the lab. 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. Disposable gloves shall not be reused.

5.4. The health and safety hazards of many of the chemicals used in this procedure have not been fully defined, therefore each chemical compound should be treated as a potential health hazard. Additional health and safety information can be obtained from the MSDS files maintained in the laboratory. The following specific hazards are known:

5.4.1. Chemicals that have been classified as carcinogens, or potential carcinogens, under OSHA include: Acrylonitrile, benzene, carbon tetrachloride, chloroform, 1,2-dibromo-3-chloropropane, 1,4-dichlorobenzene, and vinyl chloride.

5.4.2. Chemicals known to be flammable are: Methanol.

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 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 operations 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 Quanterra associate. The situation must be reported **immediately** to a laboratory supervisor.

5.8. Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices outlined in the Quanterra 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.

6. EQUIPMENT AND SUPPLIES

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

6.2. Syringe: 5 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 pipets: Pasteur.

6.7. pH paper: Wide range.

6.8. Gases:

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

6.8.2. Compressed air: Used for instrument pneumatics.

6.8.3. Liquid nitrogen: Used for cryogenic cooling if necessary.

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.

6.9.2. Trap: The trap should be at least 25 cm long and have an inside diameter of at least 0.105 inch. Starting from the inlet, the trap should contain the following amounts of absorbents: 1/3 of 2,6-diphenylene oxide polymer (Tenax-GC, 60/80 mesh or equivalent), 1/3 of silica gel (Davison Chemical, 35/60 mesh, grade 15, or equivalent), and 1/3 coconut charcoal. It is recommended to use a trap that also 1.0 cm methyl silicone packing at the inlet to extend its life. If it is not necessary to analyze for any fluorocarbons then the charcoal phase can be replaced with the polymer. Other traps. such as Supelco's Vocarb 3000 and 4000, may be used if the Quality Control criteria are met.

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 or heated bath capable of maintaining the purge device at 40°C is used for low level soil analysis only.

6.10. Gas Chromatograph/Mass Spectrometer System:

6.10.1. Gas Chromatograph: The gas chromatograph (GC) system must be capable of temperature programming. The system must include or be interfaced to a purge and trap device. All GC carrier gas lines must be made from stainless steel or copper tubing.

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

6.10.2.1. Column 1: 105m x 0.53 ID Rtx-624 with 3 µm film thickness.

6.10.2.2. Column 2: 75 m x 0.53 ID DB-624 widebore with 3 µm film thickness.

6.10.3. 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.

6.10.4. GC/MS interface: In general glass jet separators are used but any interface that achieves all acceptance criteria may be used.

6.10.5. 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.

6.10.6. Cryogenic Cooling: Some columns require the use of liquid nitrogen to achieve the subambient temperature required for the proper separation of the gases.

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.

7.2. 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. Stock standards for gases must be replaced at least every week. Other stock standards must be replaced at least every 6 months.

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 with minimal headspace and monitored for signs of degradation or evaporation, especially just prior to preparing calibration standards from them. The standards are stored for a maximum of one week.

Note: By definition in this SOP, a stock standard is one that is stored in the freezer and is only opened in order to prepare working standards. A working standard is opened more frequently in order to prepare the calibration, spiking or tuning standards used at the instrument. Stock and working standards may be at the same concentration.

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. Once the ampoule is opened the expiration dates in Section 7.2.1.1 become effective.

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 25 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. Standard 40 mL glass screw-cap VOA vials with Teflon-faced silicone septa may be used for both liquid and solid matrices. Solid samples may also be collected in wide-mouth glass jars with Teflon-lined caps. Samples should be introduced into the containers with minimum agitation to avoid loss of volatile compounds. For liquid samples, each VOA vial should be filled without introduction of bubbles. Fill until there is a meniscus over the lip of the vial. The lid with septum (Teflon side toward the sample) should be tightened onto the vial. After tightening the lid, the vial should be inverted and tapped to check for air bubbles. If there are any air bubbles present the sample must be retaken. Sample containers for solid samples should be filled as completely as possible with minimum air space.

8.2. Water samples are preserved with HCl. Aromatic compounds are particularly susceptible to biodegradation at normal pH. The pH of the sample should be adjusted to less than 2 with HCl in the field at the time of sampling.

8.2.1. If the sample is unpreserved every reasonable effort should be made to analyze the sample within 7 days from sampling. The condition should be documented as an anomaly and the normal holding time applied. If the sample requires analysis of aromatic compounds the potential impact on the data must be documented.

8.3. All samples must be iced or refrigerated at 4° ± 2°C from the time of collection until analysis or extraction.

8.4. For shipping information, see the facility Sample Procurement Protocol SOP.

8.5. The holding time is fourteen days from sampling to the completion of analysis.

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, 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 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 at least annually. The recovery limits are mean recovery +/- 3 standard deviations for surrogates and LCS, and mean recovery +/- 2 standard deviations for matrix spikes. Precision limits for matrix spikes / matrix spike duplicates are 0 to mean relative percent difference + 2 standard deviations.

9.2.1. For medium level soils only, these limits do not apply to dilutions. Surrogate and matrix spike recoveries for medium level soils will be reported unless the dilution is more than 5X.

9.2.2. All surrogate, LCS, and MS recoveries (except for dilutions) must be entered into QuantIMS (when available) or other database so that accurate historical control limits can be generated. For tests without a separate extraction, surrogates and matrix spikes will be reported for all dilutions.

9.2.3. Refer to the QC Program document (QA-003) for further details of control limits.

9.3. Surrogates

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 Tables 8 and 16. 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 or flag the data as "Estimated Concentration" if neither of the above resolves the problem.

The decision to reanalyze or flag the data should be made in consultation with the client. 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.

9.3.1. 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.

9.3.2. Refer to the Quanterra QC Program document (QA-003) for further details of the corrective actions.

9.4. Method Blanks

For each batch of samples, analyze a method blank. The method blank is normally analyzed immediately after the calibration standards. For low-level volatiles, the method blank consists of reagent water. For medium-level volatiles, the method blank consists of 9.0 mL of methanol. 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) or at or above 5% of the measured concentration of that analyte in the associated samples, whichever is higher.

- 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. Such action should be done in consultation with the client.

9.4.1. 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.

9.4.2. 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.

9.4.3. Refer to the Quanterra QC Program document (QA-003) for further details of the corrective actions.

9.5. Laboratory Control Samples (LCS)

For each batch of samples, analyze a LCS. The LCS is normally analyzed immediately after the method blank. 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. (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.)

- 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.

9.5.1. Refer to the Quanterra QC Program document (QA-003) for further details of the corrective action.

9.5.2. 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.

9.6. Matrix Spikes

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.

- 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.

9.7. Nonconformance and Corrective Action

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

9.8. Quality Assurance Summaries

Certain clients may require specific project or program QC which may supersede these method requirements. Quality Assurance Summaries should be developed to address these requirements.

9.9. Quanterra QC Program

Further details of QC and corrective action guidelines are presented in the Quanterra QC Program document (QA-003). Refer to this document if in doubt regarding corrective actions.

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 volumetric flasks or in a 5 or 25 mL Luerlok syringe. Calculate the volume of reagent water required for the dilution. Fill the 5/25 mL 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 5/25 mL mark and inject the proper aliquot of sample into the syringe. If the dilution required would use less than 5 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 calibration standards (including purge time and flow, desorb time and temperature, column temperatures, multiplier setting etc.).

11.3.2. Sample Preparation Procedure

11.3.2.1. Samples fall into three general categories: waters, low-level soils, and medium-level soils or wastes. For waters and low-level soils, no sample preparation is necessary. For those soils which contain greater than 1 mg/kg of individual purgeable compounds, a medium-level preparation is necessary.

11.3.3. 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.

11.3.3.1. 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.

11.3.3.2. One MS/MSD pair does not count towards the maximum 20 samples in the batch. Additional client requested MS/MSD samples do count towards the maximum 20 samples.

11.3.3.3. It is not necessary to reanalyze batch QC with reanalyses of samples. However, any reruns must be as part of a valid batch.

11.3.4. Water Samples

11.3.4.1. All samples and standard solutions must be at ambient temperature before analysis.

11.3.4.2. Fill a 5 or 25 mL syringe with the sample. If a dilution is necessary it may be made in the syringe if the sample aliquot is ≥ 5 µL. Check and document the pH of the remaining sample.

11.3.4.3. Add 250 ng of each internal and surrogate standard (10 µL of a 25 µg/mL solution, refer to Tables 7, 8, 15 and 16). 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.

11.3.4.3.1. For TCLP samples use 0.5 mL of TCLP leachate with 4.5 mL reagent water and spike with 10 µL of the 25 µg/mL TCLP spiking solution.

11.3.4.4. Purge the sample for eleven minutes (the trap must be below 35°C).

11.3.4.5. After purging is complete, desorb the sample, start the GC temperature program, and begin data acquisition. After desorption, bake the trap for 5-10 minutes to condition it for the next analysis. When the trap is cool, it is ready for the next sample.

11.3.4.6. 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.

11.3.5. Medium-Level Soil/Sediment and Waste Samples

11.3.5.1. Sediments/soils and waste that are insoluble in methanol.

11.3.5.1.1. Gently mix the contents of the sample container with a narrow metal or wood spatula. Weigh 4 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.

11.3.5.1.2. Quickly add 9 mL of methanol, and 1 mL of surrogate spiking solution to bring the final volume of methanol to 10 mL. For an LCS or MS/MSD

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. The use of separate calibrations is required for water and low soil matrices.

10.2. Recommended Instrument Conditions

10.2.1. General

Electron Energy:	70 volts (nominal)
Mass Range:	35–300 AMU
Scan Time:	to give at least 5 scans/peak, but not to exceed 1 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

10.2.2. Gas chromatograph suggested temperature program

10.2.2.1. BFB Analysis

Isothermal:	170°C

10.2.2.2. 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 five initial calibration standards is prepared and analyzed for the target compounds and each surrogate compound. The calibration levels for a 5 mL purge are: 10, 20, 50, 100, and 200 µg/L. Certain analytes are prepared at higher concentrations due to poor purge performance. Calibration levels for a 25 mL purge are 2, 5, 10, 30, and 60 µg/L. Again, some analytes are prepared at higher levels. Tables 2, 4, and 17 list the calibration levels for each analyte.

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 Tables 7 and 15. Target compounds should reference the nearest internal standard. In particular, the SPCC compounds bromoform and 1,1,2,2-tetrachloroethane reference chlorobenzene-d5, not 1,4-difluorobenzene, which was appropriate for packed column analysis. Note different internal standards are used for the method 8260A drinking water analyte list (Appendix A). 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. Otherwise, all CCCs must meet the 30% criterion.

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. If the %RSD of ≥ 80% of the analytes in the calibration is ≤ 15%, then all analytes may use average response factor for calibration.

10.4.6.1. If the software in use is capable of routinely reporting curve coefficients for data valivation purposes, and the necessary calibration reports can be generated, then the analyst should evaluate analytes with %RSD > 15% for calibration on a curve. If if appears that substantially better accuracy would be obtained using quantitation from a curve (e.g. R^2 >0.995) then the appropriate curve should be used for quantitation.

10.4.6.2. If less than 80% of the analytes in the calibration have %RSD ≤ 15%, then calibration on a curve must be used for all analytes with %RSD > 15%. The analyst should consider instrument maintenance to improve the linearity of response.

10.4.7. Weighting of data points

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.

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. A separate five point calibration must be prepared for analysis of low level soils. Each standard is prepared as in Section 10.4.1, <u>except</u> that 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. Medium soil extracts should be analyzed using the water (unheated) calibration curve.

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. The level 3 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 anlalytes 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. Otherwise, all CCCs must meet the 20% criterion.

10.5.3.2. Cyclohexanone, one of the components of the Appendix IX standard, is unstable in the calibration solution, forming 1,1-dimethoxycyclohexane. No calibration criteria are applied to cyclohexanone and quantitation is tentative. Cyclohexanone is included on the Universal Treatment Standard and FO-39 regulatory lists (but not on Appendix IX).

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 Nonconformance Memo and approved by a Supervisor or group leader and QA Manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file.

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

sample add 8 mL of methanol, 1 mL of surrogate spike solution, and 1 mL of matrix spike solution. Cap the vial and vortex to mix thoroughly.

NOTE: Sections 11.3.5.1.1 and 11.3.5.1.2 must be performed rapidly and without interruption to avoid the loss of volatile organics.

11.3.5.2. Liquid wastes that are soluble in methanol and insoluble in water.

11.3.5.2.1. Pipet 2 mL of the sample into a tared vial. Use a top-loading balance. Record the weight to the nearest 0.1 gram.

11.3.5.2.2. Quickly add 7 mL of methanol, then add 1 mL of surrogate spiking solution to bring the final volume to 10 mL. Cap the vial and shake for 2 minutes to mix thoroughly. For a MS/MSD or LCS, 6 mL of methanol, 1 mL of surrogate solution, and 1 mL of matrix spike solution is used.

11.3.5.3. Fill a 5 mL syringe with 5 mL of reagent water. Add 100 µL (or less if a dilution is required) of methanol extract from the sample preparation in Section 11.3.5.1 or 11.3.5.2. If less than 5 µL of the methanol extract is required, then an intermediate dilution is required. Add 10 µL of the 25 µg/L internal standard solution. (Note that the combined internal standard/surrogate standard solution is not used since surrogates have been added previously.) Inject the sample into the purging chamber and proceed with the analysis as per Sections 11.3.4.4 and 11.3.4.5.

11.3.6. Low-Level Soils

11.3.6.1. This is designed for samples containing individual purgeable compounds of < 2 mg/kg. It is limited to soil/sediment samples and waste that is of a similar consistency (granular and porous). Weigh 5 g of the sample into a tared purge vessel. If a dilution is required, a smaller sample amount can be analyzed, down to a minimum of 1.0 g. Any soil sample requiring further dilution must be run as a medium-level soil. Add 5 mL of reagent water to which 10 µL of the 25 µg/L internal standard/surrogate standard solution has been added. Proceed with the analysis as per Sections 11.3.4.4 and 11.3.4.5.

11.4. Initial review and corrective actions

11.4.1. 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.

11.4.2. 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.

11.4.3. Internal standard response in each sample should be within 50% to 200% of the response in the preceding continuing calibration standard.

11.4.3.1. Any samples that do not meet the internal standard criteria must be evaluated for validity. If the change in sensitivity is a matrix effect confined to an individual sample reanalysis may not be necessary. If the change in sensitivity is due to instrumental problems all affected samples must be reanalyzed after the problem is corrected. In any event, the reason for accepting the sample analysis must be documented. Some clients may require reanalysis of all samples with internal standard criteria outside the 50-200% criteria. Consideration should be given to reanalyzing at a dilution to reduce matrix effects. It is only necessary to reanalyze once to confirm matrix effect.

11.4.4. 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 to demonstrate matrix effect, but reanalysis at a dilution should be considered.

11.5. Dilutions

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.

11.5.1. Guidance for Dilutions Due to Matrix

If the sample is initially run at a dilution and the baseline rise is less than half the height of the peaks in the level 3 standard, then the sample should be reanalyzed at a more concentrated dilution.

11.5.2. Reporting Dilutions

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

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.
- 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.
- 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.)

12.1.1. 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

$$SD = \sqrt{\sum_{i=1}^{N} \frac{(Xi - X)^2}{N - 1}}$$

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

$$\%\ \textbf{Drift} = \frac{C_{expected} - C_{found}}{C_{expected}} \times 100$$

Where

$C_{expected}$ = Known concentration in standard

C_{found} = Measured concentration using selected quantitation method

12.3.5. Target compound and surrogate concentrations:

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%.

12.3.5.1. Calculation of concentration using Quadratic fit

Equation 5

$$\textbf{Concentration } \mu g / L = A + Bx + Cx^2$$

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

12.3.5.2. Calculation of concentration using Linear fit

Equation 6

$$\textbf{Concentration } \mu g / L = A + Bx$$

12.3.5.3. Calculation of concentration using Average Response Factors

Equation 7

$$\textbf{Concentration } \mu g / L = \frac{x}{RF}$$

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:

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)

A_{is} = Area of the characteristic ion for the internal standard

I_s = Amount of internal standard added in ng

$$\text{Dilution Factor} = D_f = \frac{\text{Total volume purged (mL)}}{\text{Volume of original sample used (mL)}}$$

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:

A_x, I_s, D_f, A_{is}, same as for water.

V_t = Volume of total extract, mL (Typically 10 mL)

V_a = Volume of extract added for purging, µL

W_s = Weight of sample extracted, g

$$D = \frac{100 - \%moisture}{100}$$

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:

A_x, I_s, A_{is}, same as for water.

D is as for medium level soils

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:

A_x = Area in 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

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

$$\mathbf{RPD} = \frac{|\mathbf{MSR - MSDR}|}{\frac{1}{2}(\mathbf{MSR + MSDR})} \times 100$$

Where:

RPD = Relative percent difference

MSR = Matrix spike result

MSDR = Matrix spike duplicate result

13. METHOD PERFORMANCE

13.1. Method Detection Limit

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 #: QA-005.

13.2. Initial Demonstration

Each laboratory must make a one time 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. The QC check sample is made up at 20 µg/L. (Some compounds will be at higher levels, refer to the calibration standard levels for guidance.)

13.2.1. Four aliquots of the QC check sample are analyzed using the same procedures used to analyze samples, including sample preparation.

13.2.2. Calculate the average recovery and standard deviation of the recovery for each analyte of interest. The %RSD should be ≤ 15% for each analyte, and the % recovery should be within 80-120%.

13.2.3. If any analyte does not meet the acceptance criteria, check the acceptance limits in the reference methods (Table 6 of method 8240B, paragraph 8.3.5 of method 8260A). If the recovery or precision is outside the limits in the reference methods, 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. Training Qualification

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

15. WASTE MANAGEMENT

15.1. Waste generated in the procedure must be segregated and disposed according to the facility hazardous waste procedures. The Health and Safety Director should be contacted if additional information is required.

16. REFERENCES

16.1. SW846, *Test Methods for Evaluating Solid Waste*, Third Edition, Gas Chromatography/Mass Spectrometry for Volatile Organics, Method 8240B, Update II, September 1994.

16.2. SW846, *Test Methods for Evaluating Solid Waste,* Third Edition, Gas Chromatography/Mass Spectrometry for Volatile Organics, Method 8260A, Update II, September 1994.

17. MISCELLANEOUS

17.1. Modifications from the reference method

17.1.1. Method 8240B has been modified in this SOP to use capillary columns rather than the packed columns listed in the reference method. This provides improved separation of the target analytes and improved detection limits.

17.1.2. Ion 119 is used as the quantitation ion for chlorobenzene-d5 for 25 mL purge tests.

17.1.3. The internal standard control criteria of 50% to 200% is applied to each sample, rather than the subsequent continuing calibration standard as recommended in the reference method.

17.1.4. 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.

17.1.5. 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.

17.1.6. Method 8260A recommends that the purge vessel is run through an additional purge cycle after 25 mL sample analysis to remove carryover. Instead, purge vessels are oven baked between analyses or disposable vessels are used one time only.

17.1.7. Matrix spikes and surrogates are spiked at the levels specified in methods 3500 and 5030.

17.1.8. SW-846 recommends that a curve be used for any analytes with %RSD of the response factors > 15%. However, some industry standard data systems and forms generation software cannot report this data with the necessary information for data validation. In addition most software available does not allow weighting of the curve. Unweighted curves may exibit serious errors in quantitation at the low end, resulting in possible false positives or false negatives. Therefore, this SOP allows used of average response factors in 80% of the analytes have %RSDs ≤ 15%.Modifications from previous revision

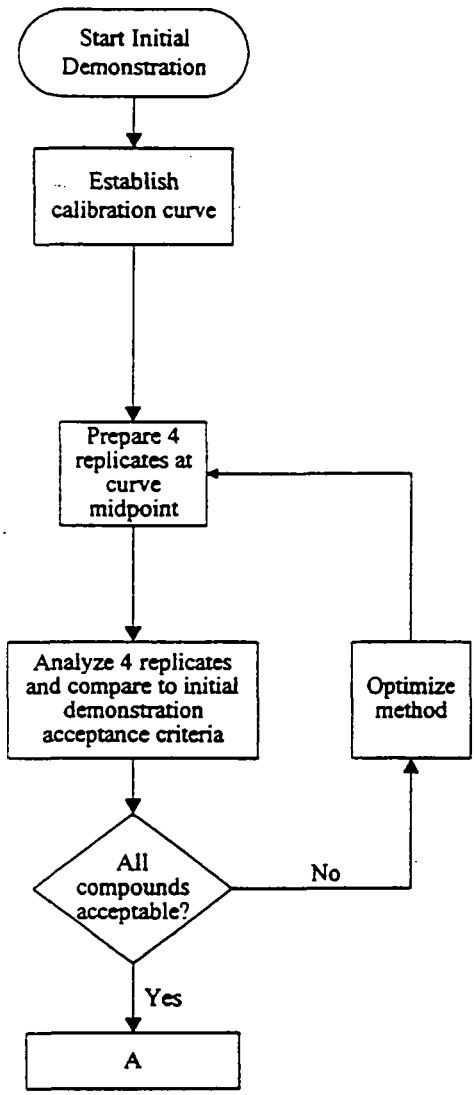
17.1.9. If at least 80% of the analytes in the initial calibration have %RSD < 15%, average response factor calibration may be used far all analytes.

17.2. Facility specific SOPs

Each facility shall attach a list of facility-specific SOPs or approved attachments (if applicable) which are required to implement this SOP or which are used in conjunction with this SOP. If no facility specific SOPs or amendments are to be attached, a statement must be attached specifying that there are none.

17.3. Flow diagrams

17.3.1. Initial Demonstration and MDL



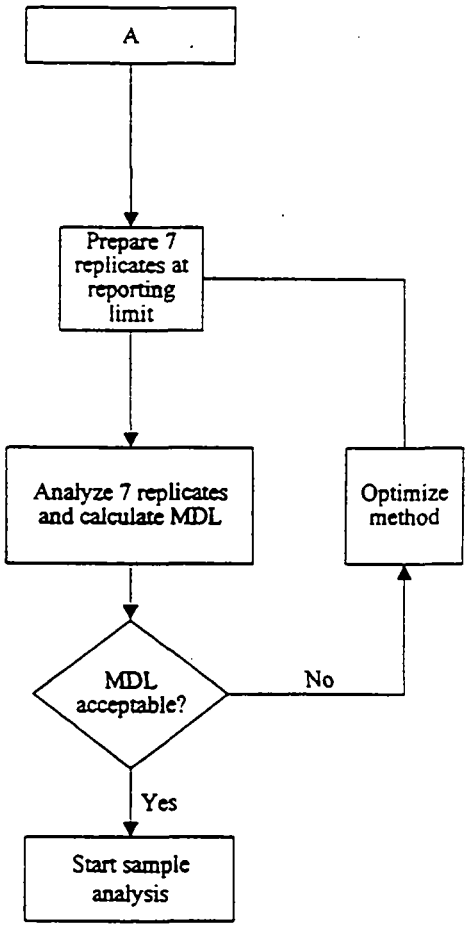


Table 1

Quanterra Primary Standard and Reporting Limits

Compound	CAS Number	Reporting Limits[1]			
		5 mL Water µg/L	25 mL water µg/L	Low soil µg/kg	Med. Soil µg/kg
Dichlorodifluoromethane	75-71-8	10	2	10	1200
Chloromethane	74-87-3	10	2	10	1200
Bromomethane	74-83-9	10	2	10	1200
Vinyl chloride	75-01-4	10	2	10	1200
Chloroethane	75-00-3	10	2	10	1200
Trichlorofluoromethane	75-69-4	10	2	10	1200
Acrolein	107-02-8	100	20	100	12000
Acetone	67-64-1	20	10	20	2500
Trichlorotrifluoroethane	76-13-1	5	1	5	620
Ethanol	64-17-5	500	200	500	62,000
Iodomethane	74-88-4	5	1	5	620
Carbon disulfide	75-15-0	5	1	5	620
Methylene chloride	75-09-2	5	1	5	620
tert-Butyl alcohol	75-65-0	200	50	200	25,000
1,1-Dichloroethene	75-35-4	5	1	5	620
1,1-Dichloroethane	75-34-3	5	1	5	620
trans-1,2-Dichloroethene	156-60-5	2.5	0.5	2.5	310
Acrylonitrile	107-13-1	100	20	100	12000
Methyl *tert*-butyl ether (MTBE)	1634-04-4	20	5	20	2500
Hexane	110-54-3	5	1	5	620
cis-1,2-Dichloroethene	156-59-2	2.5	0.5	2.5	310
1,2-Dichloroethene (Total)	540-59-0	5	1	5	620
Tetrahydrofuran	109-99-9	20	5	20	2500
Chloroform	67-66-3	5	1	5	620
1,2-Dichloroethane	107-06-2	5	1	5	620
Dibromomethane	74-95-3	5	1	5	620
2-Butanone	78-93-3	20	5	20	2500
1,4-Dioxane	123-91-1	500	200	500	62000
1,1,1-Trichloroethane	71-55-6	5	1	5	620
Carbon tetrachloride	56-23-5	5	1	5	620
Bromodichloromethane	75-27-4	5	1	5	620
1,2-Dichloropropane	78-87-5	5	1	5	620
cis-1,3-Dichloropropene	10061-01-5	5	1	5	620
Trichloroethene	79-01-6	5	1	5	620

Table 1

Quanterra Primary Standard and Reporting Limits

Compound	CAS Number	Reporting Limits[1]			
		5 mL Water µg/L	25 mL water µg/L	Low soil µg/kg	Med. Soil µg/kg
Dibromochloromethane	124-48-1	5	1	5	620
1,2-Dibromoethane	106-93-4	5	1	5	620
1,2,3-Trichloropropane	96-18-4	5	1	5	620
1,1,2-Trichloroethane	79-00-5	5	1	5	620
Benzene	71-43-2	5	1	5	620
Ethylmethacrylate	97-63-2	5	1	5	620
trans-1,3-Dichloropropene	10061-02-6	5	1	5	620
Bromoform	75-25-2	5	1	5	620
4-Methyl-2-pentanone	108-10-1	20	5	20	2500
2-Hexanone	591-78-6	20	5	20	2500
Tetrachloroethene	127-18-4	5	1	5	620
Toluene	108-88-3	5	1	5	620
1,1,2,2-Tetrachloroethane	79-34-5	5	1	5	620
2-Chloroethyl vinyl ether	110-75-8	N/A[2]	N/A	50	6200
Vinyl acetate	108-05-4	10	2	10	1200
Chlorobenzene	108-90-7	5	1	5	620
Ethylbenzene	100-41-4	5	1	5	620
Styrene	100-42-5	5	1	5	620
t-1,4-Dichloro-2-butene	110-57-6	5	1	5	620
m and p Xylenes		2.5	0.5	2.5	310
o-xylene	95-47-6	2.5	0.5	2.5	310
Total xylenes	1330-20-7	5	1	5	620
1,3-Dichlorobenzene	541-73-1	5	1	5	620
1,4-Dichlorobenzene	106-46-7	5	1	5	620
1,2-Dichlorobenzene	95-50-1	5	1	5	620

[1] Reporting limits listed for soil/sediment are based on wet weight. The reporting limits calculated by the laboratory for soil/sedim calculated on dry weight basis, will be higher.

[2] 2-Chloroethyl vinyl ether cannot be reliably recovered from acid preserved samples

Table 2

Quanterra Primary Standard Calibration Levels, 5 mL purge[1]

Compound	Calibration Level ug/L				
	Level 1	Level 2	Level 3	Level 4	Level 5
1,2-Dichloroethane-d4 (Surrogate)	10	20	50	100	200
Toluene-d8 (Surrogate)	10	20	50	100	200
4-Bromofluorobenzene (Surrogate)	10	20	50	100	200
Dichlorodifluoromethane	10	20	50	100	200
Chloromethane	10	20	50	100	200
Bromomethane	10	20	50	100	200
Vinyl chloride	10	20	50	100	200
Chloroethane	10	20	50	100	200
Trichlorofluoromethane	10	20	50	100	200
Acrolein	100	200	500	1000	2000
Acetone	10	20	50	100	200
Trichlorotrifluoroethane	10	20	50	100	200
Ethanol	500	1000	5000	10,000	20,000
Iodomethane	10	20	50	100	200
Carbon disulfide	10	20	50	100	200
Methylene chloride	10	20	50	100	200
tert-Butyl alcohol	200	400	1,000	2,000	4,000
1,1-Dichloroethene	10	20	50	100	200
1,1-Dichloroethane	10	20	50	100	200
trans-1,2-Dichloroethene	10	20	50	100	200
Acrylonitrile	100	200	500	1,000	2,000
Methyl *tert*-butyl ether (MTBE)	10	20	50	100	200
Hexane	10	20	50	100	200
cis-1,2-Dichloroethene	10	20	50	100	200
Tetrahydrofuran	10	20	50	100	200
Chloroform	10	20	50	100	200
1,2-Dichloroethane	10	20	50	100	200
Dibromomethane	10	20	50	100	200
2-Butanone	10	20	50	100	200
1,4-Dioxane	500	1000	2,500	5,000	10,000
1,1,1-Trichloroethane	10	20	50	100	200
Carbon tetrachloride	10	20	50	100	200
Bromodichloromethane	10	20	50	100	200
1,2-Dichloropropane	10	20	50	100	200
cis-1,3-Dichloropropene	10	20	50	100	200

Table 2

Quanterra Primary Standard Calibration Levels, 5 mL purge[1]

Compound	Calibration Level ug/L				
	Level 1	Level 2	Level 3	Level 4	Level 5
Trichloroethene	10	20	50	100	200
Dibromochloromethane	10	20	50	100	200
1,2-Dibromoethane	10	20	50	100	200
1,2,3-Trichloropropane	10	20	50	100	200
1,1,2-Trichloroethane	10	20	50	100	200
Benzene	10	20	50	100	200
Ethylmethacrylate	10	20	50	100	200
trans-1,3-Dichloropropene	10	20	50	100	200
Bromoform	10	20	50	100	200
4-Methyl-2-pentanone	10	20	50	100	200
2-Hexanone	10	20	50	100	200
Tetrachloroethene	10	20	50	100	200
Toluene	10	20	50	100	200
1,1,2,2-Tetrachloroethane	10	20	50	100	200
2-Chloroethyl vinyl ether	20	40	100	200	400
Vinyl acetate	10	20	50	100	200
Chlorobenzene	10	20	50	100	200
Ethylbenzene	10	20	50	100	200
Styrene	10	20	50	100	200
t-1,4-Dichloro-2-butene	10	20	50	100	200
m and p Xylenes	20	40	100	200	400
o-xylene	10	20	50	100	200
1,3-Dichlorobenzene	10	20	50	100	200
1,4-Dichlorobenzene	10	20	50	100	200
1,2-Dichlorobenzene	10	20	50	100	200

[1] **Levels for 25 mL purge are 5 times lower in all cases**

Table 3

Quanterra Appendix IX Standard and Reporting Limits, 5 mL purge[1]

Compound	CAS Number	Reporting Limits			
		5 mL Water µg/L	25 mL water µg/L	Low Soil µg/kg	Medium Soil µg/mL
Allyl Chloride	107-05-1	10	2	10	1,200
Acetonitrile	75-05-8	100	20	100	12,000
Dichlorofluoromethane		10	2	10	1,200
Isopropyl ether	108-20-3	50	10	50	6,200
Chloroprene	126-99-8	5	1	5	620
n-Butanol	71-36-3	200	50	200	25,000
Propionitrile	107-12-0	20	4	20	2500
Methacrylonitrile	126-98-7	5	1	5	620
Isobutanol	78-83-1	200	50	200	25,000
Methyl methacrylate	80-62-6	5	1	5	620
1,1,1,2-Tetrachloroethane	630-20-6	5	1	5	620
1,2-Dibromo-3-chloropropane	96-12-8	10	2	10	1,200
Ethyl ether	60-29-7	10	2	10	1,200
Ethyl Acetate	141-78-6	20	4	20	2500
2-Nitropropane	79-46-9	10	2	10	1,200
Cyclohexanone	108-94-1	N/A[2]	N/A[2]	N/A[2]	N/A[2]
Isopropylbenzene	98-82-8	5	1	5	620

[1] **Levels for 25 mL purge are 5 times lower in all cases**

[2] Cyclohexanone decomposes to 1,1-dimethoxycyclohexane in methanolic solution. Reporting limits cannot be accurately determined.

Table 4

Quanterra Appendix IX Standard Calibration Levels, µg/L

Compound	Level 1	Level 2	Level 3	Level 4	Level 5
Allyl Chloride	10	20	50	100	200
Acetonitrile	100	200	500	1,000	2,000
Dichlorofluoromethane	10	20	50	100	200
Isopropyl ether	50	100	250	500	1,000
Chloroprene	10	20	50	100	200
n-Butanol	200	400	1,000	2,000	4,000
Propionitrile	20	40	100	200	400
Methacrylonitrile	10	20	50	100	200
Isobutanol	200	400	1,000	2,000	4,000
Methyl methacrylate	10	20	50	100	200
1,1,1,2-Tetrachloroethane	10	20	50	100	200
1,2-Dibromo-3-chloropropane	20	40	100	200	400
Ethyl ether	10	20	50	100	200
Ethyl Acetate	20	40	100	200	400
2-Nitropropane	20	40	100	200	400
Cyclohexanone	100	200	500	1,000	2,000
Isopropylbenzene	10	20	50	100	200

Table 5

Reportable Analytes for Quanterra Standard Tests, Primary Standard

Compound	CAS Number	Quanterra Standard List	TCLP	TCL	Appendix IX	UTS
Dichlorodifluoromethane	75-71-8				X	X
Chloromethane	74-87-3	X		X	X	X
Bromomethane	74-83-9	X		X	X	X
Vinyl chloride	75-01-4	X	X	X	X	X
Chloroethane	75-00-3	X		X	X	X
Trichlorofluoromethane	75-69-4				X	X
Acrolein	107-02-8				X	X
Acetone	67-64-1	X		X	X	X
Trichlorotrifluoroethane	76-13-1					X
Ethanol	64-17-5					
Iodomethane	74-88-4				X	X
Carbon disulfide	75-15-0	X		X	X	X
Methylene chloride	75-09-2	X		X	X	X
tert-Butly alcohol	75-65-0					
1,1-Dichloroethene	75-35-4	X	X	X	X	X
1,1-Dichloroethane	75-34-3	X		X	X	X
trans-1,2-Dichloroethene	156-60-5	X		X	X	X
Total dichloroethene		X		X	X	X
Acrylonitrile	107-13-1					X
Methyl *tert*-butyl ether (MTBE)	1634-04-4					
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	X
1,2-Dichloroethane	107-06-2	X	X	X	X	X
Dibromomethane	74-95-3				X	X
2-Butanone	78-93-3	X	X	X	X	X
1,4-Dioxane	123-91-1				X	X
1,1,1-Trichloroethane	71-55-6	X		X	X	X
Carbon tetrachloride	56-23-5	X	X	X	X	X
Bromodichloromethane	75-27-4	X		X	X	X
1,2-Dichloropropane	78-87-5	X		X	X	X
cis-1,3-Dichloropropene	10061-01-	X		X	X	X

Table 5

Reportable Analytes for Quanterra Standard Tests, Primary Standard

Compound	CAS Number	Quanterra Standard List	TCLP	TCL	Appendix IX	UTS
	5					
Trichloroethene	79-01-6	X	X	X	X	X
Dibromochloromethane	124-48-1	X		X	X	X
1,2-Dibromoethane	106-93-4				X	X
1,2,3-Trichloropropane	96-18-4				X	X
1,1,2-Trichloroethane	79-00-5	X		X	X	X
Benzene	71-43-2	X	X	X	X	X
Ethylmethacrylate	97-63-2				X	X
trans-1,3-Dichloropropene	10061-02-6	X		X	X	X
Bromoform	75-25-2	X		X	X	X
4-Methyl-2-pentanone	108-10-1	X		X	X	X
2-Hexanone	591-78-6	X		X	X	
Tetrachloroethene	127-18-4	X	X	X	X	X
Toluene	108-88-3	X		X	X	X
1,1,2,2-Tetrachloroethane	79-34-5	X		X	X	X
2-Chloroethyl vinyl ether	110-75-8					
Vinyl acetate	108-05-4				X	
Chlorobenzene	108-90-7	X	X	X	X	X
Ethylbenzene	100-41-4	X		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	X
o-xylene	95-47-6	X		X	X	X
Total xylenes	1330-20-7	X		X	X	X
1,3-Dichlorobenzene	541-73-1					
1,4-Dichlorobenzene	106-46-7					
1,2-Dichlorobenzene	95-50-1					

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Quanterra Primary Standard Retention Times

Compound	Column1 RTX502.2	Column 2 DB-624
Dichlorodifluoromethane	3.903	2.389
Chloromethane	4.344	2.647
Bromomethane	5.341	3.176
Vinyl chloride	4.527	2.761
Chloroethane	5.476	3.291
Trichlorofluoromethane	5.956	3.620
Acrolein	6.703	4.149
Acetone	6.809	4.349
Iodomethane	7.582	4.478
Allyl chloride	7.668	4.736
Carbon disulfide	7.940	4.550
Methylene chloride	7.873	4.893
1,1-Dichloroethene	7.058	4.264
1,1-Dichloroethane	9.111	5.809
trans-1,2-Dichloroethene	8.392	5.237
Acrylonitrile	8.065	5.222
cis-1,2-Dichloroethene	10.136	6.610
1,2-Dichloroethene (Total)		
Chloroform	10.405	7.082
1,2-Dichloroethane	11.739	7.955
Dibromomethane	13.602	9.529
2-Butanone	9.791	6.624
1,4-Dioxane	13.516	9.557
1,1,1-Trichloroethane	11.096	7.340
Carbon tetrachloride	11.537	7.583
Bromodichloromethane	13.505	9.786
1,2-Dichloropropane	13.092	9.314
cis-1,3-Dichloropropene	14.397	10.573
Trichloroethene	12.814	8.928
Dibromochloromethane	16.489	12.734
1,2-Dibromoethane	16.851	12.948
1,2,3-Trichloropropane	19.826	16.854
1,1,2-Trichloroethane	15.539	11.961
Benzene	11.806	7.912
Ethylmethacrylate	15.184	11.804
trans-1,3-Dichloropropene	15.242	11.618

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Continued

Bromoform	19.310	15.681
4-Methyl-2-pentanone	13.994	10.859
2-Hexanone	15.491	12.462
Tetrachloroethene	16.144	12.204
Toluene	14.992	11.174
1,1,2,2-Tetrachloroethane	19.540	16.783
2-Chloroethyl vinyl ether	13.946	10.316
Vinyl acetate	9.072	5.866
Chlorobenzene	17.601	13.935
Ethylbenzene	17.669	14.164
Styrene	18.667	15.295
t-1,4-Dichloro-2-butene	19.912	16.926
m and p Xylenes	17.803	14.422
o-Xylene	18.609	15.252
Total xylenes		
1,3-Dichlorobenzene	21.813	18.843

Table 6

Reportable Analytes for Quanterra Standard Tests, Appendix IX standard

Compound	Number	Quanterra Standard List	TCLP	TCL	Appendix IX	UTS
Allyl Chloride	107-05-1				X	
Acetonitrile	75-05-8				X	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	X
Isobutanol	78-83-1				X	X
Methyl methacrylate	80-62-6				X	X
1,1,1,2-Tetrachloroethane	630-20-6				X	X
1,2-Dibromo-3-chloropropane	96-12-8				X	X
Ethyl ether	60-29-7					X
Ethyl Acetate	141-78-6					X
2-Nitropropane	79-46-9					
Cyclohexanone	108-94-1					X
Isopropylbenzene	98-82-8					

Table 7

Internal Standards

	Standard Concentration µg/mL	Quantitation ion (5 mL purge)	Quantitation ion (25 mL purge)
Bromochloromethane	25	128	128
1,4-Difluorobenzene	25	114	114
Chlorobenzene d5	25	117	119

Notes:

1) 10 µL of the internal standard is added to the sample. This results in a concentration of each internal in the sample of 50µg/L for a 5 mL purge or 10 µg/L for a 25 mL purge.

2) 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	25
Toluene-d_8	25
4-Bromofluorobenzene	25

Notes:

1) 10 µL of the surrogate standard is added to the sample. This results in a concentration of each surrogate in the sample of 50µg/L for a 5 mL purge or 10 µg/L for a 25 mL purge.

2) Except for medium level soils, the surrogate and internal standards may be combined in one solution.

3) Recovery limits for surrogates are generated from historical data and are maintained by the QA department.

Table 9

Matrix Spike / LCS Compounds

Compound	Standard Concentration µg /mL
1,1-Dichloroethene	25
Trichloroethene	25
Toluene	25
Benzene	25
Chlorobenzene	25

Notes:

1) 10 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 the QA dedartment.

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	8240B Min. RF	8260A Min. RF
Chloromethane	0.300	0.100
1,1-Dichloroethane	0.300	0.100
Bromoform	>0.100	>0.100
1,1,2,2-Tetrachloroethane	0.300	0.300
Chlorobenzene	0.300	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

Table 13

Characteristic ions

Compound	Primary*	Secondary	Tertiary
Bromochloromethane (Internal Standard)	128	49	130, 51
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

Table 13

Characteristic ions

Compound	Primary*	Secondary	Tertiary
Iodomethane	142	127	141
Carbon disulfide	76	78	
Trichlorotrifluoroethane	151	101	153
Ethanol	45	46	
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**	
Tetrahydrofuran	42	71	
Chloroform	83	85	47
1,2-Dichloroethane	62	64	98
Dibromomethane	93	174	95, 172, 176
1,4-Dioxane	88	58	
1,4-Difluorobenzene (Internal Standard)	114	63	88
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
Chlorobenzene-d_5 (Internal Standard)	117,119	117,119	
Toluene-d_8 (Surrogate)	98	70	100
4-Bromofluorobenzene (Surrogate)	95	174	176
Toluene	91	92	65

Table 13

Characteristic ions

Compound	Primary*	Secondary	Tertiary
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
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	

* 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.

1. SUMMARY

A target analyte list based on the list in method 524.2 is frequently requested for analysis by method 8260A. Quanterra's standard analyte list for this test, and the internal and surrogate standards used, are listed in Tables below.. In all other respects the method is as described in the main body of this SOP. Note that this SOP is ***not*** appropriate for drinking water analysis by method 524.2.

Table 14

Quanterra 8260 Drinking Water List Standard and Reporting Limits

Compound	CAS Number	Reporting Limits[1]			
		5 mL water µg/L	25 mL water µg/L	Low soil µg/kg	Med. Soil µg/kg
Dichlorodifluoromethane	75-71-8	10	2	10	1200
Chloromethane	74-87-3	10	2	10	1200
Bromomethane	74-83-9	10	2	10	1200
Vinyl chloride	75-01-4	10	2	10	1200
Chloroethane	75-00-3	10	2	10	1200
Trichlorofluoromethane	75-69-4	10	2	10	1200
Acetone[1]	67-64-1	20	10	20	2500
Methylene chloride	75-09-2	5	2	5	620
1,1-Dichloroethene	75-35-4	5	1	5	620
1,1-Dichloroethane	75-34-3	5	1	5	620
trans-1,2-Dichloroethene	156-60-5	2.5	0.5	2.5	310
Methyl *tert*-butyl ether (MTBE)	1634-04-4	20	5	20	620
2,2-Dichloropropane	590-20-7	5	1	5	620
cis-1,2-Dichloroethene	156-59-2	2.5	0.5	2.5	310
1,2-Dichloroethene (Total)	540-59-0	5	1	5	620
Chloroform	67-66-3	5	1	5	620
Bromochloromethane	74-97-5	5	1	5	620
1,2-Dichloroethane	107-06-2	5	1	5	620
Dibromomethane	74-95-3	5	1	5	620
2-Butanone[1]	78-93-3	20	5	20	2500
1,1,1-Trichloroethane	71-55-6	5	1	5	620
Carbon tetrachloride	56-23-5	5	1	5	620
Bromodichloromethane	75-27-4	5	1	5	620
1,2-Dichloropropane	78-87-5	5	1	5	620
cis-1,3-Dichloropropene	10061-01-5	5	1	5	620

Table 14

Quanterra 8260 Drinking Water List Standard and Reporting Limits

Compound	CAS Number	Reporting Limits[1]			
		5 mL water µg/L	25 mL water µg/L	Low soil µg/kg	Med. Soil µg/kg
Trichloroethene	79-01-6	5	1	5	620
Dibromochloromethane	124-48-1	5	1	5	620
1,2-Dibromoethane	106-93-4	5	1	5	620
1,2,3-Trichloropropane	96-18-4	5	1	5	620
1,1,2-Trichloroethane	79-00-5	5	1	5	620
Benzene	71-43-2	5	1	5	620
trans-1,3-Dichloropropene	10061-02-6	5	1	5	620
Bromoform	75-25-2	5	1	5	620
4-Methyl-2-pentanone[1]	108-10-1	20	5	20	2500
2-Hexanone[1]	591-78-6	20	5	20	2500
Tetrachloroethene	127-18-4	5	1	5	620
Toluene	108-88-3	5	1	5	620
1,1,2,2-Tetrachloroethane	79-34-5	5	1	5	620
Chlorobenzene	108-90-7	5	1	5	620
Ethylbenzene	100-41-4	5	1	5	620
Styrene	100-42-5	5	1	5	620
m and p Xylenes		2.5	0.5	2.5	310
o-xylene	95-47-6	2.5	0.5	2.5	310
Total xylenes	1330-20-7	5	1	5	620
Isopropylbenzene	98-82-8	5	1	5	620
Bromobenzene	108-86-1	5	1	5	620
n-Propylbenzene	103-65-1	5	1	5	620
2-Chlorotoluene	95-49-8	5	1	5	620
4-Chlorotoluene	106-43-4	5	1	5	620
1,3,5-Trimethylbenzene	108-67-8	5	1	5	620
tert-Butylbenzene	98-06-6	5	1	5	620
1,2,4-Trimethylbenzene	95-63-6	5	1	5	620
sec-butylbenzene	135-98-8	5	1	5	620
1,3-Dichlorobenzene	541-73-1	5	1	5	620
1,4-Dichlorobenzene	106-46-7	5	1	5	620
1,2-Dichlorobenzene	95-50-1	5	1	5	620
4-Isopropyltoluene	99-87-6	5	1	5	620
n-Butylbenzene	104-51-8	5	1	5	620
1,2-Dibromo-3-chloropropane	96-12-8	5	1	5	620
1,2,4-Trichlorobenzene	120-82-1	5	1	5	620

Table 14

Quanterra 8260 Drinking Water List Standard and Reporting Limits

Compound	CAS Number	Reporting Limits[1]			
		5 mL water µg/L	25 mL water µg/L	Low soil µg/kg	Med. Soil µg/kg
Napthalene	91-20-3	5	1	5	620
Hexachlorobutadiene	87-68-3	5	1	5	620
1,2,3-Trichlorobenzene	87-61-6	5	1	5	620

[1] Not included on the method 524.2 analyte list, but includes in the calibration standard as an add on frequently requested by method 8260A.

Table 15

Internal Standards, Method 8260A Drinking water list

	Standard Concentration µg/mL	Quantitation ion
Fluorobenzene	25	128
Chlorobenzene-d5	25	114
1,4-Dichlorobenzene-d4	25	119

Notes:

1) 10 µL of the internal standard is added to the sample. This results in a concentration of each internal in the sample of 50µg/L for a 5 mL purge or 10 µg/L for a 25 mL purge.

2) Except for medium level soils, the surrogate and internal standards may be combined in one solution.

Table 16

Surrogate Standards, Method 8260B Drinking water list

Surrogate Compounds	Standard Concentration µg/mL
1,2-Dichloroethane-d_4	25
Toluene-d_8	25
4-Bromofluorobenzene	25

Notes:

1) 10 µL of the surrogate standard is added to the sample. This results in a concentration of each surrogate in the sample of 50µg/L for a 5 mL purge or 10 µg/L for a 25 mL purge.

2) Except for medium level soils, the surrogate and internal standards may be combined in one solution.

Table 17

Quanterra 8260 Drinking water list Standard: Calibration Levels

Compound	Level 1		Level 2		Level 3		Level 4		Level 5	
	5 mL	25 mL	5 mL	25 mL	5 mL	25 mL	5 mL	25 mL	5 mL	25 mL
Dichlorodifluoromethane	20	4	40	10	100	20	200	60	400	120
Chloromethane	20	4	40	10	100	20	200	60	400	120
Bromomethane	20	4	40	10	100	20	200	60	400	120
Vinyl chloride	20	4	40	10	100	20	200	60	400	120
Chloroethane	20	4	40	10	100	20	200	60	400	120
Trichlorofluoromethane	20	4	40	10	100	20	200	60	400	120
Acetone[1]	20	4	40	10	100	20	200	60	400	120
Methylene chloride	10	2	20	5	50	10	100	30	200	60
1,1-Dichloroethene	10	2	20	5	50	10	100	30	200	60
1,1-Dichloroethane	10	2	20	5	50	10	100	30	200	60
trans-1,2-Dichloroethene	10	2	20	5	50	10	100	30	200	60
Methyl *tert*-butyl ether (MTBE)	20	4	40	10	100	20	200	60	400	120
2,2-Dichloropropane	10	2	20	5	50	10	100	30	200	60
cis-1,2-Dichloroethene	10	2	20	5	50	10	100	30	200	60

Table 17

Quanterra 8260 Drinking water list Standard: Calibration Levels

Compound	Level 1		Level 2		Level 3		Level 4		Level 5	
Chloroform	10	2	20	5	50	10	100	30	200	60
Bromochloromethane	10	2	20	5	50	10	100	30	200	60
1,2-Dichloroethane	10	2	20	5	50	10	100	30	200	60
Dibromomethane	10	2	20	5	50	10	100	30	200	60
2-Butanone[1]	20	4	40	10	100	20	200	60	400	120
1,1,1-Trichloroethane	10	2	20	5	50	10	100	30	200	60
Carbon tetrachloride	10	2	20	5	50	10	100	30	200	60
Bromodichloromethane	10	2	20	5	50	10	100	30	200	60
1,2-Dichloropropane	10	2	20	5	50	10	100	30	200	60
cis-1,3-Dichloropropene	10	2	20	5	50	10	100	30	200	60
Trichloroethene	10	2	20	5	50	10	100	30	200	60
Dibromochloromethane	10	2	20	5	50	10	100	30	200	60
1,2-Dibromoethane	10	2	20	5	50	10	100	30	200	60
1,2,3-Trichloropropane	10	2	20	5	50	10	100	30	200	60
1,1,2-Trichloroethane	10	2	20	5	50	10	100	30	200	60
Benzene	10	2	20	5	50	10	100	30	200	60
trans-1,3-Dichloropropene	10	2	20	5	50	10	100	30	200	60
Bromoform	10	2	20	5	50	10	100	30	200	60
4-Methyl-2-pentanone[1]	20	4	40	10	100	20	200	60	400	120
2-Hexanone[1]	20	4	40	10	100	20	200	60	400	120
Tetrachloroethene	10	2	20	5	50	10	100	30	200	60
Toluene	10	2	20	5	50	10	100	30	200	60
1,1,2,2-Tetrachloroethane	10	2	20	5	50	10	100	30	200	60
Chlorobenzene	10	2	20	5	50	10	100	30	200	60
Ethylbenzene	10	2	20	5	50	10	100	30	200	60
Styrene	10	2	20	5	50	10	100	30	200	60
m and p Xylenes	10	2	20	5	50	10	100	30	200	60
o-xylene	10	2	20	5	50	10	100	30	200	60

Table 17

Quanterra 8260 Drinking water list Standard: Calibration Levels

Compound	Level 1		Level 2		Level 3		Level 4		Level 5	
Isopropylbenzene	10	2	20	5	50	10	100	30	200	60
Bromobenzene	10	2	20	5	50	10	100	30	200	60
n-Propylbenzene	10	2	20	5	50	10	100	30	200	60
2-Chlorotoluene	10	2	20	5	50	10	100	30	200	60
4-Chlorotoluene	10	2	20	5	50	10	100	30	200	60
1,3,5-Trimethylbenzene	10	2	20	5	50	10	100	30	200	60
tert-Butylbenzene	10	2	20	5	50	10	100	30	200	60
1,2,4-Trimethylbenzene	10	2	20	5	50	10	100	30	200	60
sec-butylbenzene	10	2	20	5	50	10	100	30	200	60
1,3-Dichlorobenzene	10	2	20	5	50	10	100	30	200	60
1,4-Dichlorobenzene	10	2	20	5	50	10	100	30	200	60
1,2-Dichlorobenzene	10	2	20	5	50	10	100	30	200	60
4-Isopropyltoluene	10	2	20	5	50	10	100	30	200	60
n-Butylbenzene	10	2	20	5	50	10	100	30	200	60
1,2-Dibromo-3-chloropropane	10	2	20	5	50	10	100	30	200	60
1,2,4-Trichlorobenzene	10	2	20	5	50	10	100	30	200	60
Napthalene	10	2	20	5	50	10	100	30	200	60
Hexachlorobutadiene	10	2	20	5	50	10	100	30	200	60
1,2,3-Trichlorobenzene	10	2	20	5	50	10	100	30	200	60

[1] Not included in the Quanterra Standard test, but included in the standard as a frequently requested add-on.

Table 4	Matrix spike and LCS solutions
Table 5	Surrogate spike components
Table 6	Matrix spike components
Table A1	Herbicide surrogate spiking solutions
Table A2	Herbicide matrix spike and LCS solutions
Table A3	Herbicide surrogate spike components
Table A4	Herbicide matrix spike and LCS components

1. SCOPE AND APPLICATION

This SOP describes procedures for preparation (extraction and cleanup) 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:
8080A, 8100, 8140, 8141A, 8150B, 8151A, 8270B, 8310
608, 610, and 625

1.2. The extraction procedures here may be appropriate for other determinative methods when appropriate spiking mixtures are used.

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 methylene chloride 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

A 30 g sample is mixed with anhydrous sodium sulfate to form a free flowing powder. This is extracted with refluxing solvent.

2.5. Cleanup and Concentration

Procedures are presented for removing interferents from sample extracts, and for drying and concentration of the extract to final volume for analysis.

2.6. Phenoxy acid herbicide extractions

Procedures for the extraction and cleanup of phenoxy acid herbicides are presented in Appendix A.

3. DEFINITIONS

Definitions of terms used in this SOP may be found in the glossary of the Quality Assurance Management Plan (QAMP).

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 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. Procedures shall be carried out in a manner that protects the health and safety of all Quanterra associates. The following requirements must be met:

5.2. Eye protection that satisfies ANSI Z87.1 (as per the Chemical Hygiene Plan), 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. Viton gloves may be worn when halogenated solvents are used for extractions or sample preparation. Nitrile gloves may be used when other solvents are handled. [Note: VITON is readily degraded by acetone]. When good manual dexterity is needed, for example, when handling small quantities/containers, disposable gloves (such as latex or N-DEX®) shall be used. While these gloves protect against splashes, they give little or no protection against contact with large quantities of solvent, and no protection against spills or immersion.

5.3. The health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the MSDS files maintained in the laboratory. The following specific hazards are known:

Chemicals that have been classified as **carcinogens** or **potential carcinogens** under OSHA include: Methylene chloride, PCBs, certain pesticides.

The following materials are known to be **corrosive**: Concentrated sulfuric acid, sodium hydroxide, 1N nitric acid.

Sulfuric acid cleanup must not be performed on any matrix that may have water present as a violent reaction between the acid and water may result in acid exploding out of the vessel.

Chemicals known to be **flammable** are: Diethyl ether, acetone, hexane, 2-propanol.
Mercury is a highly toxic compound that must be handled with care. The analyst must be aware of the handling and clean-up techniques before handling this material.

5.4. 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.

5.5. 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.

5.6. All work must be stopped in the event of a known or potential compromise to the health and safety of a Quanterra associate. The situation must be reported **immediately** to a laboratory supervisor.

6. EQUIPMENT AND SUPPLIES

6.1. Glassware should be cleaned with soap and water, rinsed with water and dried in an oven at 400°C for at least 2 hours. Alternatively the glassware can be solvent rinsed with acetone or methanol followed by methylene chloride after the water rinse.

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)	√	√			
Erlenmeyer Flask or Fleaker: 125 & 300 mL (other sizes optional)	√		√		
Solvent Dispenser Pump or 100 mL Graduated Cylinder	√		√		
Continuous Liquid/Liquid Extractor		√			
Round or flat Bottom: 250, 500 mL or 1 L		√			

EQUIPMENT AND SUPPLIES	Sep fun.	CLLE	Soni	Sox	Conc
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			√		
Balance: >100 g capacity, accurate ±0.1 g			√	√	
Soxhlet Extractor				√	
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					√
Nitrogen Blowdown Apparatus					√
Nitrogen: reagent grade.					√
Culture tubes: 10 mL, 16 mmx100 mm					√
Syringe: 1 mL	√	√	√	√	
Phase Separation Paper	√	√	√	√	
Glass Wool	√	√	√	√	
Glass Funnel: 75 X 75 mm	√	√	√	√	√
Disposable Pipets	√	√	√	√	√
Aluminum foil	√	√	√	√	√
Paper Towels	√	√	√	√	√

6.3. Equipment and Supplies for Cleanup Procedures

EQUIPMENT AND SUPPLIES	GPC	Florosil	Sulfur	Acid	A/B
Gel permeation chromatography system (GPC Autoprep Model 1002A or 1002B Analytical Biochemical Laboratories, Inc. or Zymark Benchmate or equivalent).	√				
Bio Beads: (S-X3) -200-400 mesh, 70 gm (Bio-Rad Laboratories, Richmond, CA, Catalog 152-2750 or equivalent).	√				
Chromatographic column: 700 mm x 25 mm ID glass column. Flow is upward.	√				
Ultraviolet detector: Fixed wavelength (254 nm) and a semi-prep flow-through cell.	√				
Strip chart recorder, recording integrator, or laboratory	√				

EQUIPMENT AND SUPPLIES	GPC	Florosil	Sulfur	Acid	A/B
data system.					
Syringe: 10 mL with Luerlok fitting.	√				
Syringe filter assembly, with disposable 5 um filter discs, Millipore No. LSWP 01300 or equivalent.	√				
Chromatographic column: 250 mm long x 10 mm ID; with Pyrex glass wool at the bottom and a Teflon stopcock (for silica gel cleanup).	√				
Vacuum system for eluting multiple cleanup cartridges. Vac Elute Manifold - Analytichem International, J.T. Baker, or Supelco (or equivalent). The manifold design must ensure that there is no contact between plastics containing phthalates and sample extracts.		√			
Vacuum trap made from a 500 mL sidearm flask fitted with a one-hole stopper and glass tubing.		√			
Vacuum pressure gauge.		√			
Rack for holding 10 mL volumetric flasks in the manifold.		√			
Mechanical shaker or mixer: Vortex Genie or equivalent.			√	√	
Separatory Funnels with Ground-Glass Stoppers: 250 mL					√
Erlenmeyer Flasks: 125 mL					√
Disposable Pipets		√	√	√	√
Culture tubes: 10 mL, 16 mmx100 mm	√	√	√	√	√

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.	√	√			
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: Used for cleaning	√	√	√	√	√

7.2. Reagents for Cleanup Procedures

REAGENTS	GPC	Florisil	Sulfur	Acid	A/B
Florisil: 500 mg or 1 g cartridges with stainless steel or Teflon frits (calalog 694-313, Analytichem, 24201 Frampton Ave., Harbor City, CA, or equivalent.)		√			
Mercury: triple distilled			√		
Tetrabutylammonium hydrogen sulfate			√		
Sodium sulfite			√		
Tetrabutylammonium (TBA) sulfite reagent: Prepare reagent by dissolving 3.39 g of Tetrabutylammonium hydrogen sulfate in 100 mL organic-free reagent water. Extract this solution 3 times with 20 mL portions of hexane. Discard the hexane extracts. Add 25 g sodium sulfite to the water solution.			√		
2-Propanol			√		
Nitric acid: 1N			√		
Copper powder: remove oxides (if powder is dark) by treating with 1N nitric acid, rinse with organic-free reagent water to remove all traces of acid, rinse with acetone, and dry under a stream of nitrogen.			√		
Sulfuric acid, Concentrated				√	
Sodium hydroxide, Pellets					√
Sodium hydroxide, 10N: Dissolve 40 g of NaOH in 100 mL of reagent water					√
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.					√

7.3. Standards

7.3.1. 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 six months (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.

7.3.2. Surrogate Spiking Standards

Prepare or purchase surrogate spiking standards at the concentrations listed in Table 5. Surrogate spiking standards are 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. 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.

7.3.4. GPC calibration solution - prepare or purchase a solution in methylene chloride that contains the following analytes in the concentrations listed below:

Analyte	mg/mL
Corn Oil	25.0
Bis (2-ethylhexyl) phthalate	1.0
Methoxychlor	0.2
Perylene	0.02
Sulfur	0.08

NOTE: Sulfur is not very soluble in methylene chloride, however, it is soluble in warm corn oil. Therefore, one approach is to weigh out the corn oil, warm it, and transfer the weighed amount of sulfur into the warm corn oil. Mix it and then transfer into a volumetric flask with methylene chloride, along with the other calibration compounds. This standard has a lifetime of 6 months.

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 leaching procedure is completed.

8.3.3. Analysis of the extracts is completed within forty days of extraction.

9. QUALITY CONTROL

9.1. Quality Control Batch

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.

9.2. Definition of matrix

The possible matrix types are aqueous, soil, waste and TCLP leachate.

9.3. Insufficient Sample

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. Use of a LCS pair in place of a MS/MSD must be documented as a nonconformance.

9.4. Sample count

Laboratory generated QC samples (method blanks, LCS, MS/MSD) are not included in the sample count. Field QC samples and multiple dilutions of samples are included.

9.5. Method Blank

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.

9.5.1. Aqueous Method Blanks use 1000 mL of reagent water spiked with the surrogates. The method blank goes through the entire analytical procedure, including any cleanup steps.

9.5.2. Solid method blanks use 90 g of sodium sulfate spiked with the surrogates. The method blank goes through the entire analytical procedure, including any cleanup steps.

9.5.3. TCLP method blanks use 200 mL of leachate fluid (100 mL for pesticides or herbicides) 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, including any cleanup steps.

9.6. Laboratory Control Sample (LCS)

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, including any cleanup steps.

9.6.1. The LCS is made up in the same way as the method blank, (except that soil LCS consist of 30 g of reagent sand and 60 g of sodium sulfate) (See sections 9.5.1 - 9.5.3) but spiked with the LCS standard and the surrogates.

9.7. Surrogates

9.7.1. 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.

9.7.2. 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.

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

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.

9.9. Initial Demonstration of Capability

The initial demonstration and method detection limit studies described in section 13 must be acceptable before analysis of samples may begin.

9.10. Quality Assurance Summaries

Certain clients may require specific project or program QC which may supersede these method requirements. Quality Assurance Summaries (QAS) should be developed to address these requirements.

9.11. Quanterra QC Program

Further details of QC and corrective action guidelines are presented in the Quanterra QC Program document (QA-003). Refer to this document if in doubt regarding corrective actions.

10. CALIBRATION AND STANDARDIZATION

Refer to section 11.8.1.2 for calibration of the GPC. Otherwise this section is not applicable.

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), waste dilution (11.6), extract concentration (11.7), and extract cleanup (11.8) are presented in this section.

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.

A flow chart for this procedure is included in Section 17. There are slight differences in the initial steps for SW-846 and 600 series methods, as defined below.

11.2.1. Sample preparation for SW-846 methods

11.2.1.1. For pesticides and TCLP leachates, 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.

11.2.1.2. If the entire sample will be used (about 1 L), weigh the sample container on a balance (± 1 g), taring the sample and container. Transfer the sample to the separatory funnel. Decant the water and leave the sediment on the bottom of the container. Reweigh the container. Assume a density of 1 g/mL and record the difference as the sample volume on the benchsheet to the nearest milliliter. Add 60 mL of methylene chloride directly to the separatory funnel. If the entire sample is not used the sample volume is measured using a graduated cylinder.

11.2.1.3. 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.

11.2.1.4. Use 100 mL of leachate for TCLP pesticides, and 200 mL of leachate for TCLP semivolatiles, measured in a graduated cylinder. The leachate should be made up to 1 L in volume with reagent water.

11.2.1.5. For a TCLP method blank, measure 100 mL (200 mL for semivolatiles) of the buffer solution used in the leaching procedure and transfer to the separatory funnel. Dilute to about 1 liter with reagent water. Add 60 mL of methylene chloride to the separatory funnel.

- The sample volume may also be determined by marking the meniscus level on the sample container. Mark the meniscus and transfer the sample to the separatory funnel. Fill the sample container with water up to the marked level. Transfer the measured amount of water to a graduated cylinder and record the volume on the benchsheet to the nearest 5 mL.
- Less than one liter of sample may be used. If necessary, dilute the sample to about 1 liter with reagent water.

11.2.1.6. Proceed to section 11.2.3 (SW-846 and 600 series).

11.2.2. 600 Series methods

11.2.2.1. Mix the sample well by shaking the container.

11.2.2.2. Measure the initial sample pH with wide-range pH paper and record on the extraction benchsheet.

11.2.2.3. If the entire sample will be used (about 1 L), weigh the sample container on a balance (± 1 g), taring the sample and container. Transfer the sample to the separatory funnel. Empty the container completely. Reweigh the container. Assume a density of 1 g/mL and record the difference as the sample volume on the benchsheet to the nearest milliliter. Add 60 mL of methylene chloride to the sample container, seal and shake to rinse the inner surface and remove residual analytes adhering to the glass walls. Transfer this solvent to the separatory funnel.

- **Warning:** Dichloromethane creates excessive pressure very rapidly! Therefore, initial venting should be done immediately after the sample container has been sealed and inverted. Vent into hood away from analysts and other samples. The sample volume may also be determined by marking the meniscus level on the sample container. Transfer the sample to the extractor (see 11.1.3). Fill the sample container with water up to the marked level. Transfer the measured amount of water to a graduated cylinder and record the volume on the benchsheet to the nearest 5 mL.
- Less than one liter of sample may be used. Dilute the sample to about 1 liter with reagent water.

11.2.2.4. 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.

11.2.2.5. Proceed to section 11.2.3 (SW-846 and 600 series)

11.2.3. Add 1 mL of the surrogate spiking solution (Table 3) to each sample, method blank, Laboratory Control Sample (LCS), and Matrix Spike/Matrix Spike Duplicate (MS/MSD). Add 1 mL of the matrix spiking solution (Table 4) to each LCS and MS/MSD. Note that different matrix spiking solutions are used for 600 series, 8000 series and TCLP batches. Swirl liquid in separatory funnel gently to homogenize sample and surrogate/spiking compounds. Note that the surrogate and matrix spiking solutions should be brought to room temperature before spiking the samples.

11.2.4. 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 by dipping a disposable pipette into the sample and wetting the pH paper. Record adjusted pH, spiking volumes and standard numbers on the benchsheet. Return spiking solutions to the refrigerator as soon as possible.

11.2.5. Seal and shake the separatory funnel vigorously for 2 minutes with periodic venting to release excess pressure.

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.

11.2.6. Allow the organic layer to separate from the water phase until complete visible separation has been achieved (approximately 10 minutes). If the emulsion interface between layers is more than one-third the size of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample and may include stirring, 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 11.2.). 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.

11.2.7. Fill a funnel with 10-20 g of anhydrous sodium sulfate. The funnel can be plugged with glass wool or filter paper may be used 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.

11.2.8. Repeat the extraction process two more times using fresh 60 mL portions of solvent, combining the three solvent extracts in the collection container.

11.2.9. If extraction at a secondary pH is required, 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 11.1.7 to 11.1.9. Collect these three extracts in the same container used for the acid fraction.

Note: Alternatively, the acid and base fractions may be kept separate. This may be required for method 625. Separate analysis of the acid and base fractions may also be required for method 625. Individual client requirements must be checked before starting the extraction.

11.2.10. 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.

11.2.11. Dispose of solvent and water remaining in the extractor into the appropriate waste container.

11.2.12. Cover with aluminum foil if the extract is not concentrated immediately. Refer to Section 11.7 for concentration and Section 11.8 for cleanup.

11.3. Continuous Liquid/Liquid Extraction from Water Samples.

A flow chart for this procedure is included in Section 17. There are slight differences in the initial steps for SW-846 and 600 series methods, as defined below.

11.3.1. Sample preparation for SW-846 methods.

11.3.1.1. Assemble the apparatus. Add 450 mL of methylene chloride to the extractor body. Add 3 to 5 boiling chips to the round bottom distilling flask.

11.3.1.2. 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.

11.3.1.3. If the entire sample will be used (about 1 L), weigh the sample container on a balance (± 1 g), taring the sample and container. Transfer the sample to the continuous extractor body. Decant the water and leave the sediment on the bottom of the container. Reweigh the container. Assume a density of 1 g/mL and record the difference as the sample volume on the benchsheet to the nearest milliliter.

11.3.1.4. 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.

11.3.1.5. Use 100 mL of leachate for TCLP pesticides, and 200 mL of leachate for TCLP semivolatiles, measured in a graduated cylinder. The leachate may be made up to 1 L in volume with reagent water.

11.3.1.6. For a TCLP method blank, measure 100 mL (200 mL for semivolatiles) of the buffer solution used in the leaching procedure and transfer to the separatory funnel. Dilute to about 1 liter with reagent water.

11.3.1.7. The sample volume may also be determined by marking the meniscus level on the sample container. Transfer the sample to the extractor (see 11.1.3). Fill the sample container with water up to the marked level. Transfer the measured amount of water to a graduated cylinder and record the volume on the benchsheet to the nearest 5 mL.

11.3.1.8. 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.

11.3.1.9. Proceed to section 11.3.4 (SW-846 and 600 series methods).

11.3.2. Sample preparation for 600 series methods.

11.3.2.1. Assemble the apparatus. Add 400 mL of methylene chloride to the extractor body. Add 3 to 5 boiling chips to the round bottom distilling flask.

11.3.2.2. Mix the sample well by shaking the container.

11.3.2.3. Measure the initial sample pH with wide-range pH paper and record on the extraction benchsheet.

11.3.2.4. If the entire sample will be used (about 1 L), weigh the sample container on a balance (± 1 g), taring the sample and container. Transfer the sample to the continuous extractor body. Empty the container completely. Reweigh the container. Assume a density of 1 g/mL and record the difference as the sample volume on the benchsheet to the nearest milliliter. Add 50 mL of methylene chloride to the sample container, seal and shake to rinse the inner surface and remove residual analytes adhering to the glass walls. Transfer this solvent to the continuous extractor body. If the entire sample is not used the sample volume is measured using a graduated cylinder.

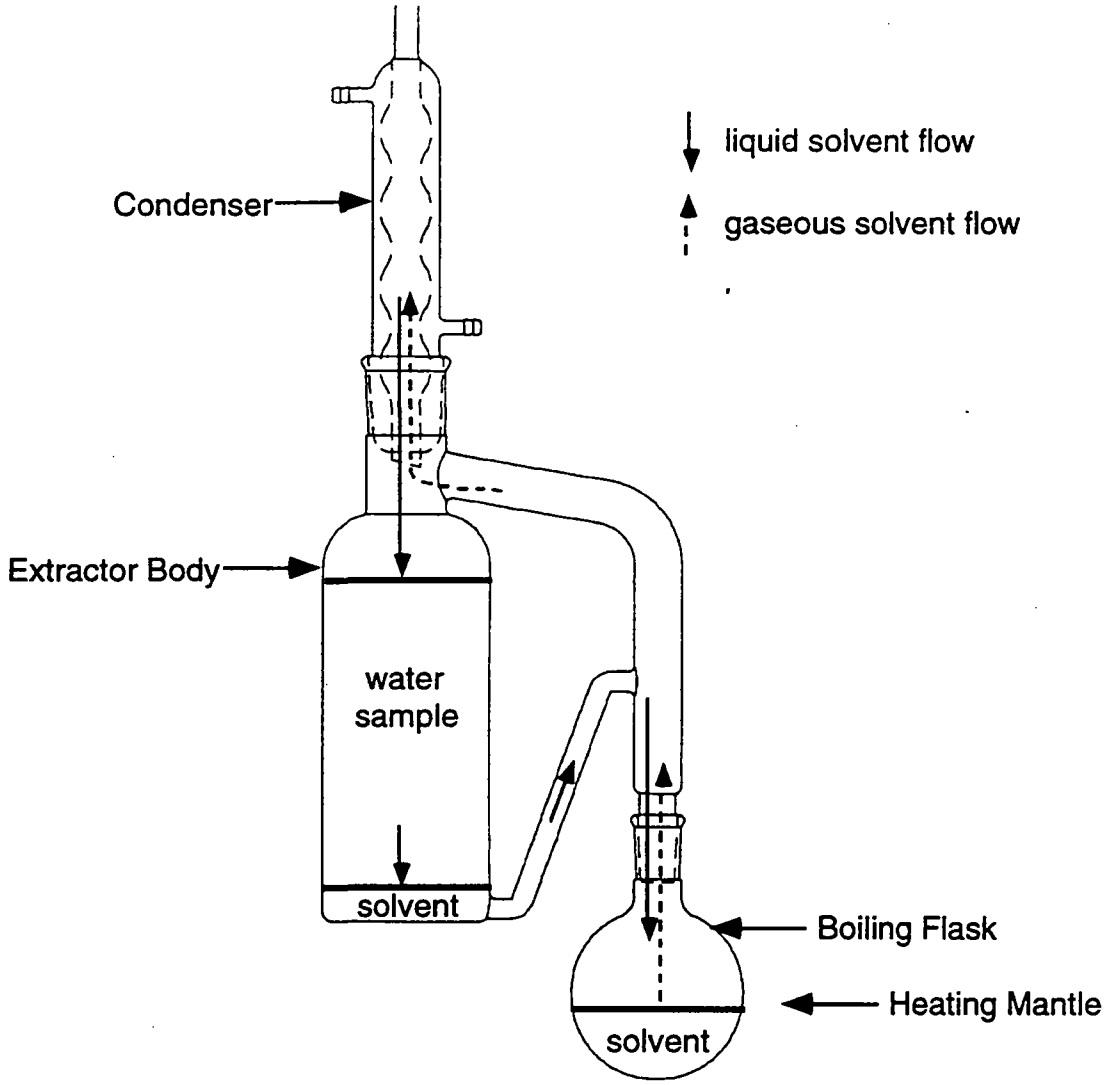
Warning: Dichloromethane creates excessive pressure very rapidly! Therefore, initial venting should be done immediately after the sample container has been sealed and inverted. Vent into hood away from analysts and other samples.

11.3.2.5. 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.

11.3.2.6. The sample volume may also be determined by marking the meniscus level on the sample container. Transfer the sample to the extractor (see 11.1.3). Fill the sample container with water up to the marked level. Transfer the measured amount of water to a graduated cylinder and record the volume on the benchsheet to the nearest 5 mL.

11.3.2.7. 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.

11.3.2.8. Proceed to section 11.3.4 (SW-846 and 600 series methods).



11.3.3. Add 1 mL of the surrogate spiking solution (Table 3) to each sample, method blank, Laboratory Control Sample (LCS), and Matrix Spike/Matrix Spike Duplicate (MS/MSD). Add 1 mL of the matrix spiking solution (Table 4) to each LCS and MS/MSD.

- **Different matrix spiking solutions are used for 600 series, 8000 series and TCLP batches.**
- Surrogate and matrix spiking solutions should be brought to room temperature before spiking the samples.

11.3.4. 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.

11.3.5. 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)

11.3.6. 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. If desired, the acid and base fractions may be kept separate by replacing the boiling flask with a clean flask and fresh solvent. Reattach the condenser and turn on heating mantle. Extract for 18-24 hours.

Note: Alternatively, the acid and base fractions may be kept separate. This may be required for method 625. Separate analysis of the acid and base fractions may also be required for method 625. Individual client requirements must be checked before starting the extraction.

11.3.7. Turn off the heating mantle and allow the extractor to cool.

11.3.8. 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 or phase separation filter paper may be used.

11.3.9. Dry the extract in the round bottom flask by filtering it through the sodium sulfate filled funnel. Note that it is not necessary nor advisable to attempt to add the solvent remaining in the continuous extractor body to the extract.

11.3.10. Collect the dried extract in a K-D or other glass container . Rinse the flask which contained the solvent extract with 20-30 mL of methylene chloride and add it to the funnel to complete the quantitative transfer. Dispose of solvent and water remaining in the extractor in the appropriate waste container.

Note: Some types of CLLE apparatus have built in drying columns. If this type of apparatus is used then a drying step subsequent to the extraction may not be necessary.

11.3.11. Cover with aluminum foil if the extract is not concentrated immediately. Refer to Section 11.7 for concentration and Section 11.8 for cleanup.

11.4. Sonication

11.4.1. A flow chart for this procedure is included in Section 17.

11.4.2. Determination of percent moisture (Optional - if a different group performs this test, refer to the facility SOP.)

In some cases, sample results are needed on a dry weight basis. If this is the case, weigh 5-10 g of sample into a suitable tared container (typically an aluminum weigh pan. Determine the % moisture by drying overnight (at least 12 hours) at 105°C. Allow to cool in a desiccator before weighing.

$$\% \text{ Moisture} = \frac{(\text{weight of wet sample} - \text{weight of dry sample})}{\text{weight of wet sample}} \times 100$$

11.4.3. Determination of pH (Optional - if a different group performs this test, refer to the facility SOP.)

If pH determination is required, transfer 10 g of soil to a beaker. Add 10 mL of water. Stir for 1 hour. Determine the pH of the sample with a glass electrode and pH meter.

11.4.4. Sonication Procedure

11.4.4.1. Decant and discard any water layer on a sediment/soil sample. Homogenize the sample by mixing thoroughly. Discard any 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). Document if a water layer was discarded.

11.4.4.2. Remove surrogate and matrix spiking solutions from refrigerator and allow to warm to room temperature.

11.4.4.3. Weigh 30 g of sample ± 1.0 g into a 250 or 400 mL beaker. Record the weight to the nearest 0. 1 g in the appropriate column on the benchsheet. Use 90 g of sodium sulfate for the method blank and 60 g of sodium sulfate with 30 g of reagent sand for the LCS.

11.4.4.4. Mix weighed sample with a spatula adding enough anhydrous sodium sulfate (approximately 60 g) to be free flowing. (If the sample is not free flowing extraction efficiency may be reduced)

11.4.4.5. Prepare a method blank, LCS and MS/MSD for each batch as specified in section 9 of this SOP.

11.4.4.6. Add 1 mL of the surrogate spiking solution to each sample, method blank, Laboratory Control Sample (LCS), and matrix spikes. Add 1 mL of the appropriate matrix spiking solution to each Matrix Spike/Matrix Spike Duplicate (MS/MSD) and LCS. Refer to Table 3 and 5 for details of the spiking solutions. Record spiking volumes and standard numbers on the benchsheet. Return spiking solutions promptly to refrigerator.

Note: The same volume of surrogate and matrix spiking solution is used if GPC is indicated since the final volume would be reduced to compensate for loss of extract during the GPC procedure.

11.4.4.7. Immediately add a minimum of 100 mL of 1:1 methylene chloride:acetone to the beaker.

Note: Use methylene chloride only if the extract is for Diesel Range Organics or similar tests that require determination of the total area of the chromatogram by GC-FID. If acetone is used the aldol condensation product will interfere with these tests.

Note: Steps 11.4.4.2 - 11.4.4.6 should be performed rapidly to avoid loss of the more volatile extractables.

11.4.4.8. Place the bottom surface of the appropriate disrupter horn tip approximately ½ inch below the surface of the solvent, but above the sediment layer.

11.4.4.9. Sonicate for 3 minutes, making sure the entire sample is agitated. If the W-380 or W-385 sonicator is used the output should be set at 6 for the 3/4 inch high gain (Q) horn or 10 for the 3/4 inch standard horn. with mode switch on pulse, and percent-duty cycle knob set at 50%.

Note: Do ***not*** use ***Microtip*** probe.

11.4.4.10. Loosely plug the stem of a 75 mm x 75 mm glass funnel with glass wool and/or line the funnel with filter paper. Add 10-20 g of anhydrous sodium sulfate to the funnel cup.

11.4.4.11. Place the prepared funnel on a collection apparatus (beaker or K-D Apparatus.

11.4.4.12. Decant and filter extracts through the prepared funnel into a clean beaker or K-D Apparatus.

11.4.4.13. Repeat the extraction two more times with additional 100 mL minimum portions of methylene chloride / acetone 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.

Note: Alternatively, the three extracts may be collected together and then filtered through the sodium sulfate.

11.4.4.14. Cover with aluminum foil if the extract is not concentrated immediately. Refer to Section 11.7 for concentration and Section 11.8 for cleanup.

11.4.5. Sonicator Tuning.

11.4.5.1. Tune the sonicator according to manufacturer's instructions. The sonicator must be tuned at least every time a new horn is installed.

11.5. Soxhlet

11.5.1. Determination of % moisture

In some cases, sample results are needed on a dry weight basis. If this is the case, weigh 5-10 g of sample into a suitable tared container (typically an aluminum weigh pan. Determine the % moisture by drying overnight at 105°C. Allow to cool in a desiccator before weighing.

$$\% \text{ Moisture} = \frac{(\text{weight of wet sample} - \text{weight of dry sample})}{\text{weight of wet sample}} \times 100$$

11.5.2. Determination of pH

If pH determination is required, transfer 10 g of soil to a beaker. Add 10 mL of water. Stir for 1 hour. Determine the pH of the sample with a glass electrode and pH meter.

11.5.3. Decant and discard any water layer on a sediment/soil sample. Homogenize the sample by mixing thoroughly. Discard any 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. Document on benchsheet if a water layer was discarded.

11.5.4. Remove surrogate and matrix spiking solutions from refrigerator and allow to warm to room temperature.

11.5.5. Weigh 30 g of sample ± 1.0 g into a beaker, recording the weight to the nearest 0.1 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 a 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 above and below the sample in the soxhlet extractor is an acceptable alternative for the thimble.

11.5.5.1. 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. The weight of sodium sulfate used should be approximately the weight of soil used in each sample.

11.5.7. Add 1 mL of the surrogate spiking solution to each sample, method blank, Laboratory Control Sample (LCS), and matrix spikes. Add 1 mL of the

appropriate matrix spiking solution to each Matrix Spike/Matrix Spike Duplicate (MS/MSD) and LCS. Refer to Tables 3 - 6 for details of the spiking solutions. Record spiking volumes and standard numbers on the benchsheet. Return spiking solutions promptly to refrigerator.

Note: The same volume of surrogates and matrix spiking compounds is used if GPC is indicated since the final volume would be reduced to compensate for loss of extract during the GPC procedure.

11.5.8. Place 250 mL of 1:1 methylene chloride:acetone into a 500 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: Use methylene chloride only if the extract is for Diesel Range Organics or similar tests that require determination of the total area of the chromatogram by GC-FID. If acetone is used the aldol condensation product will interfere with these tests.

11.5.9. Allow the extract to cool after the extraction is complete, then disassemble by gently twisting the soxhlet from the flask. Dry the extract in the flask by filtering it through a sodium sulfate filled funnel.

11.5.10. Collect the dried extract in a K-D or other glass container . Rinse the flask which contained the solvent extract with 20-30 mL of methylene chloride and add it to the funnel to complete the quantitative transfer.

11.5.11. Cover with aluminum foil if the extract is not concentrated immediately. Refer to Section 11.7 for concentration and Section 11.8 for cleanup.

11.6. Waste Dilution

11.6.1. This method is used for materials that are soluble in an organic solvent.

11.6.2. Transfer 10 mL of the solvent to be used for dilution into a Teflon capped vial. Mark the meniscus on the vial, then discard the solvent.

11.6.3. Tare the vial, then transfer 1.0 g $\pm$ 0.1 g of sample to the vial. Record the weight to the nearest 0.1 g.

11.6.4. Add 1 mL of surrogate solution (Table 3) For GC/MS analysis, the surrogate solution should be 10x more concentrated than the normal solution (i.e. 1000/1500 ppm). For pesticides the normal surrogate solution is appropriate.

11.6.5. Dilute to 10 mL (make up to the meniscus mark) with the appropriate solvent. (Methylene Chloride for GC/MS analysis, hexane for pesticides analysis.)

11.6.6. Add 2 g + 0.1 g sodium sulfate to the sample. Cap and shake for 2 minutes.

11.6.7. Add 4-5 g sodium sulfate to a small funnel. The funnel can be plugged with glass wool or phase separation filter paper may be used to hold the sodium sulfate.

11.6.8. Pour the sample through the funnel, collecting as much as possible in a clean vial. Do NOT rinse the funnel with additional solvent, and do NOT concentrate the sample. The final volume is defined as 10 mL.

11.6.9. Label the sample, which is now ready for cleanup or analysis.

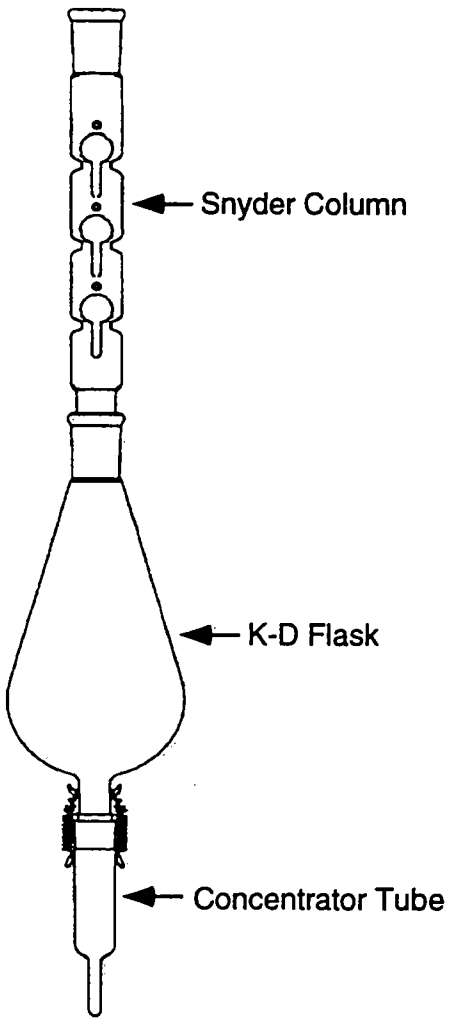
11.7. Concentration

According to the type of sample and any cleanup procedures needed, different final solvents and volumes will be required. Refer to Table 2 for the appropriate final volumes and concentrations.

11.7.1. Kuderna-Danish (KD) Method:

11.7.1.1. Assemble a Kuderna-Danish concentrator by attaching a 10 mL concentrator tube to the 500 mL KD flask. Transfer the sample to the K-D flask.

11.7.1.2. 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 that the column will work properly).



11.7.1.3. Place the KD apparatus on a water bath (80-90°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.

11.7.1.4. Concentrate to 5-15 mL. If the determinative method requires a solvent exchange add the appropriate exchange solvent (50 mL hexane, 50 mL cyclohexane, 2 mL acetonitrile or 10 mL toluene) to the top of the Snyder Column, and then continue the water bath concentration back down to 1-4 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: Add an additional boiling chip with the addition of exchange solvent.

An alternative technique for solvent exchange is to replace the macro Snyder column and KD flask with a micro Snyder column, concentrate to approximately 1 mL, add 10 mL of hexane, 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.

11.7.1.5. 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.

11.7.1.6. If the final volume is 5 or 10 mL the extract may be made up to volume in the graduated KD tube or transferred to a 12 mL vial previously marked at the appropriate volume level. Document the final volume. Otherwise proceed to section 11.7.2

11.7.2. Nitrogen Evaporation to Final Concentration

11.7.2.1. Transfer the entire extract to a calibrated evaporation tube. Rinse the concentrator tube with 1-2 mL of the appropriate solvent and transfer the solvent rinsate to the evaporation tube.

11.7.2.2. 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

11.7.2.3. During the course of the evaporation rinse the sides of the evaporation tube twice with approximately 1 mL of clean solvent. The first rinse should be about half way through the process, with the second rinse when the solvent volume gets close to 1 mL. Concentrate the solvent accurately to the calibrated volume line and transfer the extract to the appropriate storage vial.

Note: It is very important not to concentrate to dryness as analytes will be lost.

11.7.2.4. 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.

11.7.2.5. *Note:* The final concentration and volume measurement steps are critical. Use care when concentrating and make certain that the final volume measurement is accurate.

11.7.3. Turbovap Method

11.7.3.1. Turn on the Turbovap and adjust the water temperature to 5-10°C less than the boiling point of the solvent to be evaporated.

11.7.3.2. Switch all endpoint sensors to the "NO" position.

11.7.3.3. Adjust the water bath level

11.7.3.4. Adjust the nitrogen gas pressure to approximately 12 psi.

11.7.3.5. Transfer the extract into the Turbovap tube and load into the Turbovap. Do not fill the Turbovap tubes over approximately 3/4 full.

11.7.3.6. Reset the sensor and close the lid.

11.7.3.7. *Note:* If the extract splashes when the nitrogen flow starts, reduce the nitrogen flow or transfer a portion of the extract back into the original extract container.

11.7.3.8. As the extract concentrates, transfer the remainder of the extract into the appropriate Turbovap tube. After all of the extract has been transferred, rinse the flask with a few mL of methylene chloride and add to the Turbovap tube.

11.7.3.9. During the concentration rinse the Turbovap tube walls with a few mL of solvent 1 or 2 times.

11.7.3.10. Concentrate the extract to slightly less than the required final volume.

11.7.3.11. If solvent exchange is required, concentrate to 1-4 mL and add 50 mL of the exchange solvent. Concentrate back down to the appropriate volume. Refer to table 2 for details of exchange solvents and final volumes.

11.7.3.12. Transfer the concentrated extract to volumetric glassware for adjustment of final volume, using a small amount of solvent to rinse the tube and complete the transfer.

Note: Water contamination from condensation during concentration is not acceptable. If water is present, remove the Turbovap tube and filter the extract through sodium sulfate. Transfer to a clean Turbovap tube and continue the concentration.

Note 2: Dark, opaque or turbid samples may not concentrate. If this occurs, set the concentrator sensor to dryness and supervise the entire concentration procedure.

11.8. Cleanup Techniques

The following techniques may be used to remove interfering peaks, and /or to remove materials that may cause column deterioration and/ or loss of detector sensitivity. *Gel Permeation Chromatography* (Section 11.8.1) is a generally applicable technique which can be used to prepare extracts for Semivolatiles (8270), PAH (8100) and pesticides (8080) analysis. It is capable of separating high molecular weight material from the sample analytes, and so is particularly useful if tissue or vegetable matter is part of the sample, and for many soil samples.

Florisil column cleanup (Section 11.8.2) is particularly useful for cleanup of pesticides for analysis by method 8080 and should normally be applied to these samples unless the matrix is clean. It separates compounds with a different polarity from the target analytes.

Gel Permeation Chromatography and Florisil column cleanup may both be applied to samples for analysis by method 8080. In this case the GPC should be performed first.

Sulfur cleanup (Section 11.8.3) is generally applied to samples for analysis by method 8080, since the Electron Capture Detector responds strongly to sulfur. It is performed after GPC and Florisil cleanup.

Sulfuric acid cleanup (Section 11.8.4) is applied to samples requiring analysis for Polychlorinated Biphenyls (PCBs) only. Most organic matter is destroyed by the sulfuric acid.

Acid Base Partition Cleanup (Section 11.8.5) is useful for separating organic acids and phenols from basic and neutral organics.

Silica gel cleanup (Section 11.8.6) may be used to separate polynuclear aromatic hydrocarbons from interfering aliphatic hydrocarbons prior to analysis by GC/FID.

11.8.1. Gel Permeation Chromatography (GPC)

Note: GPC systems include the GPC Autoprep Model 1002A or 1002B Analytical Biochemical Laboratories, Inc., Zymark Benchmate, or equivalent.

11.8.1.1. GPC Column Preparation

11.8.1.1.1. Weigh out 70 g of Bio Beads (SX-3) into a 400-mL beaker.

11.8.1.1.2. Add approximately 300 mL of methylene chloride and stir gently.

11.8.1.1.3. Cover with aluminum foil and allow the beads to swell for a minimum of two hours. Maintain enough solvent to sufficiently cover the beads at all times.

11.8.1.1.4. Position and tighten the outlet bed support (top) plunger assembly in the tube by inserting the plunger and turning it clockwise until snug. Install the plunger near the column end but no closer than 5 cm (measured from the gel packing to the collar).

11.8.1.1.5. Turn the column upside down from its normal position with the open end up. Place the tubing from the top plunger assembly into a waste beaker below the column.

11.8.1.1.6. Swirl the bead/solvent slurry to get a homogeneous mixture and pour the mixture into the open end of the column. Transfer as much as possible with one continuous pour trying to minimize bubble formation. Pour enough to fill the column. Wait for the excess solvent to drain out before pouring in the rest. Add additional methylene chloride to transfer the remaining beads and to rinse the beaker and the sides of the column. If the top of the gel begins to look dry, add more methylene chloride to rewet the beads.

11.8.1.1.7. Wipe any remaining beads and solvent from the inner walls of the column with a laboratory tissue. Loosen the seal slightly on the other plunger assembly (long plunger) and insert it into the column. Make the seal just tight enough so that any beads on the glass surface will be pushed forward, but loose enough so that the plunger can be pushed forward.

CAUTION: Do not tighten the seal if beads are between the seal and the glass surface because this can damage the seal and cause leakage.

11.8.1.1.8. Push the plunger until it meets the gel, then compress the column bed about 4 cm.

11.8.1.1.9. Connect the column inlet to the solvent reservoir and place the column outlet tube in a waste container. Pump methylene chloride through the column at a rate of 5 mL/min. for one hour.

11.8.1.1.10. After washing the column for at least one hour, connect the column outlet tube to the inlet side of the UV detector. Connect the system outlet to the outlet side of the UV detector. Placing a restrictor (made from a piece of capillary tubing of 1/16"OD x 10/1000"ID x 2") in the outlet tube from the UV detector will prevent bubble formation which causes a noisy UV baseline. The restrictor will not effect the flow rate. After pumping methylene chloride through the column for an additional 1-2 hours, adjust the inlet bed support plunger until

approximately 6-10 psi back-pressure is achieved. Push the plunger in to increase pressure or slowly pull outward to reduce pressure.

11.8.1.1.11. When the GPC column is not to be used for several days, connect the column inlet and outlet lines to prevent column drying and/or channeling. If channeling occurs, the gel must be removed from the column, re-swelled, and re-poured as described above. If drying occurs, pump methylene chloride through the column until the observed column pressure is constant and the column appears wet. Always recalibrate after column drying has occurred to verify that retention volumes have not changed.

11.8.1.2. Initial Calibration of the GPC Column

11.8.1.2.1. Before use, the GPC must be calibrated based on monitoring the elution of standards with a UV detector connected to the GPC column.

11.8.1.2.2. Pump solvent through the GPC column for 2 hours. Verify that the flow rate is 4.5-5.5 mL/min. Corrective action must be taken if the flow rate is outside this range. Record the column pressure (should be 6-10 psi) and room temperature (22°C is ideal).

Note: Changes in pressure, solvent flow rate, and temperature conditions can affect analyte retention times and must be monitored. If the flow rate and/or column pressure do not fall within the above ranges, a new column should be prepared.

11.8.1.2.3. Inject the calibration solution and retain a UV trace that meets the following requirements (See resolution calculation in section 11.8.1.6):

- Peaks must be observed and should be symmetrical for all compounds in the calibration solution.
- Corn oil and phthalate peaks must exhibit >85% resolution.
- Phthalate and methoxychlor peaks must exhibit >85% resolution.
- Methoxychlor and perylene peaks must exhibit >85% resolution.
- Perylene and sulfur peaks must not be saturated and must exhibit >90% baseline resolution.

11.8.1.2.4. A UV trace that does not meet the criteria in paragraph 11.8.1.2.3 indicates the need for system maintenance and/or the need for a new column.

11.8.1.2.5. Determine appropriate collect and dump cycles.

11.8.1.2.6. The calibrated GPC program for pesticides/PCB should dump >85% of the phthalate and should collect >95% of the methoxychlor and perylene. Use a wash time of 10 minutes.

11.8.1.2.7. For semivolatile extracts, initiate a column eluate collection just before the elution of bis (2-ethylhexyl) phthalate and after the elution of the corn oil. Stop eluate collection shortly after the elution of perylene. Stop collection before sulfur elutes. Use a wash time of 10 minutes after the elution of sulfur.

11.8.1.2.8. Reinject the calibration solution after appropriate dump and collect cycles have been set.

11.8.1.2.9. Measure and record the volume of collected GPC eluate in a graduated cylinder.

11.8.1.2.10. The retention times for both bis(2-ethylhexyl) phthalate and perylene must not vary more than +/- 5% between calibrations.

11.8.1.3. GPC calibration check

Check the calibration of the GPC immediately after the initial calibration and at least every 7 days thereafter, while the column is in use.

11.8.1.3.1. Inject the calibration solution, and obtain a UV trace. If the retention times of bis(2-ethylhexyl)phthalate or perylene have changed by more than ± 5% use this run as the start of a new initial calibration. Otherwise, proceed with the recovery check. Excessive retention time shifts may be caused by poor laboratory temperature control or system leaks, an unstabilized column, or high laboratory temperature causing outgassing of methylene chloride. Pump methylene chloride through the system and check the retention times each day until stabilized.

11.8.1.4. GPC Recovery Check for Pesticides/ PCBs

11.8.1.4.1. The recovery from the GPC must be verified immediately after the initial calibration and at least every 7 days, when the instrument is in use. Two recovery check solutions are used. The first mixture is prepared by diluting 1.0 mL of the pesticide matrix spiking solution (Table 6) to 10 mL in methylene chloride. The second mixture is prepared by diluting 1 mL of the PCB only matrix spiking solution (Table 6) to 10 mL with methylene chloride.

11.8.1.4.2. Load the pesticide matrix spike mixture, the PCB mixture, and a methylene chloride blank onto the GPC using the GC dump and collect values.

Note: If the analysis is for PCBs only, then the pesticide recovery check is not necessary.

11.8.1.4.3. After collecting the GPC calibration check fraction, concentrate, solvent exchanging to hexane. Adjust the final volume to 5.0 mL, and analyze by GC/EC. Refer to concentration, section 11.7.

11.8.1.4.4. The methylene chloride blank may not exceed more than one half the reporting limit of any analyte. And if the recovery of each of the single component analytes is 80-110% and if the Aroclor pattern is the same as previously run standards, then the analyst may use the column. If the above criteria are not met, there may be a need for system maintenance.

11.8.1.5. GPC Recovery Check for Semivolatiles

11.8.1.5.1. The recovery from the GPC must be verified immediately after the initial calibration and at least every 7 days, when the instrument is in use. Dilute 1.0 mL of the semivolatiles matrix spiking solution (Table 6) to 10 mL in methylene chloride.

11.8.1.5.2. Load the matrix spike mixture and a methylene chloride blank onto the GPC using the semivolatiles dump and collect values.

11.8.1.5.3. After collecting the GPC recovery check fraction, concentrate to 0.5 mL, and analyze by GC/MS. Refer to the concentration section 11.7.

11.8.1.5.4. Recovery of the matrix spike analytes should be at least 85%. The blank should not contain any analytes at or above the reporting limit. If these conditions are met the column may be used for sample analysis. Otherwise correct the contamination problem, or extend the collect time to improve recovery of target analytes.

11.8.1.6. Sample Extract Cleanup

11.8.1.6.1. Reduce the sample extract volume to 1-2 mL, then adjust to 10 mL with methylene chloride prior to cleanup. This reduces the amount of acetone in the extract. Refer to section 11.7.

11.8.1.6.2. Start the pump and let the flow stabilize for 2 hours. The solvent flow rate should be 4.5-5.5 mL/min. The ideal laboratory temperature to

prevent outgassing of the methylene chloride is 22°C. The normal backpressure is 6-10 psi.

11.8.1.6.3. In order to prevent overloading of the GPC column, highly viscous sample extracts must be diluted prior to cleanup. Any sample extract with a viscosity greater than that of a 1:1 glycerol:water solution (by visual comparison) must be diluted and loaded into several loops.

11.8.1.6.4. Samples being loaded onto the GPC should be filtered with a 5 micron (or less) filter disk. Attach a filter to a 10 mL Luerlok syringe and filter the 10 mL sample extract into the sample tube.

Note: The Zymark Benchmate automatically filters the sample extracts, but manual prefiltration of very dirty extracts may be necessary.

11.8.1.6.5. Load the filtered (or unfiltered if using the Benchmate) samples into the proper sample tubes and place on the GPC.

Note: For the GPC Autoprep Model 1002A, wash the loading port with methylene chloride after loading each sample loop in order to minimize cross contamination. This step is automated on the GPC Autoprep 1002B and on the Benchmate.

11.8.1.6.6. Set the collect, dump, and wash times determined by the calibration procedure.

11.8.1.6.7. Switch to the run mode and start the automated sequence. Process each sample using the collect and dump cycle times established by the calibration procedure.

11.8.1.6.8. Collect each sample in a suitable glass container. Monitor sample volumes collected.

11.8.1.6.9. Any samples that were loaded into 2 or more positions must be recombined.

11.8.1.6.10. Concentrate semivolatile sample extracts to 0.5 mL in methylene chloride. Refer to the concentration section 11.7.

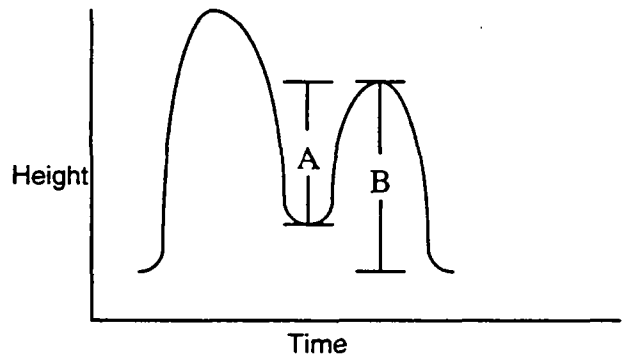
11.8.1.6.11. Solvent exchange pesticide/PCB sample extracts into hexane and concentrate to 5.0 mL. Refer to the concentration section 11.7.

11.8.1.7. Calculations

11.8.1.7.1. Resolution

To calculate the resolution between two peaks on a chromatograph, divide the depth of the valley between the peaks by the peak height of the smaller peak being resolved and multiply by 100.

Resolution Calculation



$$\% \text{ Resolution} = \frac{A}{B} \times 100$$

Where: A = depth of valley to height of smaller peak
B = peak height of smaller peak

11.8.1.7.2. Dump Time

Mark on the chromatograph the point where collection is to begin. Measure the distance from the injection point. Divide the distance by the chart speed. Alternatively the collect and dump times may be measured by means of an integrator or data system.

$$\text{Dump time (min)} = \frac{\text{Distance (cm) from injection to collection start}}{\text{Chart speed (cm / min)}}$$

11.8.1.7.3. Collection Time

$$\text{Collection time (min)} = \frac{\text{Distance (cm) between collection start and stop}}{\text{Chart speed (cm / min)}}$$

11.8.2. Florisil Cartridge Cleanup

Note 1: Systems for eluting multiple cleanup cartridges include the Supelco, Inc. Solid Phase Extraction (SPE) assembly, Zymark Benchmate, or equivalent.

Note 2: Follow the lab specific procedure when using the Zymark benchmate.

11.8.2.1. Before Florisil cleanup sample volume must be reduced to 10 mL (5 mL if GPC cleanup was used) and the solvent must be hexane. Refer to Section 11.7 for details of concentration.

11.8.2.2. Attach a vacuum manifold to a vacuum pump or water aspirator with a trap installed between the manifold and the vacuum. Adjust the vacuum in the manifold to 5-10 psi.

11.8.2.3. Place one Florisil cartridge into the vacuum manifold for each sample extract. Prior to cleanup of samples, pre-elute each cartridge with 5 mL of hexane/acetone (9:1). Adjust the vacuum applied to each cartridge so that the flow through each cartridge is approximately 2 mL/min. Do not allow the cartridges to go dry.

11.8.2.4. Just before the cartridges go dry, release the vacuum to the manifold and remove the manifold top.

11.8.2.5. Place a rack of clean labeled 12 mL concentrator tubes into the manifold and replace the manifold top. Make sure that the solvent line from each cartridge is placed inside the appropriate tube.

11.8.2.6. After the clean tubes are in place, vacuum to the manifold is restored and 2.0 mL of the extract is added to the appropriate Florisil cartridge.

11.8.2.7. The pesticides/aroclors in the extract concentrates are then eluted through the column with 8 mL of hexane/acetone (90:10) and are collected into the 10 mL culture tube or concentrator tube held in the rack inside the vacuum manifold.

11.8.2.8. Transfer the extract to a graduated concentrator tube and concentrate the extract to 2 mL. Refer to the concentration section. (11.7)

Note 1: A cartridge performance standard must be run with each lot of Florisil cartridges.

Note 2: Florisil cartridge performance check--every lot number of Florisil must be tested before use. Add 0.5 ug/mL of 2,4,5-trichlorophenol solution and 0.5 mL of GC Standard Mix A (midpoint concentration) to 4 mL hexane. Reduce volume to 0.5 mL. Add the concentrate to a pre-washed Florisil cartridge and elute with 9 mL hexane/acetone [(90:10)(v/v)]. Rinse cartridge with 1.0 mL hexane two additional times. Concentrate eluate to 1.0 mL final volume and transfer to vial. Analyze the solution by GC/EC. The test sample must show 80 to 120% recovery of all pesticide analytes with <5% trichlorophenol recovery, and no peaks interfering with target compounds can be detected. This standard has a lifetime of six months. Alternatively, this standard may be purchased as a stock solution.

11.8.3. Sulfur Removal

11.8.3.1. Sulfur can be removed by one of three methods: mercury, copper, or tetrabutylammonium sulfite (TBA) according to laboratory preference. If the sulfur concentration is such that crystallization occurs in the concentrated extract, centrifuge the extract to settle the crystals, and carefully draw off the sample extract with a disposable pipet, leaving the excess sulfur in the centrifuge tube. Transfer the extract to a clean concentrator tube before proceeding with further sulfur cleanup.

11.8.3.2. Sulfur Removal with Elemental Mercury

Note: Use Mercury sparingly in order to minimize exposure and disposal costs.

11.8.3.2.1. Transfer 2 mL of sample extract into a clean concentrator tube or Teflon sealed vial.

11.8.3.2.2. Add one to three drops of mercury to the extract vial and seal.

11.8.3.2.3. Shake well for 15-30 seconds. If prolonged shaking is required, use a mechanical shaker.

11.8.3.2.4. Remove the extract from the mercury using a disposable pipet and transfer to a clean vial.

11.8.3.2.5. If black precipitate forms, sulfur was present. Shake again, then centrifuge. After centrifugation, transfer the supernate to a clean test tube and repeat. Do this until relatively little precipitate remains, or the screens indicate that cleanup is complete.

11.8.3.2.6. Properly dispose of the mercury waste.

11.8.3.3. Sulfur Removal with Copper

11.8.3.3.1. Transfer 1.0 mL of sample extract into a centrifuge or concentrator tube.

11.8.3.3.2. Add approximately 2 g of cleaned copper powder (see 7.1.15.4 for copper cleaning procedure) to the sample extract tube.

11.8.3.3.3. Mix for one minute on a mechanical shaker.

11.8.3.3.4. If the copper changes color, sulfur was present. Repeat the sulfur removal procedure until the copper remains shiny.

11.8.3.3.5. Transfer the supernate to a clean vial.

11.8.3.4. Sulfur Removal with Tetrabutylammonium (TBA) Sulfite Reagent

11.8.3.4.1. Transfer 1.0 mL of sample extract into a culture tube.

11.8.3.4.2. Add 1.0 mL TBA sulfite reagent and 2 mL 2-propanol to the sample extract. Cap and shake for 1 minute. If clear crystals (precipitated sodium sulfite) form, sufficient sodium sulfite is present.

11.8.3.4.3. If a precipitate does not form, add sodium sulfite in approximately 0.1 g portions until a solid residue remains after repeated shaking.

11.8.3.4.4. Add 5 mL organic free reagent water and shake for 1 minute. Allow sample to stand for 5-10 minutes. (Centrifuge if necessary to separate the layers). Transfer the sample extract (top layer) to a vial. The final volume is defined as 1.0 mL in section 11.8.3.4.1.

11.8.4. Sulfuric Acid Cleanup

11.8.4.1. Add approximately 2-5 mL of concentrated sulfuric acid to 2 mL of sample extract in a Teflon capped vial.

Caution: There must be no water present in the extract or the reaction may shatter the sample container.

11.8.4.2. Shake for about thirty seconds and allow to settle. (Centrifuge if necessary)

11.8.4.3. Remove the sample extract (top layer) from the acid using a Pasteur pipet and transfer to a clean vial. ***CAUTION:*** It is not necessary to remove all the extract since the final volume is already determined. Transfer of small amounts of sulfuric acid along with the extract will result in extremely rapid degradation of the chromatographic column.

11.8.4.4. If the sulfuric acid layer becomes highly colored after shaking with the sample extract, transfer the hexane extract to a clean vial and repeat the cleanup procedure until color is no longer being removed by the acid, or a maximum of 5 acid cleanups.

11.8.4.5. Properly dispose of the acid waste.

11.8.5. **Acid/Base Partition Cleanup**

11.8.5.1. Place 10 mL of the solvent extract from a prior extraction procedure into a 125 mL separatory funnel.

11.8.5.2. Add 20 mL of methylene chloride to the separatory funnel.

11.8.5.3. Slowly add 20 mL of DI water which has been previously adjusted to a pH of 12 to 13 with 10 N sodium hydroxide.

11.8.5.4. Seal and shake the separatory funnel for at least two minutes with periodic venting to release excess pressure.

CAUTION: Methylene chloride creates excessive pressure very rapidly. Initial venting should be done immediately after the separatory funnel has been sealed.

11.8.5.5. Allow the organic layer to separate from the aqueous phase for a minimum of ten minutes.

11.8.5.6. If an 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.

11.8.5.7. Separate the aqueous phase and transfer it to a 125 mL Erlenmeyer flask. Repeat the extraction two more times using fresh 20 mL aliquots of dilute sodium hydroxide (pH 12-13) . Combine the aqueous extracts.

11.8.5.8. Water soluble organic acids and phenols will be primarily in the aqueous phase. Base/neutral analytes will be in the methylene chloride. If the analytes of interest are only in the aqueous phase discard the methylene chloride and proceed to Section 11.8.5.9. If the analytes of interest are only in the methylene chloride, discard the aqueous phase and proceed to Section 11.8.5.11.

11.8.5.9. Adjust the aqueous phase to a pH of 1-2 with sulfuric acid (1:1). Allow to cool and transfer the cool aqueous phase to a clean 125 mL separatory funnel.

11.8.5.10. Add 20 mL of methylene chloride to the separatory funnel and shake for at least two minutes. Allow the methyene chloride to separate from the aqueous phase and collect the methylene chloride in an Erlenmeyer flask.

Repeat the extraction two more times using fresh methylene chloride and extracting at pH 1-2. Combine the three extracts.

11.8.5.11. Dry the extract by passing through a funnel containing 10-20 g anhydrous sodium sulfate. Rinse the funnel with an additional 20-30 mL of clean methylene chloride

11.8.5.12. Cover with aluminum foil if the extract is not concentrated immediately. Refer to section 11.7 for concentration.

11.8.5.13. Dispose of solvent and water remaining in the separatory funnel into the appropriate waste container.

11.8.6. Silica Gel Cleanup

This procedure is appropriate for cleanup of extracts prior to determination of polynuclear aromatic hydrocarbons by GC/FID.

11.8.6.1. Exchange the extract solvent to cyclohexane and reduce the volume to 2 mL prior to cleanup.

11.8.6.2. Prepare a slurry of approximately 10 g of activated silica gel in about 15 mL of methylene chloride. Place this into a 10 mm ID chromatographic column. Tap the column to settle the silica gel. Add 1-2 cm of anhydrous sodium sulfate to the top of the silica gel.

11.8.6.3. Preelute the column with 40 mL of pentane. Elution rate should be approximately 2 mL/min. Discard the eluate and just prior to exposure of the sodium sulfate to air, transfer the 2 mL cyclohexane sample extract onto the column using an additional 2 mL of cyclohexane to complete the transfer. Just prior to exposure of the sodium sulfate layer to the air, add 25 mL of pentane and continue the elution of the column. Discard this pentane elute.

11.8.6.4. Elute the column with 25 mL of methylene chloride/pentane (2:3 v/v). Since the polynuclear aromatic hydrocarbons elute in this fraction, collect the eluate and concentrate to the required volume.

12. DATA ANALYSIS AND CALCULATIONS

Not applicable

13. METHOD PERFORMANCE

13.1. Method detection limit

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 Quanterra QA Policy #: QA-005

13.2. Initial demonstration

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.)

13.2.1. Four aliquots of the QC check sample are analyzed using the same procedures used to analyze samples, including sample preparation.

13.2.2. Calculations and acceptance criteria for the QC check samples are given in the determinative SOPs. (CORP-GC-0001, CORP-MS-0001, 0002)

13.3. Training Qualification

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

Within the constraints of following the methodology in this SOP, use of organic solvents should be minimized.

15. WASTE MANAGEMENT

Waste generated in this procedure will be segregated, and disposed according to the facility hazardous waste procedures. The Health and Safety Director should be contacted if additional information is required.

15.1. Solvent waste must be disposed of in the clearly labeled waste cans.

15.2. Acid waste must be collected in the clearly labeled acid waste containers.

15.3. Solid materials (soil, gloves, soiled paper products) are placed in the solid debris container. Do not put liquids in the solid waste container.

15.4. Methylene chloride saturated water and remaining sample after the extraction is dumped into Methylene chloride waste cans.

16. REFERENCES

Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW846, 3rd Edition, Final Update II (September 1994). Sections 3500A, 3510B, 3520B, 3540B, 3550A, 3600B, 3610A, 3620A, 3640A, 3650A, and 3660A.

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. Aqueous sample volumes may be determined by weight.

17.1.3. In the CLLE procedure the same solvent is used for the acid and base neutral extractions.

17.1.4. 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.

17.1.5. 10 g of soil is used for pH determination, rather than the 50 g suggested in the reference method. The volume of water is also adjusted to maintain the sample / water ratio specified in the method.

17.2. Modifications from previous revision

17.2.1. Sonicator tuning directions have been changed

17.2.2. Use of phase separation filter paper is not recommended, since organic solvents may leach siloxanes from the filter paper.

17.2.3. The quantity of sulfuric acid used in sulfuric acid cleanup has been reduced.

17.2.4. Allowance for different final solvents for organophosphorous pesticides has been added.

17.2.5. Some typographical errors have been corrected.

17.3. Facility Specific SOPs

Each facility shall attach a list of facility specific SOPs or approved attachments (if applicable) which are required to implement this SOP or which are used in conjunction with this SOP. If no facility specific SOPs or amendments are to be attached, a statement must be attached specifying that there are none.

17.4. Tables

Table 1
Liquid /Liquid Extraction Conditions

Determinative Method	Initial Ext. pH	Secondary Ext. pH
BNA: 8270	1-2	11-12
625	11-12	1-2
Pest/PCB: 8080 & 608	5-9	None
OPP: 8140	6-8	None
OPP: 8141	as received	None
Hydrocarbons: 8015	as received	None
PAH: 8310, 8100 & 610	as received	None

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
Semivolatiles	N/A	1.0
Pesticides	Hexane	10.0
PAH by HPLC	Acetonitrile	Refer to facility SOP for HPLC
PAH by GC	N/A	1.0
TPH	N/A	1.0
OPP	Toluene, hexane or isooctane	10.0

Final Volumes and exchange solvents if GPC cleanup is used			
Type	Exchange Solvent for GPC	Final Volume for GPC	Final Volume and solvent for Analysis
Semivolatiles	CH_2Cl_2	10 mL[1]	0.5 mL CH_2Cl_2
Pesticides	CH_2Cl_2	10 mL[1]	5 mL, hexane
OPP	CH_2Cl_2	10 mL	5 mL

[1] Final volume for GPC may be 4 mL if a 2 mL sample loop is used

Final volumes and exchange solvents if Florisil cleanup is used			
Type	Exchange Solvent for Florisil	Final Volume for Florisil	Final Volume and solvent for Analysis
Pesticides	Hexane	10 mL (2 mL aliquot used)	2 mL, hexane

Final volumes and exchange solvents if both GPC and Florisil cleanup are used					
Type	Exchange Solvent for GPC	Final Volume for GPC	Exchange Solvent for Florisil	Final Volume for Florisil	Final volume for analysis
Pesticides	Methylene Chloride	10 mL	Hexane	5 mL (2 mL aliquot used)	2 mL, hexane

Note: Different final volumes may be necessary to meet special client reporting limit requirements.

Note: If silica gel cleanup is performed, exchange solvent to cyclohexane prior to cleanup.

Table 3

Surrogate Spiking Solutions

Analyte Group	Surrogate Spike Solution ID	Volume (mL)
BNA	50/75 ppm BNA	1.0
Pest	0.2 ppm DCB/TCX	1.0
Pest/PCB	0.2 ppm DCB/TCX	1.0
PCB	0.2 ppm DCB/TCX	1.0

Table 4

Matrix Spike and LCS Solutions

Analyte Group	Matrix Spike Solution ID	Volume (mL)
BNA	50/75 ppm BNA	1.0
BNA TCLP	BNA TCLP Spike	1.0
BNA NPDES	BNA NPDES Spike	1.0
Pest	0.2/0.5 ppm Pest	1.0
Pest TCLP	Pest TCLP Spike	1.0
Pest NPDES	Pest NPDES Spike	1.0
Pest/PCB	0.5 ppm pest spike	1.0
PCB	10 ppm PCB Spike	1.0

Table 5
Surrogate Spike Components

Type	Compounds	Solvent	Conc. (µg/mL)
BNA	2-Fluorobiphenyl	Methanol	50
	Nitrobenzene-d5		50
	p-Terphenyl-d14		50
	2-Fluorophenol		75
	Phenol-d6		75
	2,4,6-Tribromophenol		75
	1,2-Dichlorobenzene-d4		50
	2-Chlorophenol-d4		75
Pest/PCB	Decachlorobiphenyl	Acetone	0.2
	Tetrachloro-m-xylene		0.2

Table 6
Matrix Spike Components

Type	Compounds	Solvent	Conc. (µg/mL)
TCL BNA	Acenaphthene	Methanol	50
	4-Chloro-3-Methylphenol		75
	2-Chlorophenol		75
	1,4-Dichlorobenzene		50
	2,4-Dinitrotoluene		50
	4-Nitrophenol		75
	N-Nitroso-Di-n-Propylamine		50
	Pentachlorophenol		75

Table 6

Matrix Spike Components

Type	Compounds	Solvent	Conc. (µg/mL)
	Phenol		75
	Pyrene		50
	1,2,4-Trichlorobenzene		50
BNA TCLP	1,4-Dichlorobenzene	Methanol	50
	2,4-Dinitrotoluene		50
	Hexachlorobenzene		50
	Hexachlorobutadiene		50
	Hexachloroethane		50
	2-Methylphenol		50
	3-Methylphenol		50
	4-Methylphenol		50
	Nitrobenzene		50
	Pentachlorophenol		50
	Pyridine		50
	2,4,5-Trichlorophenol		50
	2,4,6-Trichlorophenol		50
BNA NPDES		Methanol	
	Acenaphthene		50
	Acenaphthylene		50
	Anthracene		50
	Benzo(a)anthracene		50
	Benzo(b)fluoranthene		50
	Benzo(k)fluoranthene		50
	Benzo(a)pyrene		50

Table 6

Matrix Spike Components

Type	Compounds	Solvent	Conc. (µg/mL)
	Benzo(ghi)perylene		50
	Benzyl butyl phthalate		50
	Bis(2-chloroethyl)ether		50
	Bis(2-chloroethoxy)methane		50
	Bis(2-ethylhexyl)phthalate		50
	Bis(2-chloroisopropyl)ether		50
	4-Bromophenyl phenyl ether		50
	2-Chloronaphthalene		50
	4-Chlorophenyl phenyl ether		50
	Chrysene		50
	Dibenzo(a,h)anthracene		50
	Di-n-butylphthalate		50
	1,3-Dichlorobenzene		50
	1,2-Dichlorobenzene		50
	1,4-Dichlorobenzene		50
	3,3'-Dichlorobenzidine		50
	Diethyl phthalate		50
	Dimethyl phthalate		50
	2,4-Dinitrotoluene		50
	2,6-Dinitrotoluene		50
	Di-n-octylphthalate		50
	Fluoranthene		50
	Fluorene		50
	Hexachlorobenzene		50
	Hexachlorobutadiene		50

Table 6

Matrix Spike Components

Type	Compounds	Solvent	Conc. (µg/mL)
	Hexachloroethane		50
	Indeno(1,2,3-cd)pyrene		50
	Isophorone		50
	Naphthalene		50
	Nitrobenzene		50
	N-Nitrosodi-n-propylamine		50
	Phenanthrene		50
	Pyrene		50
	1,2,4-Trichlorobenzene		50
	4-Chloro-3-methylphenol		50
	2-Chlorophenol		50
	2,4-Dichlorophenol		50
	2,4-Dimethylphenol		50
	2,4-Dinitrophenol		50
	2-Methyl-4,6-dinitrophenol		50
	2-Nitrophenol		50
	4-Nitrophenol		50
	Pentachlorophenol		50
	Phenol		50
	2,4,6-Trichlorophenol		50
Pest	Aldrin	Acetone	0.2
	gamma-BHC (Lindane)		0.2
	4,4'-DDT		0.5
	Dieldrin		0.5

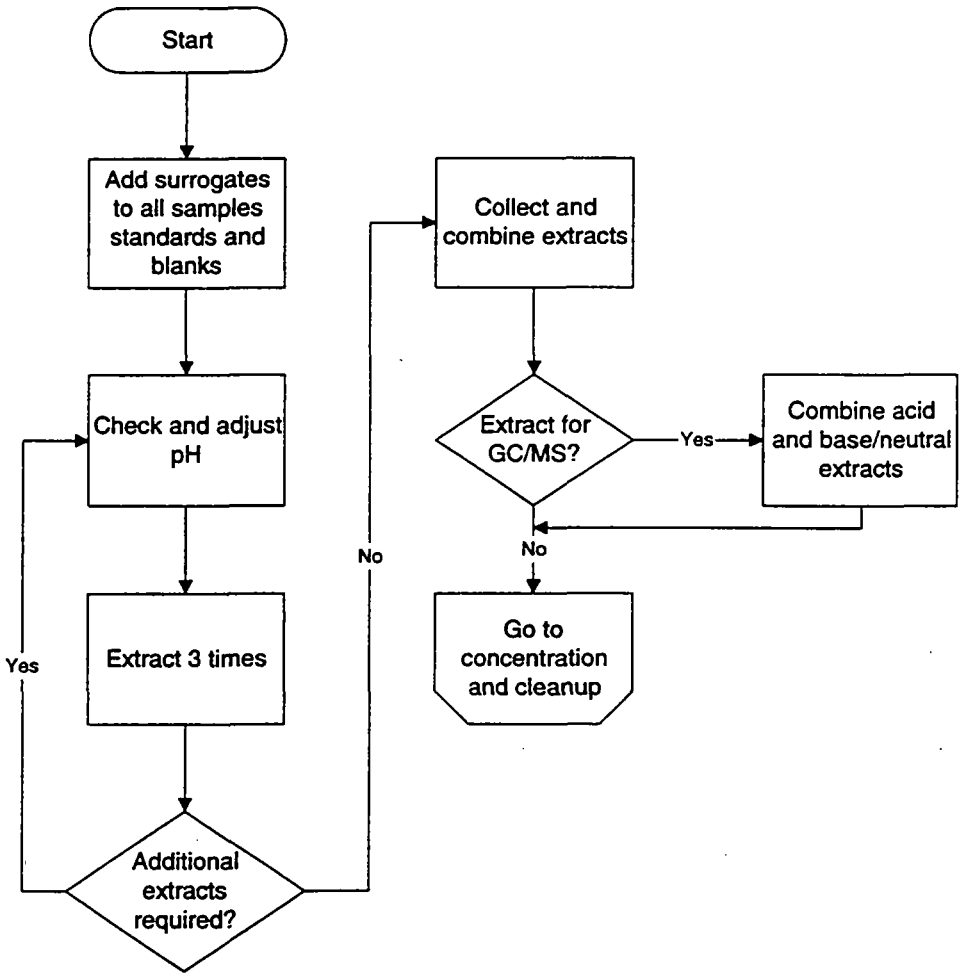
Table 6

Matrix Spike Components

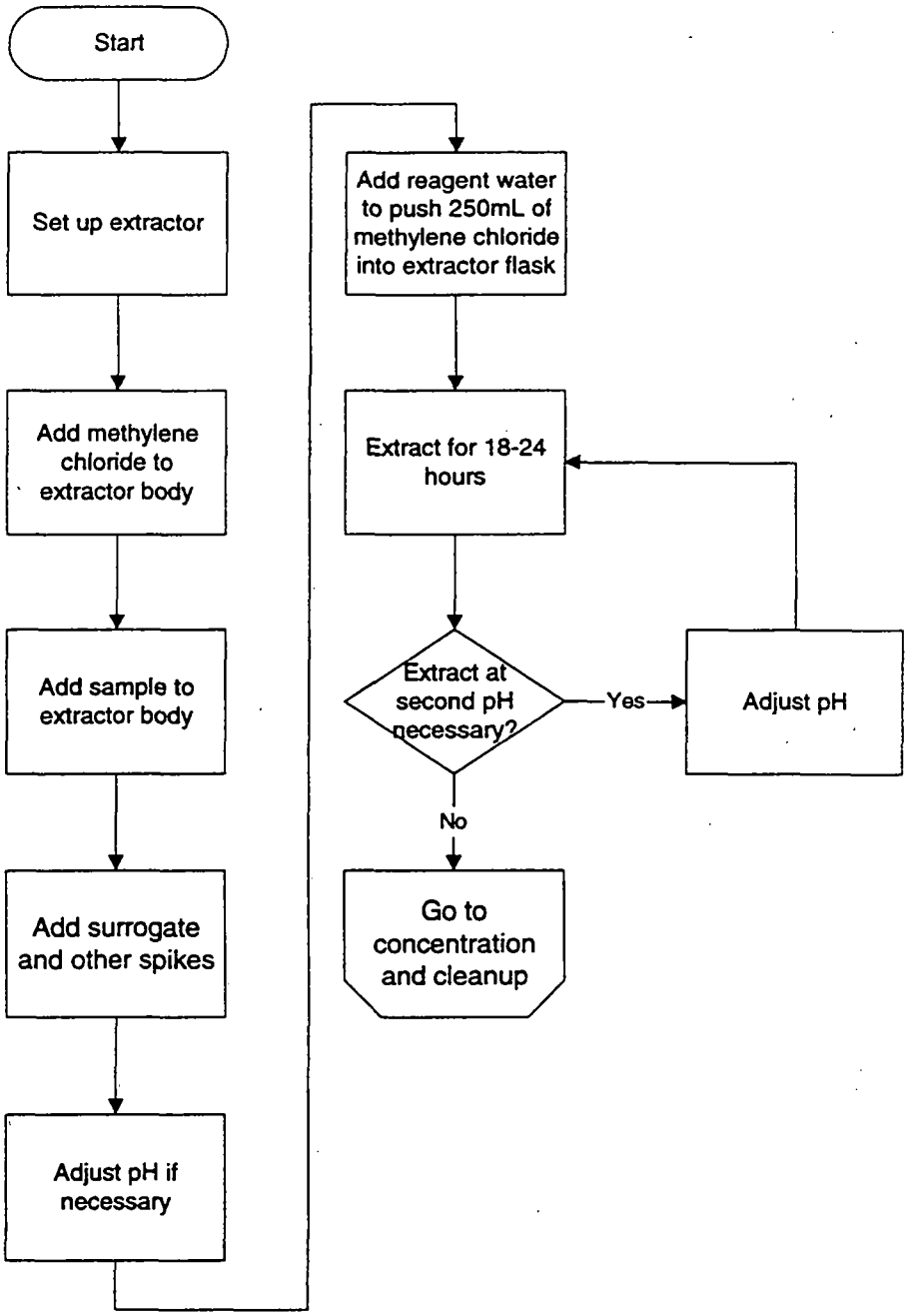
Type	Compounds	Solvent	Conc. (µg/mL)
	Endrin		0.5
	Heptachlor		0.2
Pest TCLP	Heptachlor	Acetone	0.5
	Heptachlor epoxide		0.5
	Lindane		0.5
	Endrin		0.5
	Methoxychlor		1.0
Pest NPDES	Aldrin	Acetone	0.2
	alpha-BHC		0.2
	beta-BHC		0.2
	delta-BHC		0.2
	gamma-BHC (Lindane)		0.2
	4,4'-DDD		1.0
	4,4'-DDE		0.2
	4,4'-DDT		1.0
	Dieldrin		0.2
	alpha-Endosulfan		0.2
	beta-Endosulfan		1.0
	Endosulfan Sulfate		1.0
	Endrin		1.0
	Heptachlor		0.2
	Heptachlor Epoxide		0.2
PCB only	PCB 1016/1260	Acetone	10

17.5 Flow diagrams

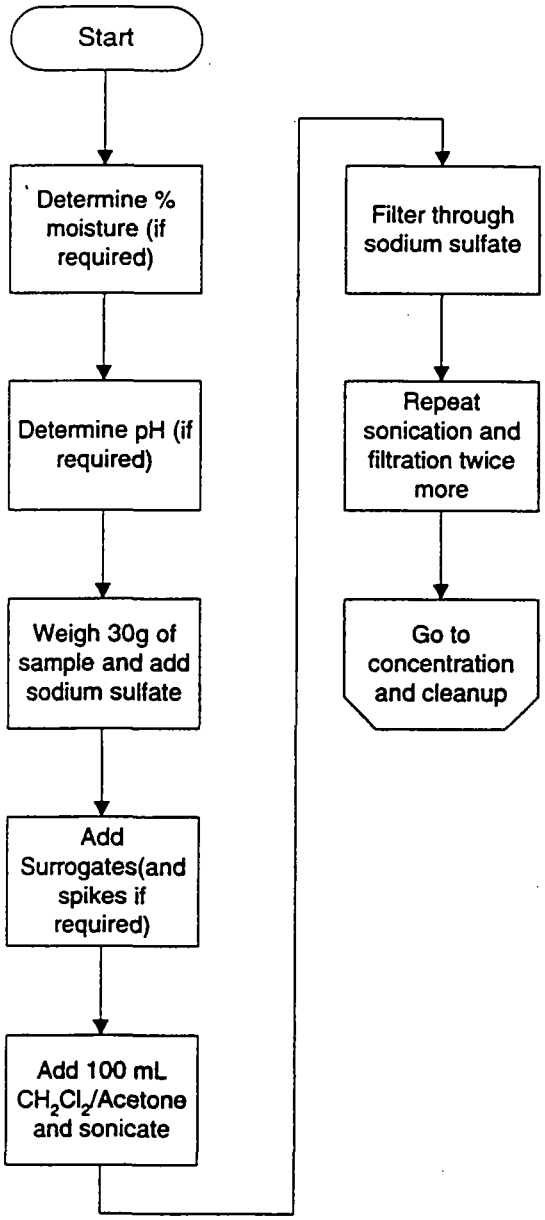
17.4.1. Separatory funnel extraction



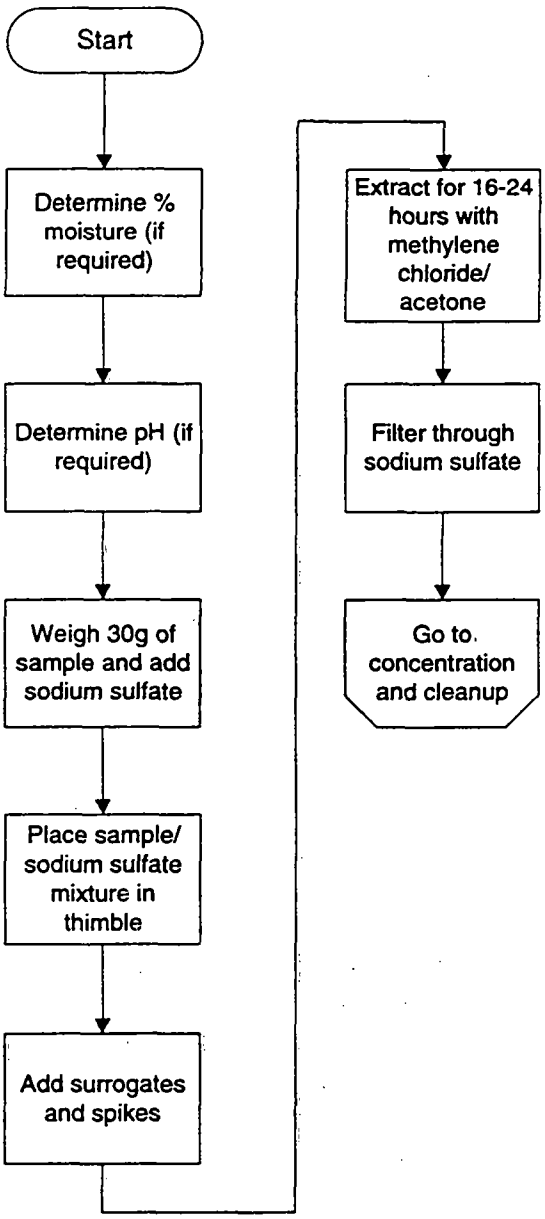
17.4.2. Continuous liquid/liquid extraction



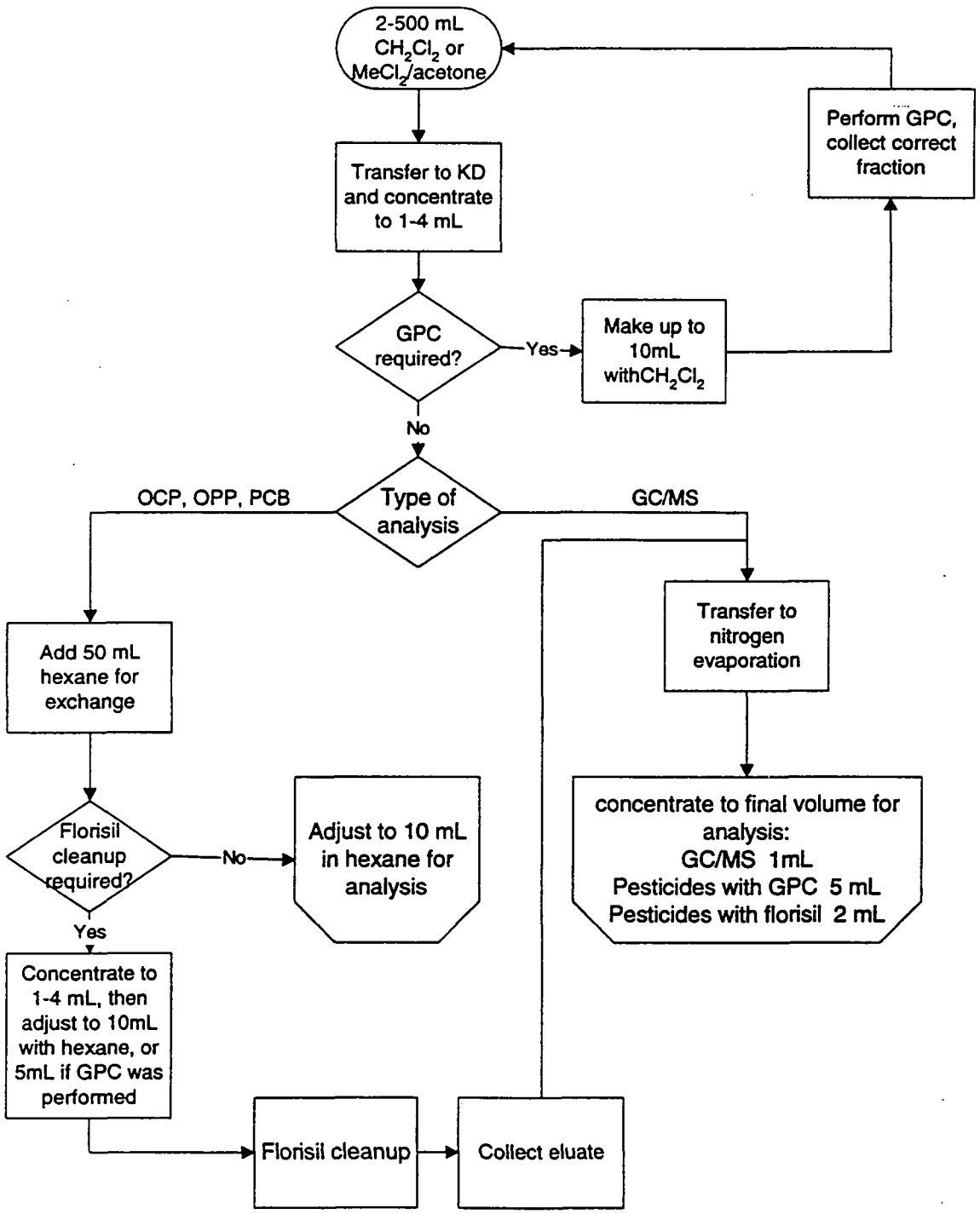
17.4.3. Sonication Extraction



17.4.4. Soxhlet extraction



17.4.5. Concentration and cleanup



QUANTERRA STANDARD OPERATING PROCEDURE

TITLE: GC/MS ANALYSIS BASED ON METHOD 8270B, SW-846

(SUPERSEDES: Revision 0)

Prepared by: Richard Burrows

Reviewed by: _____
Technology Standardization Committee

Approved by: _____
Director, Quality Assurance

Approved by: _____
Director, Environmental Health and Safety

Approved by: _____
Management

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1. SCOPE AND APPLICATION

1.1. This method is based upon SW846 8270B, 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 (SRL) 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.

2. SUMMARY OF METHOD

2.1. A measured amount of sample is serially extracted with methylene chloride using a separatory funnel, a continuous extractor, Accelerated One-Step™, or with methylene chloride / acetone using Soxhlet or sonication. Waste dilution is used for samples that are miscible with the solvent. The extract is dried, concentrated to a volume of 1 mL, and analyzed by GC/MS. Extraction procedures are detailed in SOP# CORP-OP-0001. 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. In some cases, at client request, the MS/MSD may be replaced with a matrix spike and sample duplicate. 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 Quanterra 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.

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. Procedures shall be carried out in a manner that protects the health and safety of all Quanterra associates. The following requirements must be met:

5.1.1. Eye protection that satisfies ANSI Z87.1 (as per the Chemical Hygiene Plan), 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.

5.1.2. The health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the MSDS files maintained in the laboratory. The following specific hazards are known:

5.1.2.1. 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. Primary standards should be purchaced in solution. If neat materials must be obtained, they shall be handled in a hood.

5.1.3. 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.

5.1.4. All work must be stopped in the event of a known or potential compromise to the health and safety of a Quanterra associate. The situation must be reported immediately to a laboratory supervisor.

6. EQUIPMENT AND SUPPLIES

6.1.1. 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.

6.1.2. Column: 30 m x 0.32 mm I.D. (or 0.25 mm I.D.) 0.5-µm 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.

6.1.3. 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 50 ng of the GC/MS tuning standard is injected through the GC.

6.1.4. GC/MS Interface: Any GC-to-MS interface that gives acceptable calibration points and achieves acceptable tuning performance criteria may be used.

6.1.5. 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.

6.2. Syringe: 10 µL Hamilton Laboratory grade syringes or equivalent. A selection of syringe sizes should be on hand so that the minimum volume dispensed is never less than 10% of total syringe volume (i.e., 10 mL syringe for 1 mL measured volume).

6.3. Carrier gas: Ultra high purity helium.

7. REAGENTS AND STANDARDS

7.1. A minimum five point calibration curve is prepared at nominal concentrations of 10, 25, 40, 60 and 80 µg/mL for each parameter of interest. Some compounds are prepared at higher levels due to chromatographic performance, stability, and sensitivity. Refer to Tables 12 and 13 for calibration levels for all analytes.

7.2. A 400 µg/mL Internal Standard solution is prepared. Compounds in the I.S. Mix are: acenaphthene-d10, chrysene-d12, 1,4-dichlorobenzene-d4, naphthalene-d8, perylene-d12, and phenanthrene-d10

7.2.1. Internal Standards are added to all standards and extracts at 20 µg per mL of extract. For example, if the volume of an extract used was 200 µL, 10 µL of the 400 µg/mL internal standard solution would be added.

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 25 µg/mL of decafluorotriphenylphosphine (DFTPP) is prepared. Pentachlorophenol, benzidine, and DDT, should also be included in the Tuning Standard at 25 µg/mL.

7.5. Laboratory Control Spiking Solution: Prepare as indicated in the preparative methods. See appropriate preparation SOP. LCS compounds and levels are listed in Tables 9 and 10.

7.6. Matrix Spike Solution: Prepare as indicated in the preparative methods. See preparation SOP. The matrix spike compounds and levels are the same as the LCS compounds.

7.7. The working standards listed in 7.1 to 7.6 should be refrigerated at 4 ± 2°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. The continuing calibration standard must be replaced every week and is stored at 4 ± 2°C.

8. SAMPLE PRESERVATION AND STORAGE

8.1. Reference appropriate facility SOP for sample bottle preservation and storage.

8.2. Samples are stored at 4 ± 2°C. Samples and extracts should be stored in suitable glass containers with Teflon lined caps. (Extracts will normally 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. Refer to the flow chart in section 17.4.1.

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 at least annually. The recovery limits are mean recovery +/- 3 standard deviations for surrogates and LCS, and mean recovery +/- 2 standard deviations for matrix spikes. Precision limits for matrix spikes / matrix spike duplicates are mean relative percent difference +/- 2 standard deviations.

9.2.1. These limits do not apply to dilutions (except for tests without a separate extraction), but surrogate and matrix spike recoveries will be reported unless the dilution is more than 5X.

9.2.2. All surrogate, LCS, and MS recoveries (except for dilutions) must be entered into QuantIMS (when available) or other database so that accurate historical control limits can be generated. For tests without a separate extraction, surrogates and matrix spikes will be reported for all dilutions.

9.2.3. Refer to the QC program document (QA-003) for further details of control limits.

9.3. Method Blank

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-0001 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 laboratory contaminants, see below) or at or above 5% of the measured concentration of that analyte in the associated samples, whichever is higher.

- 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.

- Reanalysis of all samples associated with an unacceptable method blank is required when concentrations above the reporting limit 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. Such action should be taken in consultation with the client.

9.3.1. 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.

9.3.2. 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.

9.3.3. Refer to the Quanterra QC Program document (QA-003) for further details of the corrective actions.

9.3.4. Sample results are NOT blank subtracted unless specific requests and arrangements have been made with a client or agency.

9.4. Instrument Blank

9.4.1. Instruments must be evaluated for contamination during each 12 hour analytical run. This may be accomplished by analysis of a method blank. If a method blank is not available, an instrument blank must be analyzed. An instrument blank consists of methylene chloride with the internal standards added. It is evaluated in the same way as the method blank.

9.5. Laboratory Control Sample (LCS)

9.5.1. A laboratory control sample (LCS) is prepared and analyzed with every batch of samples. All 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. The compounds must be spiked at a concentration equivalent to 100 or 150 ng on-column depending on the analyte.

9.5.2. If any 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.

- 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).

- 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.

9.5.3. Ongoing monitoring of the LCS provides evidence that the laboratory is performing the method within accepted QC guidelines for accuracy and precision.

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

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.

- 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 repreparation and 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.

9.7. Surrogates

9.7.1. 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. Surrogate compounds must be spiked at either 100 or 150 ng on-column, depending on the surrogate. The compounds routinely included in the surrogate spiking solution, along with recommended standard concentrations, are listed in Table 11.

9.7.2. 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 the extract if either of the above checks reveal a problem.
- Reprepare and reanalyze the sample or flag the data as "Estimated Concentration" if neither of the above resolves the problem.

The decision to reanalyze or flag the data should be made in consultation with the client. 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.

9.7.3. 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.

9.7.4. 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.)

9.7.5. If the reanalysis does confirm the original results, the original analysis is reported and the data flagged as estimated due to matrix effect.

9.8. Nonconformance and Corrective Action

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

9.9. Quality Assurance Summaries

Certain clients may require specific project or program QC which may supersede these method requirements. Quality Assurance Summaries should be developed to address these requirements.

9.10. Quanterra QC Program

Further details of QC and corrective action guidelines are presented in the Quanterra QC Program document (QA-003). Refer to this document if in doubt regarding corrective actions.

10. CALIBRATION AND STANDARDIZATION

10.1. Summary

10.1.1. The instrument is tuned for DFTPP, calibrated initially with a 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

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).

10.3.1. Inject 50 ng of the GC/MS tuning standard (Section 7.4) into the GC/MS system. (2µL of the 25µg/mL solution). 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.

10.3.2. The GC/MS tuning standard should also be used to evaluate the inertness of the chromatographic system. Benzidine and pentachlorophenol should not exhibit

excessive tailing. 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. Add the internal standard mixture at 20 µg per mL of calibration standard. (For example, if the volume of the calibration standard used is 1 mL, add 50 µL of the 400 µg/mL internal standard solution). The working range of the GC/MS system is defined by calibration standards at concentrations of 10 to 80 µg/mL. The exact concentrations of all analytes are listed in tables 12 and 13.

10.4.4. Using injections of 2 µL, 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 section 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. Otherwise, all compounds must meet the 20% criterion.

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 %RSD of $\geq$ 80% of the analytes in the calibration is $\leq$ 15%, then all analytes may use average response factor for calibration.

10.4.7.1. If the software in use is capable of routinely reporting curve coefficients for data valivation purposes, and the necessary calibration reports can be generated, then the analyst should evaluate analytes with %RSD > 15% for calibration on a curve. If if appears that substantially better accuracy would be obtained using quantitation from a curve (e.g. R^2 >0.995) then the appropriate curve should be used for quantitation.

10.4.7.2. If less than 80% of the analytes in the calibration have %RSD $\leq$ 15%, then calibration on a curve must be used for all analytes with %RSD > 15%. The analyst should consider instrument maintenance to improve the linearity of response.

10.4.8. Weighting of data points

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.

10.4.9. 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.

10.4.10. Quantitation is performed using the calibration curve or average response factor form the initial curve, not the continuing calibration.

10.5. Continuing Calibration

10.5.1. At the start of each 12-hour period, the GC/MS tuning standard must be analyzed. A 50 ng injection of DFTPP must result in a mass spectrum for DFTPP which meets the criteria given in Table 6.

10.5.2. Following a successful DFTPP analysis the continuing calibration standard(s) are analyzed. The standards must contain all semivolatile analytes, including all required surrogates. The level 2 calibration standard is used for the continuing calibration.

10.5.3. The following criteria must be met for the continuing calibration to be acceptable:

- The SPCC compounds must have a response factor of ≥ 0.05.
- The percent drift of the CCC compounds from the initial calibration must be $\leq$ 20%. (see section 12 for calculations) In addition, the percent drift of all analytes must be $\leq$ 50%, with allowance being made for up to six target compounds to have percent drift greater than 50%.

10.5.3.1. If none of the CCCs are required analytes, project specific calibration specifications must be agreed with the client. Otherwise, all CCCs must meet the 20% criterion.

10.5.4. 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

Samples are prepared following SOP CORP-OP-0001.

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 preceeding continuing calibration standard.

11.2.3. Add internal standard at 20 µg per mL of extract (for example, 25 µL internal standard solution in 0.5 mL of extract) to the sample extract and mix thoroughly before injection into the instrument.

11.2.4. Inject 2 µL of 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.

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 12.3.

11.3. Dilutions

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

If the sample is initially run at a dilution and the baseline rise is less than the height of the internal standards, the sample should be reanalyzed at a more concentrated dilution.

11.3.2. Reporting Dilutions

The most concentrated dilution with no target compounds above the calibration range will be reported. Other dilutions will only be reported at client request.

11.4. 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. Internal Standard Criteria for Samples

Internal standard response in each sample should be within 50% to 200% of the response in the preceding continuing calibration standard.

11.5.1. Any samples that do not meet the internal standard criteria must be evaluated for validity. If the change in sensitivity is a matrix effect confined to an individual sample reanalysis may not be necessary. If the change in sensitivity is due to instrumental problems all affected samples must be reanalyzed after the problem is corrected. In any event, the reason for accepting the sample analysis must be documented. Some clients may require reanalysis of all samples with internal standard criteria outside the 50-200% criteria. Consideration should be given to reanalyzing at a dilution to reduce matrix effects. It is only necessary to reanalyze once to confirm matrix effect.

11.6. Retention time criteria for samples

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.

11.6.1. If the retention time of any internal standard in any sample varies by more than 0.1 minute from the preceeding continuing calibration standard, the data must be carefully evaluated to ensure that no analytes have shifted outside their retention time windows.

11.7. Percent Moisture

Analytical results may be reported as dry or wet weight, as required by the client. Percent moisture must be determined if results will be reported as dry weight. Refer to the facility specific SOP for determination of percent moisture.

11.8. Procedural Variations

11.8.1. 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 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. Any unauthorized deviations from this procedure must also be documented as a non-conformance, with a cause and corrective action described.

11.9. Troubleshooting Guide

11.9.1. Daily Instrument Maintenance

In addition to the checks listed in the instrument maintenance schedule in the Quanterra QAMP, the following daily maintenance should be performed.

11.9.1.1. Clip Column as necessary.

11.9.1.2. Install new or cleaned injection port liner as necessary.

11.9.1.3. Install new septum as necessary.

11.9.1.4. Perform mass calibration as necessary.

11.9.2. Major Maintenance

11.9.2.1. If minor maintenance does not result in acceptable chromatography, it may be necessary to change the column.

11.9.2.2. Clean ion volume or repeller. Cleaning is indicated when DFTPP does not pass spectral criteria.

11.9.2.3. Clean source. If after cleaning ion volume or repeller, tune still does not meet criteria, or if overall sensitivity is poor, the source is removed and cleaned.

11.9.2.4. Replace filaments, replace filters and change pump oil. All of these may be done at the same time as source cleaning. The frequency of changing filters and pump oil is about every 6-12 months.

11.9.2.5. A multiplier gain check is performed if sensitivity is still poor and/or analyst suspects that the multiplier is going bad.

11.9.2.6. Mass calibration is performed if the analyst notices mass misassignments.

11.9.2.7. Refer to the manufacturer's manual for specific guidance.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Qualitative identification

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 libary. 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.

- 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.

- The characteristic ions of a compound must maximize in the same scan or within one scan of each other.

- 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%.)

12.1.1. 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.

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. Hexachlorophene

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:

- Relative intensities of major ions in the reference spectrum (ions >10% of the most abundant ion) should be present in the sample spectrum.

- 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%.)

- Molecular ions present in the reference spectrum should be present in the sample spectrum.

- Ions present in the sample spectrum, but not in the reference spectrum, should be reviewed for possible background contamination or presence of coeluting compounds.

- Ions present in the reference spectrum, but not in the sample spectrum, should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks. Data system library reduction programs can sometimes create these discrepancies.

- Automatic background subtraction can severely distort spectra from samples with unresolved hydrocarbons.

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

$$\% \text{ RSD} = \frac{SD}{\overline{RF}} \times 100$$

$\overline{RF}$ = Mean of RFs from initial calibration for a compound

SD = Standard deviation of RFs from initial calibration for a compound,

$$SD = \sqrt{\sum_{i=1}^{N} \frac{\left(RF_i - \overline{RF}\right)^2}{N-1}}$$

RF_i = RF for each of the calibration levels

N = Number of RF values

12.5.2. Continuing calibration percent drift

$$\% \text{ Drift} = \frac{C_{expected} - C_{found}}{C_{expected}} \times 100$$

$C_{expected}$ = 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. 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

R_{is} = Response for internal standard

C_{is} = Concentration of internal standard

A = Intercept

B = Slope

12.5.3.2. Quadratic fit

$$C_{ex} = A + B\left(\frac{R_x C_{is}}{R_{is}}\right) + C\left(\frac{R_x C_{is}}{R_{is}}\right)^2$$

Where: C = Curvature

12.5.3.3. Average response factor

Alternatively, if the %RSD the response factors of at least 80% of the analytes in the initial calibration is ≤ 15%, the average response factor from the initial calibration may be used.

$$C_{ex} = \frac{R_x C_{is}}{R_{is}\overline{RF}}$$

Where: $\overline{RF}$ = Average response factor

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 1 for a wet weight basis

12.6. MS/MSD percent recovery calculation.

$$\text{Matrix Spike recovery} = \frac{SSR - SR}{SA} \times 100$$

Where:

SSR = Spike sample result

SR = Sample result

SA = Spike added

12.7. Relative % Difference calculation for the MS/MSD

$$RPD = \frac{|MSR - MSDR|}{\frac{1}{2}(MSR + MSDR)} \times 100$$

Where:

RPD = Relative percent difference

MSR = Matrix spike result

MSDR = 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

$$\% \text{ DDT breakdown} = \frac{\text{DDE area} + \text{DDD area}}{\text{DDT area} + \text{DDE area} + \text{DDD area}} \times 100$$

The total ion current areas are used for this calculation

13. METHOD PERFORMANCE

13.1. Method Detection Limit

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 #: QA-005.

13.2. Initial Demonstration

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. Four aliquots of the QC check sample are analyzed using the same procedures used to analyze samples, including sample preparation. The concentration of the QC check sample should be equivalent to the level 4 calibration standard.

13.2.2. Calculate the average recovery and standard deviation of the recovery for each analyte of interest. Compare these results with the acceptance criteria given in table 14.

13.2.3. 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

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

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.

13.5. Data Quality Objectives (DQO). Refer to project-specific Quality Assurance plans for DQO information.

14. POLLUTION PREVENTION

14.1. This section is not applicable to this procedure.

15. WASTE MANAGEMENT

15.1. Waste generated during aliquotting and from used vials must be disposed of in accordance with the facility hazardous waste procedures. The Health and Safety Director should be contacted if additional information is required.

16. REFERENCES

16.1. SW846, Test Methods for Evaluating Solid Waste, Third Edition, Update II, October 1994, Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS): Capillary Column Technique, Method 8270B.

16.2. 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)

17. MISCELLANEOUS

17.1. Modifications from Reference Method

17.1.1. Spike concentrations and Injection Volume

As allowed in section 7.3 of the reference method, a 2 µL injection volume is used. Some of the recommended spike concentrations in the reference method have been changed to bring them within the calibration range of the instrument.

17.1.2. The concentration of the internal standard spiking solution is more dilute than that recommended in the reference method. This eliminates the risk of precipitation of the internal standards from solution when the standard is stored in the freezer, and also allows more accurate internal standard addition to small volumes of extract.

17.1.3. The internal standard control criteria of 50% to 200% is applied to each sample, rather than the subsequent continuing calibration standard as listed in the reference method. This is a more rigorous criterion than that in the reference method.

17.1.4. 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.

17.1.5. 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.

17.1.6. SW-846 recommends that a curve be used for any analytes with %RSD of the response factors > 15%. However, some industry standard data systems and forms generation software cannot report this data with the necessary information for data validation. In addition most software available does not allow weighting of the curve. Unweighted curves may exibit serious errors in quantitation at the low end, resulting in possible false positives or false negatives. Therefore, this SOP allows used of average response factors in 80% of the analytes have %RSDs ≤ 15%.

17.2. Modifications from Previous Revision

17.2.1. The list of reportable analytes in Tables 3 and 4 have been changed.

17.2.2. Secondary ions for phorate, phenacitin and methapyriline in Table 8 have been corrected.

17.2.3. 1,4-Dichlorobenzene and hexachlorobenzene have been added to Table 10.

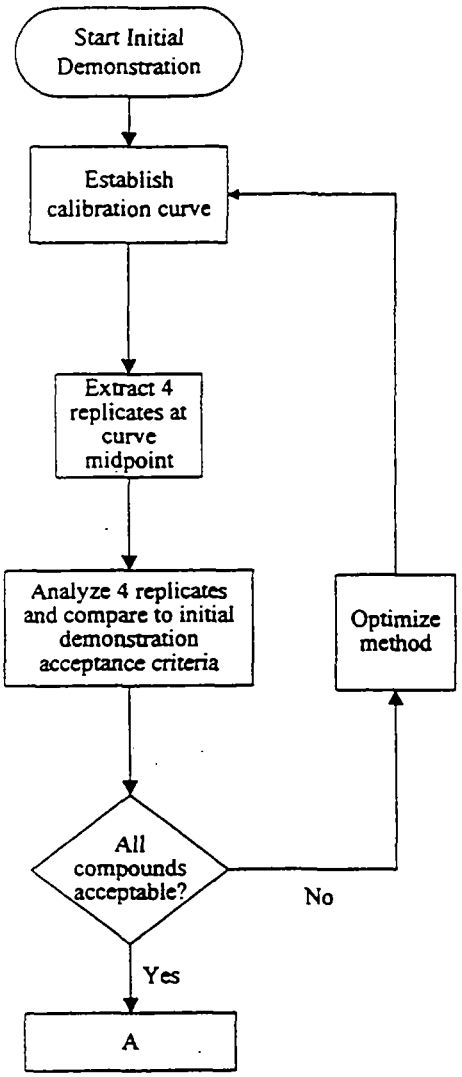
17.2.4. Use of average response factor calibration is allowed if 80% of the analytes have %RSD ≤ 15%.

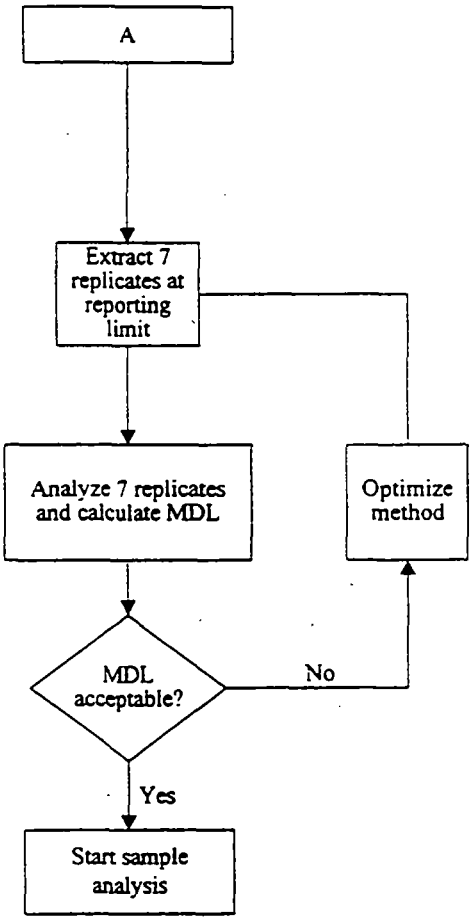
17.3. Facility Specific SOPs

Each facility shall attach a list of facility specific SOPs or approved attachments (if applicable) which are required to implement this SOP or which are used in conjunction with this SOP. If no facility specific SOPs or amendments are to be attached, a statement must be attached specifying that there are none.

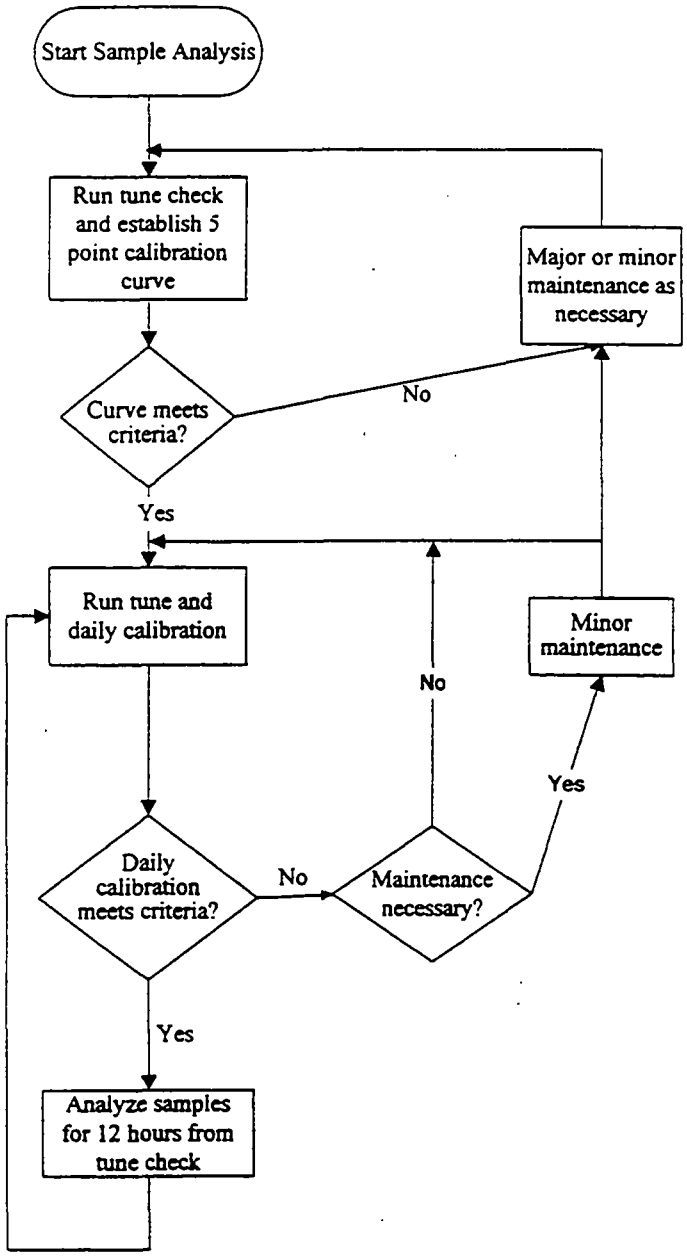
17.4. Flow Diagrams

17.4.1. Initial demonstration and MDL





17.4.2. Sample Analysis[1]



[1] This flow diagram is for guidance and cannot cover all eventualities. Consult the SOP text and a supervisor if in doubt.

17.5. Tables

Table 1

Quanterra Primary Standard[1] and Standard Reporting Limits

Analytes	CAS Number	Standard Reporting Limits	
		Aqueous µg/L	Low Soil/Sediment µg/kg
Pyridine	110-86-1	20	660
N-nitrosodimethylamine	62-75-9	10	330
Aniline	62-53-3	10	330
Phenol	108-95-2	10	330
Bis(2-chloroethyl)ether	111-44-4	10	330
2-Chlorophenol	95-57-8	10	330
1,3-Dichlorobenzene	541-73-1	10	330
1,4-Dichlorobenzene	106-46-7	10	330
Benzyl alcohol	100-51-6	10	330
1,2-Dichlorobenzene	95-50-1	10	330
2-Methylphenol	95-48-7	10	330
2,2'-oxybis(1-chloropropane)[2]	108-60-1	10	330
4-Methylphenol	106-44-5	10	330
N-Nitroso-di-n-propylamine	621-64-7	10	330
Hexachloroethane	67-72-1	10	330
Nitrobenzene	98-95-3	10	330
Isophorone	78-59-1	10	330
2-Nitrophenol	88-75-5	10	330
2,4-Dimethylphenol	105-67-9	10	330
Benzoic acid	65-85-0	50	1600
Bis(2-chloroethoxy)methane	111-91-1	10	330
2,4-Dichlorophenol	120-83-2	10	330
1,2,4-Trichlorobenzene	120-82-1	10	330
Naphthalene	91-20-3	10	330
4-Chloroaniline	106-47-8	10	330
Hexachlorobutadiene	87-68-3	10	330
4-Chloro-3-methylphenol	59-50-7	10	330
2-Methylnaphthalene	91-57-6	10	330
Hexachlorocyclopentadiene	77-47-4	50	1600
2,4,6-Trichlorophenol	88-06-2	10	330
2,4,5-Trichlorophenol	95-95-4	10	330
2-Chloronaphthalene	91-58-7	10	330
2-Nitroaniline	88-74-4	50	1600
Dimethyl phthalate	131-11-3	10	330
Acenaphthylene	208-96-8	10	330
3-Nitroaniline	99-09-2	50	1600
Acenaphthene	83-32-9	10	330
2,4-Dinitrophenol	51-28-5	50	1600
4-Nitrophenol	100-02-7	50	1600

Table 1

Quanterra Primary Standard[1] and Standard Reporting Limits

Analytes	CAS Number	Standard Reporting Limits	
		Aqueous µg/L	Low Soil/Sediment µg/kg
Dibenzofuran	132-64-9	10	330
2,4-Dinitrotoluene	121-14-2	10	330
2,6-Dinitrotoluene	606-20-2	10	330
Diethylphthalate	84-66-2	10	330
4-Chlorophenyl phenyl ether	7005-72-3	10	330
Fluorene	86-73-7	10	330
4-Nitroaniline	100-01-6	50	1600
4,6-Dinitro-2-methylphenol	534-52-1	50	1600
N-Nitrosodiphenylamine	86-30-6	10	330
Azobenzene	103-33-3	10	330
4-Bromophenyl phenyl ether	101-55-3	10	330
Hexachlorobenzene	118-74-1	10	330
Pentachlorophenol	87-86-5	50	1600
Phenanthrene	85-01-8	10	330
Anthracene	120-12-7	10	330
Carbazole	86-74-8	10	330
Di-n-butyl phthalate	84-74-2	10	330
Fluoranthene	206-44-0	10	330
Benzidine	92-87-5	100	3300
Pyrene	129-00-0	10	330
Butyl benzyl phthalate	85-68-7	10	330
3,3'-Dichlorobenzidine	91-94-1	50	1600
Benzo(a)anthracene	56-55-3	10	330
Bis(2-ethylhexyl)phthalate	117-81-7	10	330
Chrysene	218-01-9	10	330
Di-n-octylphthalate	117-84-0	10	330
Benzo(b)fluoranthene	205-99-2	10	330
Benzo(k)fluoranthene	207-08-9	10	330
Benzo(a)pyrene	50-32-8	10	330
Indeno(1,2,3-cd)pyrene	193-39-5	10	330
Dibenz(a,h)anthracene	53-70-3	10	330
Benzo(g,h,i)perylene	191-24-2	10	330

[1] The Quanterra primary standard is the standard normally used at Quanterra. Additional standards, such as the Appendix IX standard may be necessary to include all target analytes required for some clients.

[2] 2,2'oxybis(1-chloropropane) was formally known as bis(2-chloroisopropyl)ether

Table 2

Quanterra Appendix IX[1] Standard Reporting Limits

Semivolatiles	CAS Number	Standard Reporting Limits	
		Aqueous µg/L	Low Soil/Sediment µg/kg
2-Picoline	109-06-8	20	660
N-Nitrosomethylethylamine	10595-95-6	10	330
Methyl methanesulfonate	66-27-3	10	330
N-Nitrosodiethylamine	55-18-5	10	330
Ethyl methanesulfonate	62-50-0	10	330
Pentachloroethane	76-01-7	50	1600
Acetophenone	98-86-2	10	330
N-Nitrosopyrrolidine	930-55-2	10	330
N-Nitrosomorpholine	59-89-2	10	330
o-Toluidine	95-53-4	20	660
3-Methylphenol	108-39-4	10	330
N-Nitrosopiperidine	100-75-4	10	330
o,o,o-Triethyl-Phosphorothioate[2]	126-68-1	50	1600
a,a-Dimethyl-phenethylamine	122-09-8	50	1600
2,6-Dichlorophenol	87-65-0	10	330
Hexachloropropene	1888-71-7	100	3300
p-Phenylenediamine	106-50-3	100	3300
n-Nitrosodi-n-butylamine	924-16-3	10	330
Safrole	94-59-7	20	660
1,2,4,5-Tetrachlorobenzene	95-94-3	10	330
Isosafrole	120-58-1	20	660
1,4-Dinitrobenzene	100-25-4	10	330
1,4-Naphthoquinone	130-15-4	50	1600
1,3-Dinitrobenzene	99-65-0	10	330
Pentachlorobenzene	608-93-5	10	330
1-Naphthylamine	134-32-7	10	330
2-Naphthylamine	91-59-8	10	330
2,3,4,6-Tetrachlorophenol	58-90-2	50	1600
5-Nitro-o-toluidine	99-55-8	20	660
Thionazin[2]	297-97-2	50	1600
1,3,5-Trinitrobenzene	99-35-4	50	1600
Sulfotepp[2]	3689-24-5	50	1600
Phorate[2]	298-02-2	50	1600
Phenacetin	62-44-2	20	660
Diallate[3]	2303-16-4	20	660
Dimethoate[2]	60-51-5	20	660
4-Aminobiphenyl	92-67-1	50	1600
Pentachloronitrobenzene	82-68-8	50	1600
Pronamide	23950-58-5	20	660
Disulfoton[2]	298-04-4	50	1600
2-secbutyl-4,6-dinitrophenol (Dinoseb)	88-85-7	20	660
Methyl Parathion[2]	298-00-0	50	1600

Table 2

Quanterra Appendix IX[1] Standard Reporting Limits

Semivolatiles	CAS Number	Standard Reporting Limits	
		Aqueous µg/L	Low Soil/Sediment µg/kg
4-Nitroquinoline-1-oxide	56-57-5	100	3300
Parathion[2]	56-38-2	50	1600
Methapyrilene	91-80-5	50	1600
Aramite	140-57-8	20	660
Isodrin[3]	465-73-6	10	330
Kepone[2]	143-50-0	100	3300
Famphur[3]	52-85-7	100	3300
p-(Dimethylamino)azobenzene	60-11-7	20	660
p-Chlorobenzilate[3]	510-15-6	10	330
3,3'-Dimethylbenzidine	119-93-7	50	1600
2-Acetylaminofluorene	53-96-3	100	3300
Dibenz(a,j)acridine	224-42-0	20	660
7,12-Dimethylbenz(a)anthracene	57-97-6	20	660
3-Methylcholanthrene	56-49-5	20	660

1 The Appendix IX standard contains additional analytes required for the Appendix IX list. The Quanterra primary standard must also be analyzed to include all of the Appendix IX list.

2 May also be analyzed by method 8140 or 8141, which can acheive lower reporting limits.

3 May also be analyzed by method 8080 or 8081, which can achieve lower reporting limits

Table 3

Reportable Analytes for Quanterra Standard Tests, Primary Standard

Analyte	CAS Number	Quanterra Standard List	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	X
Bis(2-chloroethyl)ether	111-44-4	X		X	X
2-Chlorophenol	95-57-8	X		X	X
1,3-Dichlorobenzene	541-73-1	X		X	X
1,4-Dichlorobenzene	106-46-7	X	X	X	X
Benzyl alcohol	100-51-6				X
1,2-Dichlorobenzene	95-50-1	X		X	X
2-Methylphenol	95-48-7	X	X	X	X
2,2'-oxybis(1-chloropropane)[1]	180-60-1	X		X	X
4-Methylphenol	106-44-5	X	X	X	X
N-Nitroso-di-n-propylamine	621-64-7	X		X	X
Hexachloroethane	67-72-1	X	X	X	X
Nitrobenzene	98-95-3	X	X	X	X
Isophorone	78-59-1	X		X	X
2-Nitrophenol	88-75-5	X		X	X
2,4-Dimethylphenol	105-67-9	X		X	X
Benzoic acid	65-85-0				
Bis(2-chloroethoxy)methane	111-91-1	X		X	X
2,4-Dichlorophenol	120-83-2	X		X	X
1,2,4-Trichlorobenzene	120-82-1	X		X	X
Naphthalene	91-20-3	X		X	X
4-Chloroaniline	106-47-8	X		X	X
Hexachlorobutadiene	87-68-3	X	X	X	X
4-Chloro-3-methylphenol	59-50-7	X		X	X
2-Methylnaphthalene	91-57-6	X		X	X
Hexachlorocyclopentadiene	77-47-4	X		X	X
2,4,6-Trichlorophenol	88-06-2	X	X	X	X
2,4,5-Trichlorophenol	95-95-4	X	X	X	X
2-Chloronaphthalene	91-58-7	X		X	X
2-Nitroaniline	88-74-4	X		X	X
Dimethyl phthalate	131-11-3	X		X	X
Acenaphthylene	208-96-8	X		X	X
3-Nitroaniline	99-09-2	X		X	X
Acenaphthene	83-32-9	X		X	X
2,4-Dinitrophenol	51-28-5	X		X	X
4-Nitrophenol	100-02-7	X		X	X
Dibenzofuran	132-64-9	X		X	X
2,4-Dinitrotoluene	121-14-2	X	X	X	X
2,6-Dinitrotoluene	606-20-2	X		X	X
Diethylphthalate	84-66-2	X		X	X

Table 3

Reportable Analytes for Quanterra Standard Tests, Primary Standard

Analyte	CAS Number	Quanterra Standard List	TCLP	TCL	Appendix IX
4-Chlorophenyl phenyl ether	7005-72-3	X		X	X
Fluorene	86-73-7	X		X	X
4-Nitroaniline	100-01-6	X		X	X
4,6-Dinitro-2-methylphenol	534-52-1	X		X	X
N-Nitrosodiphenylamine	86-30-6	X		X	X
Azobenzene[4]	103-33-3				
4-Bromophenyl phenyl ether	101-55-3	X		X	X
Hexachlorobenzene	118-74-1	X	X	X	X
Pentachlorophenol	87-86-5	X	X	X	X
Phenanthrene	85-01-8	X		X	X
Anthracene	120-12-7	X		X	X
Carbazole	86-74-8	X		X	
Di-n-butyl phthalate	84-74-2	X		X	X
Fluoranthene	206-44-0	X		X	X
Benzidine	92-87-5				
Pyrene	129-00-0	X		X	X
Butyl benzyl phthalate	85-68-7	X		X	X
3,3'-Dichlorobenzidine	91-94-1	X		X	X
Benzo(a)anthracene	56-55-3	X		X	X
Bis(2-ethylhexyl)phthalate	117-81-7	X		X	X
Chrysene	218-01-9	X		X	X
Di-n-octylphthalate	117-84-0	X		X	X
Benzo(b)fluoranthene	205-99-2	X		X	X
Benzo(k)fluoranthene	207-08-9	X		X	X
Benzo(a)pyrene	50-32-8	X		X	X
Indeno(1,2,3-cd)pyrene	193-39-5	X		X	X
Dibenz(a,h)anthracene	53-70-3	X		X	X
Benzo(g,h,i)perylene	191-24-2	X		X	X

[1] 2,2'oxybis(1-chloropropane) was formally known as bis(2-chloroisopropyl)ether

[2] Azobenzene is formed by decomposition of 1,2-diphenlyhydrazine. If 1,2-diphenylhydrazine is requested, it will be analyzed as azobenzene.

Table 4

Reportable analytes for Quanterra Standard Tests, Appendix IX Standard

Semivolatiles	CAS Number	Quanterra Standard List	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
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[2]	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				
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[2]	297-97-2				X
1,3,5-Trinitrobenzene	99-35-4				X
Sulfotepp[2]	3689-24-5				X
Phorate[2]	298-02-2				X
Phenacetin	62-44-2				X
Diallate	2303-16-4				X
Dimethoate[2]	60-51-5				X
4-Aminobiphenyl	92-67-1				X
Pentachloronitrobenzene	82-68-8				X
Pronamide	23950-58-5				X
Disulfoton[2]	298-04-4				X
2-secbutyl-4,6-dinitrophenol (Dinoseb)[2]	88-85-7				X
Methyl parathion[2]	298-00-0				X

Table 4

Reportable analytes for Quanterra Standard Tests, Appendix IX Standard

Semivolatiles	CAS Number	Quanterra Standard List	TCLP	TCL	Appendix IX
4-Nitroquinoline-1-oxide	56-57-5				X
Parathion[2]	56-38-2				X
Isodrin[3]	465-73-6				X
Kepone [2]	143-50-0				X
Famphur[2]	52-85-7				X
Methapyrilene	91-80-5				X
Aramite	140-57-8				X
p-(Dimethylamino)azobenzene	60-11-7				X
p-Chlorobenzilate[3]	510-15-6				X
3,3'-Dimethylbenzidine	119-93-7				X
2-Acetylaminofluorene	53-96-3				X
Dibenz(a,j)acridine	224-42-0				
7,12-Dimethylbenz(a)anthracene	57-97-6				X
3-Methylcholanthrene	56-49-5				X
Hexachlorophene[4]	70-30-4				X
Diphenylamine[5]	122-39-4				X

[2] May also be analyzed by method 8140 or 8141, which can acheive lower reporting limits.

[3] May also be analyzed by method 8080 or 8081, which can achieve lower reporting limits

[4] 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 is searched for in the chromatogram. (See section 12.2.1)

[5] 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	40°C for 2 minutes
Column Temperature Program	40 - 320°C at 11.5°C/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	2 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
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
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
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

Table 7

Analytes in Approximate Retention Time Order and Characteristic Ions, Primary Standard

Analyte	Primary	Secondary	Tertiary
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
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
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

Analytes in Approximate Retention Time Order and Characteristic Ions, Appendix IX Standard

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
Methyl parathion	109	125	263
4-Nitroquinoline-1-oxide	190	128	160

Table 8

Analytes in Approximate Retention Time Order and Characteristic Ions, Appendix IX Standard

Analyte	Primary	Secondary	Tertiary
Parathion	109	97	291
Isodrin	193	66	195
Kepone	272	274	237
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

8270B LCS Compounds

LCS Compounds	Spiking Level, ng/µL in extract
1,2,4-Trichlorobenzene	50
Acenaphthene	50
2,4-Dinitrotoluene	50
Pyrene	50
N-Nitroso-di-n-propylamine	50
1,4-Dichlorobenzene	50
Pentachlorophenol	75
Phenol	75
2-Chlorophenol	75
4-Chloro-3-methylphenol	75
4-Nitrophenol	75

Table 10

TCLP LCS Compounds

LCS Compounds	Spiking Level, ng/µL in extract
1,4-Dichlorobenzene	50
2,4-Dinitrotoluene	50
Hexachlorobenzene	50
Hexachlorobutadiene	50
Hexachloroethane	50
2-Methylphenol	50
3-Methylphenol	50
4-Methylphenol	50
Nitrobenzene	50
Pentachlorophenol	50
Pyridine	50
2,4,5-Trichlorophenol	50
2,4,6-Trichlorophenol	50

Recovery limits for the LCS and for matrix spikes are generated from historical data and are maintained by the QA department.

Table 11

8270B Surrogate Compounds

Surrogate Compounds	Spiking Level, ng/µL in extract
Nitrobenzene-d5	50
2-Fluorobiphenyl	50
Terphenyl-d14	50
1,2-Dichlorobenzene-d4[1]	50
Phenol-d5	75
2-Fluorophenol	75
2,4,6-Tribromophenol	75
2-Chlorophenol-d4[1]	75

[1] Included in standard mix, but not routinely evaluated for method 8270B

Recovery limits for surrogates are generated from historical data and are maintained by the QA department.

Table 12

Calibration Levels, Primary Standard, µg/mL

Analyte	Level 1	Level 2	Level 3	Level 4	Level 5
Pyridine	10	25	40	60	80
N-nitrosodimethylamine	10	25	40	60	80
Aniline	10	25	40	60	80
Phenol	10	25	40	60	80
Bis(2-chloroethyl)ether	10	25	40	60	80
2-Chlorophenol	10	25	40	60	80
1,3-Dichlorobenzene	10	25	40	60	80
1,4-Dichlorobenzene	10	25	40	60	80
Benzyl alcohol	10	25	40	60	80
1,2-Dichlorobenzene	10	25	40	60	80
2-Methylphenol	10	25	40	60	80
2,2'-oxybis(1-chloropropane)[1]	10	25	40	60	80
4-Methylphenol	10	25	40	60	80
N-Nitroso-di-n-propylamine	10	25	40	60	80
Hexachloroethane	10	25	40	60	80
Nitrobenzene	10	25	40	60	80
Isophorone	10	25	40	60	80
2-Nitrophenol	10	25	40	60	80
2,4-Dimethylphenol	10	25	40	60	80
Benzoic acid	10	25	40	60	80
Bis(2-chloroethoxy)methane	10	25	40	60	80
2,4-Dichlorophenol	10	25	40	60	80
1,2,4-Trichlorobenzene	10	25	40	60	80
Naphthalene	10	25	40	60	80
4-Chloroaniline	10	25	40	60	80
Hexachlorobutadiene	10	25	40	60	80

Table 12

Calibration Levels, Primary Standard, µg/mL

Analyte	Level 1	Level 2	Level 3	Level 4	Level 5
4-Chloro-3-methylphenol	10	25	40	60	80
2-Methylnaphthalene	10	25	40	60	80
Hexachlorocyclopentadiene	10	25	40	60	80
2,4,6-Trichlorophenol	10	25	40	60	80
2,4,5-Trichlorophenol	10	25	40	60	80
2-Chloronaphthalene	10	25	40	60	80
2-Nitroaniline	10	25	40	60	80
Dimethyl phthalate	10	25	40	60	80
Acenaphthylene	10	25	40	60	80
3-Nitroaniline	10	25	40	60	80
Acenaphthene	10	25	40	60	80
2,4-Dinitrophenol	10	25	40	60	80
4-Nitrophenol	10	25	40	60	80
Dibenzofuran	10	25	40	60	80
2,4-Dinitrotoluene	10	25	40	60	80
2,6-Dinitrotoluene	10	25	40	60	80
Diethylphthalate	10	25	40	60	80
4-Chlorophenyl phenyl ether	10	25	40	60	80
Fluorene	10	25	40	60	80
4-Nitroaniline	10	25	40	60	80
4,6-Dinitro-2-methylphenol	10	25	40	60	80
N-Nitrosodiphenylamine	10	25	40	60	80
Azobenzene[2]	10	25	40	60	80
4-Bromophenyl phenyl ether	10	25	40	60	80
Hexachlorobenzene	10	25	40	60	80
Pentachlorophenol	10	25	40	60	80
Phenanthrene	10	25	40	60	80
Anthracene	10	25	40	60	80
Carbazole	10	25	40	60	80
Di-n-butyl phthalate	10	25	40	60	80
Fluoranthene	10	25	40	60	80
Benzidine	10	25	40	60	80
Pyrene	10	25	40	60	80
Butyl benzyl phthalate	10	25	40	60	80
3,3'-Dichlorobenzidine	10	25	40	60	80
Benzo(a)anthracene	10	25	40	60	80
Bis(2-ethylhexyl)phthalate	10	25	40	60	80
Chrysene	10	25	40	60	80
Di-n-octylphthalate	10	25	40	60	80
Benzo(b)fluoranthene	10	25	40	60	80
Benzo(k)fluoranthene	10	25	40	60	80
Benzo(a)pyrene	10	25	40	60	80
Indeno(1,2,3-cd)pyrene	10	25	40	60	80
Dibenz(a,h)anthracene	10	25	40	60	80
Benzo(g,h,i)perylene	10	25	40	60	80

[1] 2.2'oxybis(1-chloropropane) was formally known as bis(2-chloroisopropyl)ether

[2] Azobenzene is formed by decomposition of 1,2-diphenlyhydrazine. If 1,2-diphenylhydrazine is requested, it will be analyzed as azobenzene.

Table 13

Calibration Levels, Appendix IX Standard, µg/mL

Semivolatiles	Level 1	Level 2	Level 3	Level 4	Level 5
2-Picoline	10	25	40	60	80
N-Nitrosomethylethylamine	10	25	40	60	80
Methyl methanesulfonate	10	25	40	60	80
N-Nitrosodiethylamine	10	25	40	60	80
Ethyl methanesulfonate	10	25	40	60	80
Pentachloroethane	10	25	40	60	80
Acetophenone	10	25	40	60	80
N-Nitrosopyrrolidine	10	25	40	60	80
N-Nitrosomorpholine	10	25	40	60	80
o-Toluidine	10	25	40	60	80
3-Methylphenol	10	25	40	60	80
N-Nitrosopiperidine	10	25	40	60	80
o,o,o-Triethyl-Phosphorothioate	20	50	80	120	160
a,a-Dimethyl-phenethylamine	10	25	40	60	80
2,6-Dichlorophenol	10	25	40	60	80
Hexachloropropene	20	50	80	120	160
p-Phenylenediamine	10	25	40	60	80
n-Nitrosodi-n-butylamine	10	25	40	60	80
Safrole	10	25	40	60	80
1,2,4,5-Tetrachlorobenzene	10	25	40	60	80
Isosafrole 1 + 2	20	50	80	120	160
1,4-Dinitrobenzene	10	25	40	60	80
1,4-Naphthoquinone	10	25	40	60	80
1,3-Dinitrobenzene	10	25	40	60	80
Pentachlorobenzene	10	25	40	60	80
1-Naphthylamine	10	25	40	60	80
2-Naphthylamine	10	25	40	60	80
2,3,4,6-Tetrachlorophenol	10	25	40	60	80
5-Nitro-o-toluidine	10	25	40	60	80
Thionazin	10	25	40	60	80
1,3,5-Trinitrobenzene	20	50	80	120	160
Sulfotepp	10	25	40	60	80
Phorate	10	25	40	60	80
Phenacetin	10	25	40	60	80
Diallate 1 + 2	20	50	80	120	160
Dimethoate	10	25	40	60	80
4-Aminobiphenyl	10	25	40	60	80
Pentachloronitrobenzene	20	50	80	120	160
Pronamide	10	25	40	60	80
Disulfoton	10	25	40	60	80

Table 13

Calibration Levels, Appendix IX Standard, µg/mL

Semivolatiles	Level 1	Level 2	Level 3	Level 4	Level 5
2-secbutyl-4,6-dinitrophenol (Dinoseb)	20	50	80	120	160
Methyl parathion	10	25	40	60	80
4-Nitroquinoline-1-oxide	20	50	80	120	160
Parathion	10	25	40	60	80
Isodrin	10	25	40	60	80
Kepone	40	100	160	240	320
Famphur	40	100	160	240	320
Methapyrilene	10	25	40	60	80
Aramite 1 and 2	20	50	80	120	160
p-(Dimethylamino)azobenzene	10	25	40	60	80
p-Chlorobenzilate	10	25	40	60	80
3,3'-Dimethylbenzidine	10	25	40	60	80
2-Acetylaminofluorene	10	25	40	60	80
Dibenz (a,j)acridine	10	25	40	60	80
7,12-Dimethylbenz(a)anthracene	10	25	40	60	80
3-Methylcholanthrene	10	25	40	60	80

Table 14

Initial demonstration recovery and precision limits

Compound	Spiking concentration µg/L	Limit for Relative Standard Deviation	Limit for average recovery, %
Acenaphthene	60	27.6	60.1-132.3
Acenaphthylene	60	40.2	53.5-126.0
Aldrin[1]	60	39.0	7.2-152.2
Anthracene	60	32.0	43.4-118.0
Benz(a)anthracene	60	27.6	41.8-133.0
Benzo(b)fluoranthene	60	38.8	42.0-140.4
Benzo(k)fluoranthene	60	32.3	25.2-145.7
Benzo(a)pyrene	60	39.0	31.7-148.0
Benzo(ghi)perylene	60	58.9	D-195.0
Benzylbutyl phthalate	60	23.4	D-139.9
B-BHC[1]	60	31.5	41.5-130.6
d-BHC[1]	60	21.6	D-100.0
Bis(2-chloroethyl) ether	60	55.0	42.9-126.0
Bis(2-chloroethoxy)methane	60	34.5	49.2-164.7
Bis(2-chloroisopropyl) ether	60	46.3	62.8-138.6
Bis(2-ethylhexyl) phthalate	60	41.1	28.9-136.8
4-Bromophenyl phenyl ether	60	23.0	64.9-114.4
2-Chloronaphthalene	60	13.0	64.5-113.5
4-Chlorophenyl phenyl ether	60	33.4	38.4-144.7
Chrysene	60	48.3	44.1-139.9
4,4'-DDD[1]	60	31.0	D-134.5
4,4'-DDE[1]	60	32.0	19.2-119.7
4,4'-DDT[1]	60	61.6	D-170.6
Dibenzo(a,h)anthracene	60	70.0	D-199.7
Di-n-butyl phthalate	60	16.7	8.4-111.0
1,2-Dichlorobenzene	60	30.9	48.6-112.0
1,3-Dichlorobenzene	60	41.7	16.7-153.9
1,4-Dichlorobenzene	60	32.1	37.3-105.7
3,3'-Dichlorobenzidine	60	71.4	8.2-212.5
Dieldrin[1]	60	30.7	44.3-119.3
Diethyl phthalate	60	26.5	D-100.0
Dimethyl phthalate	60	23.2	D-100.0
2,4-Dinitrotoluene	60	21.8	47.5-126.9
2,6-Dinitrotoluene	60	29.6	68.1-136.7
Di-n-octylphthalate	60	31.4	18.6-131.8
Endosulfan sulfate[1]	60	16.7	D-103.5
Endrin aldehyde	60	32.5	D-188.8
Fluoranthene	60	32.8	42.9-121.3
Fluorene	60	20.7	71.6-108.4
Heptachlor[1]	60	37.2	D-172.2
Heptachlor epoxide[1]	60	54.7	70.9-109.4
Hexachlorobenzene	60	24.9	7.8-141.5

Table 14

Initial demonstration recovery and precision limits

Compound	Spiking concentration µg/L	Limit for Relative Standard Deviation	Limit for average recovery, %
Hexachlorobutadiene	60	26.3	37.8-102.2
Hexachloroethane	60	24.5	55.2-100.0
Indeno(1,2,3-cd)pyrene	60	44.6	D-150.9
Isophorone	60	63.3	46.6-180.2
Naphthalene	60	30.1	35.6-119.6
Nitrobenzene	60	39.3	54.3-157.6
N-Nitrosodi-n-propylamine	60	55.4	13.6-197.9
PCB-1260[1]	60	54.2	19.3-121.0
Phenanthrene	60	20.6	65.2-108.7
Pyrene	60	25.2	69.6-100.0
1,2,4-Trichlorobenzene	60	28.1	57.3-129.2
4-Chloro-3-methylphenol	60	37.2	40.8-127.9
2-Chlorophenol	60	28.7	36.2-120.4
2,4-Chlorophenol	60	26.4	52.5-121.7
2,4-Dimethylphenol	60	26.1	41.8-109.0
2,4-Dinitrophenol	60	49.8	D-172.9
2-Methyl-4,6-dinitrophenol	60	93.2	53.0-100.0
2-Nitrophenol	60	35.2	45.0-166.7
4-Nitrophenol	60	47.2	13.0-106.5
Pentachlorophenol	60	48.9	38.1-151.8
Phenol	60	22.6	16.6-100.0
2,4,6-Trichlorophenol	60	31.7	52.4-129.2

[1] Since the organochlorine pesticides and PCBs are normally determined by method 8080 at Quanterra, they will not be included in the initial demonstration of capability for method 8270B.

QUANTERRA STANDARD OPERATING PROCEDURE

TITLE: GAS CHROMATOGRAPHIC ANALYSIS BASED ON METHOD 8000A, 8010B, 8020A, 8021A, 8080A, 8081, 8150B and 8151, SW-846

(SUPERSEDES: Revision 1)

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1. SCOPE AND APPLICATION

This SOP describes procedures for analysis of organic analytes by Gas Chromatography (GC). The procedures are based on SW-846 methodology and are applicable for measurements made to comply with the Resource Conservation and Recovery Act (RCRA). Individual analytes and methods are described in the appendices.

2. SUMMARY OF METHOD

In general, semivolatile analytes are prepared for analysis using continuous or separatory funnel liquid / liquid extraction (SOP # CORP-OP-0001) or sonication or soxhlet extraction (SOP # CORP-OP-0001). Volatile analytes are prepared for analysis using purge and trap methodology (Appendix A).

After the initial preparation step, the sample is introduced to the GC and concentrations of target analytes are measured by the detector response within a defined retention time window, relative to the response to standard concentrations. Internal or external standardization procedures are used as specified in the method appendices.

3. DEFINITIONS

Definitions of terms used in this SOP may be found in the glossary of the Quality Assurance Management Plan (QAMP).

4. INTERFERENCES

Contamination by carryover can occur when a low concentration sample is analyzed after a high concentration sample. In addition, some purge and trap autosamplers are susceptible to port specific contamination. Co-elution of target analytes with non-targets can occur, resulting in false positives or biased high results. In particular, this is a problem with non-selective detectors such as the Flame Ionization Detector (FID). See the appendices for interferences specific to individual tests and suggested corrective actions.

5. SAFETY

5.1. Procedures shall be carried out in a manner that protects the health and safety of all Quanterra associates. The following requirements must be met:

Eye protection that satisfies ANSI Z87.1 (as per the Chemical Hygiene Plan), 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. Refer to the Quanterra Chemical Hygiene plan for a complete description of personal protection equipment.

The health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the MSDS files maintained in the laboratory. Specific hazards are covered in the appendices.

5.1.1. Opened containers of neat standards will be handled in a fume hood.

6. EQUIPMENT AND SUPPLIES

An analytical system complete with a gas chromatograph is required. A data system capable of measuring peak area and/or height is required. Recommended equipment and supplies for individual methods are listed in each method appendix.

7. REAGENTS AND STANDARDS

7.1. Stock Standards

Stock standards are purchased as certified solutions or prepared from pure solutions. Stock standards for gases are stored at -10 to -20°C. Other volatile and semivolatile stock standard solutions are stored at ≤6°C. All stock standards must be protected from light. Stock standard solutions should be brought to room temperature before using.

Semivolatile stock standard solutions must be replaced after one year. (6 months if also used for 600 series methods). Stock standards of gases must be replaced at least every 2 months. (Every week if also used for 600 series methods). Other volatile stock standards must be replaced at least every 6 months (1 month if used for 600 series analysis) or sooner if comparison with check standards prepared from an independent source indicates a problem.

7.1.1. Expiration times for all standards are measured from the time the standard is prepared, or from the time that the standard ampoule is opened, if the standard is supplied in a sealed ampoule.

7.2. Calibration Standards

7.2.1. Volatile Calibration Standards

The procedure for preparation of volatile standards is given in Appendix A

7.2.2. Semivolatile Calibration Standards

Semivolatile calibration standards are prepared as dilutions of the stock standards. Surrogates and internal standards are used as specified in the method appendices. Semivolatile calibration solutions must be refrigerated at ≤6°C and protected from light. The standards must be replaced at least every six months or sooner if comparison with check standards indicates a problem.

7.3. Gases for carrier and make-up: Hydrogen, Helium, Nitrogen, Argon/Methane.

7.4. Quality control (QC) Standards

QC standards (matrix spiking and LCS standards) are prepared and stored in the same way as calibration standards. They must be made from a stock independent from the calibration standards.

8. SAMPLE PRESERVATION AND STORAGE

Semivolatile extracts must be refrigerated at ≤6°C and analyzed within 40 days of the start of the extraction. Volatile sample storage conditions and holding times are given in Appendix A.

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, 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 an extracted standard at the reporting limit and a single point calibration.

9.2. Batch Definition

Batches are defined at the sample preparation stage. Batches should be kept together through the whole analytical process as far as possible, but it is not mandatory to analyze prepared extracts on the same instrument or in the same

sequence. Refer to the Quanterra QC Program document (QA-003) for further details of the batch definition.

9.2.1. Quality Control 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. In some cases, at client request, the MS/MSD may be replaced with a matrix spike and sample duplicate.

9.3. Control Limits

In-house historical control limits must be determined for surrogates, matrix spikes, and laboratory control samples (LCS). These limits must be determined at least annually. The recovery limits are mean recovery +/- 3 standard deviations for surrogates and LCS, and mean recovery +/- 2 standard deviations for matrix spikes. Precision limits for matrix spikes / matrix spike duplicates are zero to mean relative percent difference + 2 standard deviations.

9.3.1. These limits do not apply to dilutions (except for tests without a separate extraction), but surrogate and matrix spike recoveries will be reported unless the dilution is more than 5X.

9.3.2. All surrogate, LCS, and MS recoveries (except for dilutions) must be entered into QuantIMS (when available) or other database so that accurate historical control limits can be generated. For tests without a separate extraction, surrogates and matrix spikes will be reported for all dilutions.

9.3.3. Refer to the QC Program document (QA-003) for further details of control limits.

9.4. Surrogates

All methods must use surrogates to the extent possible. Surrogate recoveries in samples and QC samples must be assessed to ensure that recoveries are within established limits. 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 the extract if either of the above checks reveal a problem.
- Reprepare and reanalyze the sample or flag the data as "Estimated Concentration" if neither of the above resolves the problem.

The decision to reanalyze or flag the data should be made in consultation with the client. 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.

9.4.1. If dual column analysis is used, the rules for which column's result to report are the same as for samples (Section 12.1). That is, the lower of the two results is reported.

9.4.2. 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 repreparation or flagging of the data is required.

9.4.3. Refer to the Quanterra QC Program document (QA-003) for further details of the corrective actions.

9.5. Method Blanks

For each batch of samples, analyze a method blank. The method blank consists of reagent water for aqueous semivolatiles samples, and sodium sulfate for semivolatiles soils tests (Refer to SOP No. CORP-OP-0001 for details). For low level volatiles, the method blank consists of reagent water. For medium level volatiles, the method blank consists of 9.5 mL of methanol as described in section 11.5 of Appendix A. 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) or at or above 5% of the measured concentration of that analyte in the associated samples, whichever is higher.

- If the analyte is a common laboratory contaminant (methylene chloride, acetone, 2-butanone, phthalate esters) 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.

- Re-extraction and 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. Such action should be done in consultation with the client.

9.5.1. Refer to the Quanterra QC Program document (QA-003) for further details of the corrective actions.

9.6. Instrument Blanks

9.6.1. An instrument blank must be analysed with any sequence that does not contain a method blank.

9.6.2. A new sequence starts with any new initial calibration and if there has been a break of greater than 12 hours in sample analysis.

9.6.3. An instrument blank consists of the appropriate solvent with internal standards added. If internal standards are not used the surrogates should be added.

9.6.4. Control criteria are the same as for the method blank, except that only reanalysis of affected samples would be required, not re-extraction.

9.7. Laboratory Control Samples (LCS)

For each batch of samples, analyze a LCS. The LCS contains a representative subset of the analytes of interest, 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; however, if the matrix spike and matrix spike duplicate are within limits, the batch may be acceptable.

9.7.1. Refer to the Quanterra QC Program document (QA-003) for further details of the corrective action.

9.7.2. If dual column analysis is used, the rules for which column's result to report are the same as for samples (Section 12.1). That is, the lower of the two results is reported.

9.7.3. LCS compound lists are included in the appendices.

9.7.4. 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.

9.8. Matrix Spikes

For each QC batch, analyze a matrix spike and matrix spike duplicate. Spiking compounds and levels are given in the appendices. Compare the percent recovery and relative percent difference (RPD) to that in the laboratory specific historically generated limits.

- 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 repreparation and 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.

9.8.1. If dual column analysis is used, the rules for which column's result to report are the same as for samples (Section 12.1). That is, the lower of the two results is reported.

9.9. Quality Assurance Summaries

Certain clients may require specific project or program QC which may supersede these method requirements. Quality Assurance Summaries should be developed to address these requirements.

9.10. Quanterra QC Program

Further details of QC and corrective action guidelines are presented in the Quanterra QC Program document (QA-003). Refer to this document if in doubt regarding corrective actions.

10. CALIBRATION AND STANDARDIZATION

Internal or external calibration may be used. In either event prepare standards containing each analyte of interest at a minimum of five concentration levels. The low level standard should be at the reporting limit. The other standards define the working range of the detector. Recommended calibration levels are given in the appendices.

10.1. A new calibration curve must be generated after major changes to the system or when the continuing calibration criteria cannot be met. Major changes include new columns and any changes in instrument operating parameters, including gas flows, detector temperatures, oven temperatures, etc.

10.2. With the exception of 10.3 below, it is NOT acceptable to remove points from a calibration curve for the purpose of meeting criteria, unless the points are the highest or lowest on the curve AND the reporting limit and/or linear range is adjusted accordingly. In any event, at least 5 points must be included in the calibration curve.

10.3. A level may be removed from the calibration if the reason can be clearly documented, for example a broken vial or no purge run. A minimum of five levels must remain in the calibration. The documentation must be retained with the initial calibration. Alternatively, if the analyst believes that a point on the curve is inaccurate, the point may be reanalyzed and the reanalysis used for the calibration. All initial calibration points must be analyzed without any changes to instrument conditions.

10.4. External standard calibration

Quantitation by the external standard method assumes a proportional relationship between the calibration run and the analyte in the sample. To use this approach introduce each calibration standard into the GC using the technique that will be used for samples. The ratio of the peak height or area response to the mass or concentration injected may be used to prepare a calibration curve.

Equation 1

$$\text{Calibration Factor (CF)} = \frac{\text{Area or Height of Peak}}{\text{Mass Injected (ng)}}$$

Some data systems may use the inverse of this formula. This is acceptable so long as the same formula is used for standards and samples. Use of peak area or height must be consistent. It is not permitted to switch between using peak area and height for quantitation within an analytical sequence.

10.5. Internal standard calibration

10.5.1. The internal standard approach assumes that variations in instrument sensitivity, amount injected etc. can be corrected by determining the ratio of the response of the analyte to the response of an internal standard that has been added to the extract. To use this approach, select one or more internal standard(s) that are similar in analytical behavior to the compounds of interest. Recommended internal standards are given in the appendices. The analyst must demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. If there is interference, the external standard approach must be used. In this event use the response factors from the previous continuing calibration to quantitate the analytes in the sample with the interference (applies only to the sample with the interference).

10.5.2. Introduce each calibration standard into the GC using the technique that will be used for samples. Response factors (RF) for each compound are calculated as follows:

Equation 2

$$RF = \frac{A_s \times C_{is}}{A_{is} \times C_s}$$

Where:

A_s = Response for the analyte to be measured
A_{is} = Response for the internal standard
C_{is} = Concentration of internal standard
C_s = Concentration of the analyte to be determined in the standard

10.6. Calibration curve fits

Average response factor, linear regression, or quadratic curves may be used to fit the data. Linear regression is a special case of the quadratic fit and may be used if the calibration range is sufficiently narrow so that a straight line will fit the calibration points. Average response factor may be used if the % RSD of the response factors or calibration factors is < 20%.

10.6.1. Average response factor

The average response factor may be used if the percent relative standard deviation (%RSD) of the response factors is < 20%.
The equation for average response factor is:

Equation 3

$$\text{Average response factor} = \frac{\sum RF_{1-n}}{n}$$

Where: n = Number of calibration levels

$\sum RF_{1-n}$ = Sum of response factors for each calibration level

10.6.2. Linear regression

The linear fit uses the following functions:

10.6.2.1. External Standard

Equation 4

$$Concentration = A + BR$$

Where: A = Intercept
B = Slope
R = Response

10.6.2.2. Internal Standard

Equation 5

$$Concentration = A + B\frac{(R \times C_{is})}{R_{is}}$$

Where the variables are defined in equations 2 and 4

10.6.3. Quadratic curve

The quadratic curve uses the following functions:

10.6.3.1. External standard

Equation 6

$$Concentration = A + BR + CR^2$$

10.6.3.2. Internal Standard

Equation 7

$$Concentration = A + B\left(\frac{R \times C_{is}}{R_{is}}\right) + C\left(\frac{R \times C_{is}}{R_{is}}\right)^2$$

Where: C = Curvature

10.7. Evaluation of calibration curves

10.7.1. The percent relative standard deviation (%RSD) from the calibration curve is used to evaluate the initial calibration. This provides a measure of how much error is associated with using the calibration curve for quantitation.

10.7.2. The least squares regression line is calculated and used to calculate the predicted concentration for each level. The percent relative standard deviation is calculated as follows:

Equation 8

$$\% \text{ RSD} = 100\% \times \sqrt{\frac{\sum_{i=1}^{N}\left[\frac{C_i - PC_i}{C_i}\right]^2}{(N-P)}}$$

Where:
N = Number of points in the curve
P = Number of parameters in the curve (= 1 for average response factor, 2 for linear, 3 for quadratic)
C_i = True concentration for level i
PC_i = Predicted concentration for level i

Note that when average response factors are used, this equation gives the same value as the %RSD of the response factors.

10.8. The following requirements must be met for any calibration to be used:

- Response must increase with increasing concentration.
- If a curve is used, the intercept of the curve at zero response must be less than the reporting limit for the analyte.
- Relative standard deviation of the calibration points from the curve used must be < 20%.

- Some data systems will not measure the %RSD from a linear or quadratic fit. In this case, the correlation coefficient may be used as an alternative to the %RSD, and must be greater than 0.995.

10.8.1. Weighting of data points

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.

10.9. Calibration Verification

10.9.1. Continuing Calibration

The working calibration curve or RF must be verified by the analysis of a mid point continuing calibration standard at the beginning, after every 10 samples, and at the end of the analysis sequence (QC and instrument blanks included).

10.9.2. Daily Calibration

At least every 24 hours a daily calibration must be analyzed. The requirements of the daily calibration are the same as the continuing calibration with the addition that retention times are updated.

10.9.3. Any analyte that is reportable as found must have a % difference of $\leq$15% in the preceding continuing calibration, on the column used for quantitation. For dual column analysis, the column used for quantitation will be the column with the lower result. Methods 8010B and 8020A have different continuing calibration limits that are obtained from Table 3 of the reference method and are listed in Appendix A of this SOP.

10.9.4. For any analyte that is not reportable as found, the % difference may be -15% to +30%.

10.9.5. Reportable as found is defined as any analyte that would be reported as anything other than a non-detect.

10.9.6. If dual column analysis is used, at least one column must meet the criteria listed above. The other column must be within ± 30% difference from the initial calibration.

10.9.7. It is not necessary to run a continuing calibration standard at the beginning of the sequence if the first 10 samples are analyzed immediately after the completion of the initial calibration.

10.9.8. The last sample in the sequence must be followed by an ending calibration. The ending calibration serves the analyst in judging the validity of the sequence.

10.9.9. Methods 8010B and 8020A have different continuing calibration criteria. Criteria for continuing calibrations for these methods can be found in the appendices.

10.9.10. % Difference calculation

Equation 9

$$\% \text{ Difference} = \frac{\text{Expected value} - \text{Calculated value}}{\text{Expected value}} \times 100\%$$

10.9.11. Corrective Actions for Continuing Calibration

If the % difference for any analyte is > +30 to -15% corrective action must be taken. This may include clipping the column, changing the liner or other minor instrument adjustments, followed by reanalyzing the standard. If the response for any analyte still varies by more than 30%, a new calibration curve must be prepared.

10.9.12. Corrective Action for Samples

Any samples injected *after* the standard exceeding the continuing calibration criteria must be reinjected.

11. PROCEDURE

11.1. Extraction

Extraction procedures are referenced in the appendices.

11.2. Cleanup

Cleanup procedures are referenced in the appendices.

11.3. Gas Chromatography

Chromatographic conditions for individual methods are presented in the appendices.

11.4. Sample Introduction

In general, volatiles analytes are introduced using purge and trap as described in Appendix A. Semivolatile analytes are introduced by direct injection of the extract. Samples, standards, and QC must be introduced using the same procedure.

11.5. Analytical Sequence

An analytical sequence starts with an initial calibration or a daily calibration. Refer to the individual method appendices for method specific details of daily calibrations and analytical sequences.

11.5.1. The daily calibration includes analysis of standards containing all single response analytes and updating the retention time windows.

11.5.2. If there is a break in the analytical sequence of greater than 12 hours, then a new continuing calibration run must be analyzed before proceeding with the sequence. If more than 24 hours have elapsed since the injection of the last sample in the analytical sequence, a new analytical sequence must be started with a daily calibration.

11.6. Retention Time Windows

11.6.1. Retention time windows must be determined for all analytes. Make an injection of all analytes of interest each day over a three day period. Calculate the standard deviation of the three retention times for each analyte (relative retention times may also be used). For multiresponse analytes (e.g., Aroclors) use the retention time of one major peak. Plus or minus three times the standard deviation of the retention times of each analyte defines the retention time window.

11.6.2. The center of the retention time window is the retention time from the last of the three standards. The centers of the windows are updated with

the mid point of the initial calibration and each daily calibration. The widths of the windows will remain the same until new windows are generated following the installation of a new column.

11.6.3. If the retention time window as calculated above is less than +/- 0.05 minutes, use +/- 0.05 minutes as the retention time window. This allows for slight variations in retention times caused by sample matrix.

11.6.4. The laboratory must calculate new retention time windows each time a new column is installed. The new windows must be generated within one week of the installation of the new column. Until these standards have been run on the new column, the retention time windows from the old column may be used, updated with the retention times from the new initial calibration.

11.6.5. Corrective Action for Retention Times

11.6.5.1. The retention times of all compounds in each continuing calibration must be within the retention time windows established by the daily calibration. If this condition is not met, all samples analyzed after the last compliant standard must be reanalyzed unless the following conditions are met for any compound that elutes outside the retention time window:

- The retention time of that compound in the standard must be within a retention time range equal to twice the original window.
- No peak that would be reportable may be present on the sample chromatogram within an elution time range equal to three times the original retention time window.

11.7. Daily Retention Time Windows

The center of the retention time windows determined in section 11.6 are adjusted to the retention time of each analyte as determined in the daily calibration standards. (See the method 8080A appendix for exceptions for multi-response components.) The retention time windows must be updated at the beginning of each analytical sequence and with each daily calibration, but not for the continuing calibration standards.

11.8. Percent Moisture

Analytical results may be reported as dry or wet weight, as required by the client. Percent moisture must be determined if results will be reported as dry weight. Refer to SOP CORP-OP-0001 for determination of percent moisture.

11.9. 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 shall be notified. The Nonconformance Memo shall be filed in the project file. The nonconformance is also addressed in the case narrative. 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. Qualitative Identification

12.1.1. Tentative identification occurs when a peak is found within the retention time window for an analyte, at a concentration above the reporting limit, or above the MDL if J flags are required. Normally confirmation is required on a second column, but if the detector is sufficiently specific or if the sample matrix is well enough defined, single column analysis may be adequate. In some cases GC/MS confirmation may be required. Client specific requirements may also define the need for second column confirmation and / or GC/MS confirmation. Refer to the appendices for test specific requirements for confirmation. Identification is confirmed if a peak is also present in the retention time window for that analyte on the confirmatory column, at a concentration greater than the reporting limit (MDL if J flags required). For confirmed results, the lower of the two results is reported.

12.1.2. If the % difference between the response on the two columns is greater than 50%, or if the opinion of an experienced analyst is that the complexity of the matrix is resulting in false positives, the confirmation is suspect and the results are qualified.

12.1.3. Multi-response Analytes (Aroclors)

For multi-response analytes, the analyst should use the retention time window, but should rely primarily on pattern recognition. The pattern of peaks will normally serve as confirmation.

12.1.4. The experience of the analyst should weigh heavily in the interpretation of the chromatogram. For example, sample matrix or laboratory temperature fluctuation may result in variation of retention times.

12.2. Calibration Range

If concentrations of any analytes exceed the working range as defined by the calibration standards, then the sample must be diluted and reanalyzed. Dilutions should target the most concentrated analyte in the upper half (over 50% of the high level standard) of the calibration range. It may be necessary to dilute samples due to matrix.

12.3. Dilutions

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.

12.3.1. Guidance for Dilutions Due to Matrix

If the sample is initially run at a dilution and the baseline rise is less than half the height of the peaks in the level 3 standard, then the sample should be reanalyzed at a more concentrated dilution.

12.3.2. Reporting Dilutions

The most concentrated dilution with no target compounds above the calibration range will be reported. Other dilutions will only be reported at client request.

12.4. Interferences

If peak detection is prevented by interferences, further cleanup should be attempted. If no further cleanup is reasonable, then elevation of reporting levels and/or lack of positive identification must be addressed in the case narrative.

12.5. Internal Standard Criteria for Samples

If internal standard calibration is used, then the internal standard response must be within 50 to 200% of the response in the preceding continuing calibration standard.

12.6. Calculations

Capabilities of individual data systems may require the use of different formulas than those presented here. When this is the case, the calculations used must be shown to be equivalent and must be documented in an appendix attached to this document.

12.7. External Standard Calculations

12.7.1. Aqueous Samples

Equation 10

$$\text{Concentration } (\mu g / L) = \frac{(A_x \times V_t \times D_f)}{(CF \times V_i \times V_s)}$$

Where:

A_x = Response for the analyte in the sample
V_i = Volume of extract injected, µL
D_f = Dilution factor
V_t = Volume of total extract, µL
V_s = Volume of sample extracted or purged, mL
CF = Calibration factor, area or height/ng, Section 10.1

12.7.2. Non-aqueous Samples

Equation 11

$$\text{Concentration } (\mu g / kg) = \frac{(A_x \times V_t \times D_f)}{(CF \times V_i \times W \times D)}$$

Where:

W = Weight of sample extracted or purged, g

$$D = \frac{100 - \%Moisture}{100} \qquad (D = 1 \text{ if wet weight is required})$$

A_x, V_t, D_f, CF and V_i are as defined in Equation 10

12.8. Internal Standard Calculations

12.8.1. Aqueous Samples

Equation 12

$$\text{Concentration } (\mu g / L) = \frac{(A_x \times C_{is} \times D_f)}{(A_{is} \times RF \times V_s)}$$

Where:

C_{is} = Amount of internal standard added, ng
A_{is} = Response of the internal standard
RF = Response factor for analyte
Ax, Df, Vs are as defined in Equation 10

12.8.2. Non-aqueous Samples

Equation 13

$$\text{Concentration } (\mu g / kg) = \frac{(A_x \times C_{is} \times D_f)}{(A_{is} \times RF \times W \times D)}$$

All variables are as defined in equations 11 and 12

12.9. Surrogate Recovery

Concentrations of surrogate compounds are calculated using the same equations as for the target compounds. The response factor from the initial calibration is used. Surrogate recovery is calculated using the following equation:

Equation 14

$$\% \text{ Recovery} = \frac{\text{Concentration (or amount) found}}{\text{Concentration (or amount) spiked}} \times 100$$

13. METHOD PERFORMANCE

13.1. Method Detection Limit

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 #: QA-005.

13.2. Initial Demonstration

Each laboratory must make a one time initial demonstration of capability for each individual method. Demonstration of capability for both soils 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. Four aliquots of the QC check sample are analyzed using the same procedures used to analyze samples, including sample preparation. The concentration of the QC check sample should be equivalent to a mid level calibration.

13.2.2. Calculate the average recovery and standard deviation of the recovery for each analyte of interest. Compare these results with the acceptance criteria given in each appendix.

13.2.3. 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. Training Qualification

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

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

15. WASTE MANAGEMENT

Waste generated in this procedure will be segregated and disposed according to the facility hazardous waste procedures. The Environmental Health and Safety Director should be contacted if additional information is required.

16. REFERENCES

Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW846, 3rd Edition, Final Update 1, July 1992. Section 8000A

17. MISCELLANEOUS

17.1. Modifications from Reference Method

17.1.1. Section 7.6.8 of Method 8000A in SW-846 recommends reanalysis if the continuing calibration does not meet criteria and "if the initial analysis indicated the presence of specific target analytes that exceeded the criterion." This SOP is more rigorous than the requirements in SW-846 in that reanalysis is required if the continuing calibration exceeds - 15 to + 30% difference, whether or not the initial analysis indicated the presence of specific analytes.

17.1.2. Method 8000A in SW-846 recommends that the continuing calibration be within 15% difference from the calibration curve for all analytes. This SOP allows for a % Difference of + 30% and -15% for analytes that are not detected. This is supported by the statement in Method 8000A that reanalysis is only required "if the initial analysis indicated the presence of specific target analytes that exceeded the criterion." In any event, the % difference of the continuing calibration must be $\leq$15% for any analyte that is to be quantitated and reported.

17.1.3. Chapter 1 of SW-846 states that the method blank should not contain any analyte of interest at or above the Method Detection Limit. 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 to be up to 5 times the reporting limit in the blank following consultation with the client.

17.1.4. Retention time windows are calculated as in SW-846. However, if a retention time window of less than 0.05 min. is calculated, the window defaults to 0.05 min.

17.1.5. Retention time windows are updated each day using the daily standard, as required by method 8000A. The system is not recalibrated unless the continuing calibration standards fall outside the retention time windows set by the daily standard.

17.2. Modifications from Previous Revision

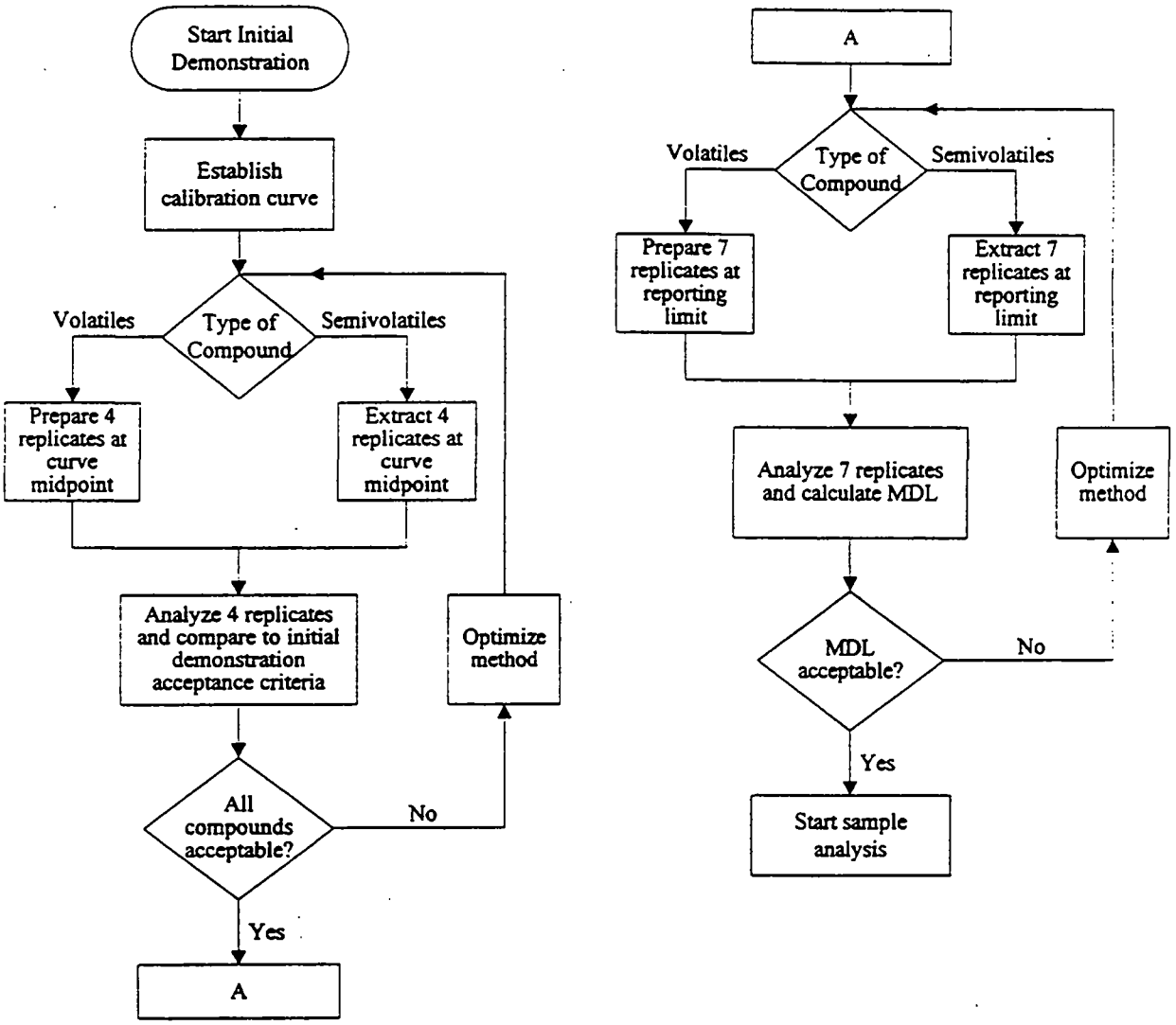
17.2.1. Directions for methods 8081 and 8151 have been added.

17.3. Facility Specific SOPs

Each facility shall attach a list of facility specific SOPs or approved attachments (if applicable) which are required to implement this SOP or which are used in conjunction with this SOP. If no facility specific SOPs or amendments are to be attached, a statement must be attached specifying that there are none.

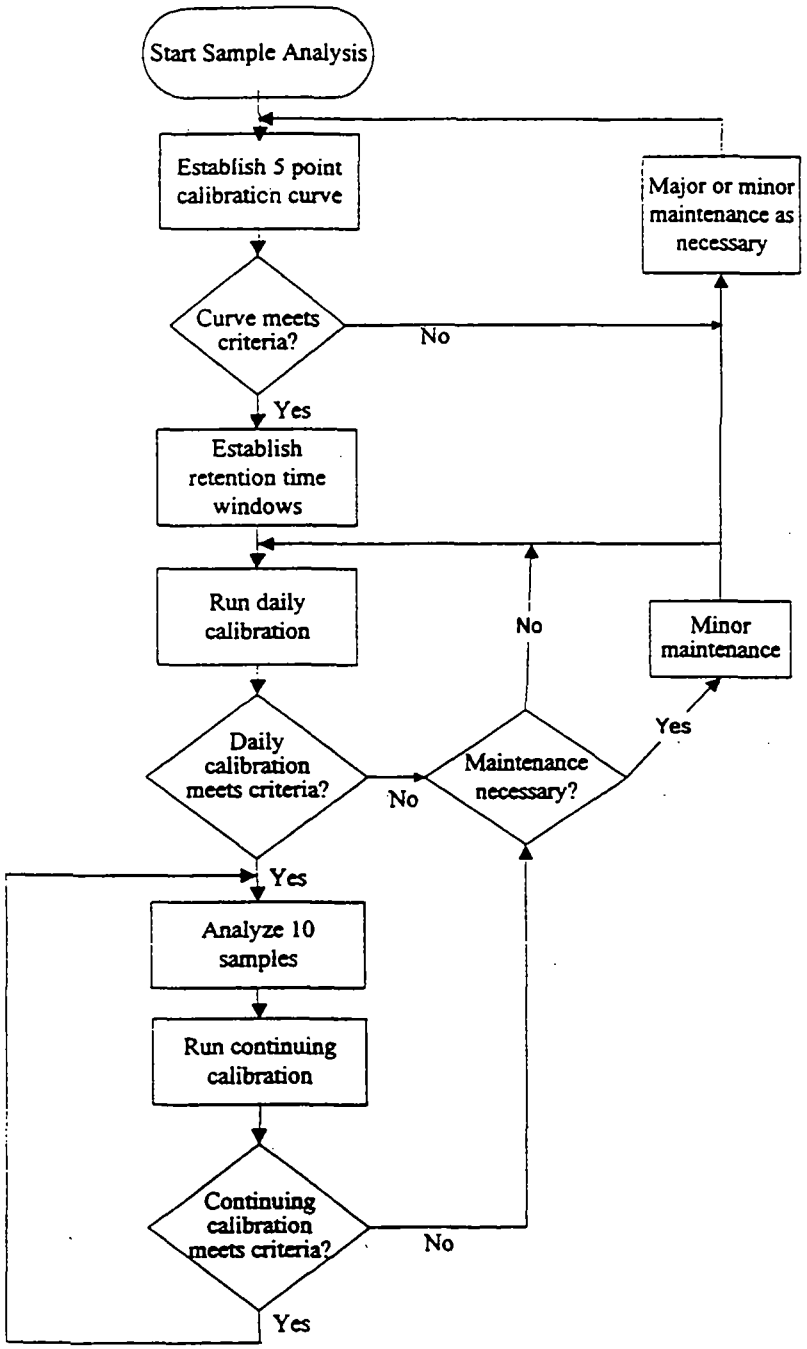
17.4. Flow Diagrams

17.4.1. Initial demonstration and MDL[1]



[1] This flow diagram is for guidance and cannot cover all eventualities. Consult the SOP text and a supervisor if in doubt.

17.4.2. Sample Analysis[1]



[1] This flow diagram is for guidance and cannot cover all eventualities. Consult the SOP text and a supervisor if in doubt.

1. SCOPE AND APPLICATION

1.1. This method describes sample preparation and extraction for the analysis of volatile organics by a purge and trap procedure. All requirements of the 8000A section of this SOP must be met except when superseded by this Appendix. Refer to Table A-1 for the individual analytes normally determined by these procedures.

1.2. Compounds within the scope of this method have boiling points below 200°C and are soluble or slightly soluble in water. Classes of compounds best suited to purge-and-trap analysis include low molecular weight halogenated hydrocarbons, aromatics, ketones, nitriles, acetates, acrylates, ethers, and sulfides.

1.3. Water samples and soils samples with low levels of contamination may be analyzed directly by purge-and-trap extraction and gas chromatography. Higher concentrations of these analytes in soil may be determined by the medium level methanol extraction procedure.

1.4. This method also describes the preparation of water-miscible liquids, non-water-miscible liquids, solids, wastes, and soils/sediments for analysis by the purge-and-trap procedure.

2. SUMMARY OF METHOD

2.1. An inert gas is bubbled through the sample at ambient temperature (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 sorbent column where the volatile components are adsorbed. After purging is completed, the sorbent column is heated and backflushed with inert gas to desorb the components onto a gas chromatographic column. Analytes are detected using a Photoionization Detector (PID, Method 8020A), an Electrolytic Conductivity Detector (ELCD, Method 8010B), or a combination of both (Method 8021A).

2.2. For soil samples with a high level of contamination, a portion of the sample is dispersed in methanol to dissolve the volatile organic constituents. A portion of the methanolic solution is combined with water. It is then analyzed by purge-and-trap GC following the normal water method.

3. DEFINITIONS

Refer to the QAMP for definitions of terms used in this SOP.

Table A-10		
Continuing Calibration and Initial Demonstration Limits		
Analyte	Continuing Calibration and Initial Demonstration Recovery Limits, +/- %	Initial Demonstration RSD Limits, %
Method 8020A		
Benzene	23.0	20.5
Chlorobenzene	19.5	17.5
1,2-Dichlorobenzene	32.0	29.0
1,3-Dichlorobenzene	27.5	25.0
1,4-Dichlorobenzene	30.5	27.5
Ethylbenzene	37.0	33.5
Toluene	22.5	20.0
Additional compounds	35.0	25.0

DELETED

1. SCOPE AND APPLICATION

This SOP Appendix describes procedures to be used when SW-846 Method 8000A is applied to the analysis of organochlorine pesticides and Aroclors (PCBs) by GC/ECD. This Appendix is to be applied when SW-846 Method 8080A is requested, and is applicable to extracts derived from any matrix which are prepared according to the appropriate Quanterra sample extraction SOPs. (CORP-OP-0001)

Table B-1 lists compounds which are routinely determined by this method and gives the Reporting Limits (RL) for each matrix. RLs given are based on the low level standard and the sample preparation concentration factors. Matrix interferences may result in higher RLs than those listed.

2. SUMMARY OF METHOD

This method presents conditions for the analysis of prepared extracts of organochlorine pesticides. The pesticides are injected onto the column and separated and detected by electron capture detection. Quantitation is by the external standard method.

3. DEFINITIONS

Refer to the QAMP for definitions of terms used in this document.

4. INTERFERENCES

4.1. Refer to the method 8000A section of this SOP for information regarding chromatographic interferences.

4.2. Interferences in the GC analysis arise from many compounds amenable to gas chromatography that give a measurable response on the electron capture detector. Phthalate esters, which are common plasticizers, can pose a major problem in the determinations. Interferences from phthalates are minimized by avoiding contact with any plastic materials.

4.3. Sulfur will interfere and can be removed using procedures described in SOP CORP-OP-0001.

4.4. Interferences co-extracted from samples will vary considerably from source to source. The presence of interferences may raise quantitation limits for individual samples. Specific cleanups may be performed on the sample extracts, including florisil cleanup (Method 3620), Gel Permeation Chromatography (Method 3640), and Sulfur cleanup (Method 3660). These cleanup procedures are included in SOP # CORP-OP-0001.

5. SAFETY

5.1. Refer to section 5 of the Method 8000A SOP for general safety requirements.

5.2. Aroclors have been classified as a potential carcinogen under OSHA. Concentrated solutions of Aroclors must be handled with extreme care to avoid excess exposure. Contaminated gloves and clothing must be removed immediately. Contaminated skin surfaces must be washed thoroughly.

6. EQUIPMENT AND SUPPLIES

6.1. Refer to Section 6 of the 8000A section of this SOP. A ^{63}Ni electron capture detector is required.

6.2. Refer to Table B-2 for analytical columns.

6.3. Microsyringes, various sizes, for standards preparation, sample injection, and extract dilution.

7. REAGENTS AND STANDARDS

7.1. Refer to the method 8000A section of this SOP for general requirements for reagents and supplies.

7.2. Refer to Table B-3 for details of calibration standards.

7.3. Surrogate Standards

Tetrachloro-m-xylene and decachlorobiphenyl are the surrogate standards. Dibutylchlorendate may be used at client request. Refer to tables B-5, B-6, and B-7 for details of surrogate standards.

7.4. Column Degradation Evaluation Mix

A mid-level standard containing 4,4'-DDT and Endrin and not containing any of their breakdown products must be prepared for evaluation of degradation of these compounds by the GC column and injection port. This mix must be replaced after one year, or whenever corrective action to columns fails to eliminate the breakdown of the compounds, whichever is shorter. This solution also contains the surrogates. Refer to Table B-4 for details of the column degradation evaluation mix.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

Refer to Section 8 of the 8000A section of this SOP.

9. QUALITY CONTROL

Refer to Section 9 of the 8000A section of this SOP.

10. CALIBRATION AND STANDARDIZATION

10.1. Refer to Section 10 of the 8000A section of this SOP for general calibration requirements.

10.2. External standard calibration is used for this method.

10.3. Refer to Table B-2 for details of GC operating conditions. The conditions listed should result in resolution of all analytes listed in Table B-1 on both columns. Closely eluting pairs are DDE and Dieldrin on the Rtx-5 or DB-5 column and Endosulfan II and DDD on the 1701 column.

10.4. Column Degradation Evaluation

Before any calibration runs, either initial or daily, the column evaluation mix must be injected. The degradation of DDT and endrin must be calculated (see equations 9 and 10) and each shown to be less than 20% before calibration can proceed. This is only necessary if the target compound list includes DDT, Endrin, or any of their degradation products.

If the breakdown of DDT and/or endrin exceeds the limits given above, corrective action must be taken. This action may include:

- Replacement of the injection port liner or the glass wool.
- Cutting off a portion of the injection end of a capillary column.
- Replacing the GC column.

10.5. Initial Calibration

Refer to Section 10 of the 8000A section of this SOP for details of calibration procedures.

10.5.1. Refer to Table B-8 for the initial calibration analytical sequence.

10.5.2. The response for each single-peak analyte will be calculated by the external standard procedure described in the general method for GC analysis.

10.5.3. The surrogate calibration curve is calculated from the Individual AB mix (or from the Aroclor 1016/1260 mix if the analysis is for acid cleaned

Aroclor only). Surrogates in the other calibration standards are used only as retention time markers.

10.5.4. For multi-component pesticides and Aroclors:

Two options are possible for quantitation of multicomponent pesticides and Aroclors. The same quantitation option must be used for standards and samples.

10.5.4.1. Multiple peak option

Select 3-10 major peaks in the analyte pattern. Calculate the response using the total area or total height of these peaks. Alternatively, find the response of each of the 3-10 peaks per multi-peak pesticide or Aroclor, and use these responses independently, averaging the resultant concentrations found in samples for a final concentration result. When using this option, it is appropriate to remove peaks that appear to be coeluting with contaminant peaks from the quantitation. (i.e. peaks which are significantly larger than would be expected from the rest of the pattern.)

10.5.4.2. Total area option

The total area of the standards and samples may be used for quantitation of multicomponent analytes. Any surrogate or extraneous peaks within the envelope must be subtracted from the total area. This option should not be used if there are significant interference peaks within the multicomponent pattern in the samples. The retention time window for total area measurement must contain at least 90% of the area of the analyte.

10.5.5. For multicomponent analytes, the low level standard must be analyzed as part of the initial calibration. If multicomponent analytes are present above half the reporting limit in any of the samples, these samples must be reanalyzed and quantitated against a valid five point calibration (unless a 5 point calibration for multicomponent was included as part of the initial calibration).

10.5.6. The analyst may include a full 5 point calibration for any of the multicomponent analytes with the initial calibration.

10.5.7. For Aroclor only analysis, a five point calibration of the 1016/1260 mix is generated with at least low level single points for the other Aroclor mixes. If multicomponent analytes are present above half the reporting limit in any of the samples, these samples must be reanalyzed and quantitated against a valid five point calibration.

10.6. Daily Calibration Verification

The daily calibration verification must be analyzed within 24 hours of the start of the initial calibration and at least once every 24 hours thereafter if samples are being analyzed. If there is a break in the analytical sequence of greater than 12 hours, then a new continuing calibration run must be analyzed before proceeding with the sequence. If more than 24 hours have elapsed since the injection of the last sample in the analytical sequence, a new analytical sequence must be started with a daily calibration.

10.6.1. At a minimum, the daily calibration includes analysis of the breakdown mix followed by mid level standards of any single component analytes. (The individual mix AB and any additional single component analytes.)

10.6.2. If any multicomponent analytes are to be quantitated, then the daily calibration must include mid level standards of the appropriate multicomponents.

10.6.3. If multicomponent analytes do not have a full five point initial calibration or are not included with the daily calibration, then any multicomponent analytes found at greater than half the reporting limit must be reanalyzed and quantitated against a five point. Note that, at a minimum, all multicomponent analytes of interest must have a low level standard analyzed as part of the initial calibration to ensure that the sensitivity of the instrument is sufficient for pattern recognition.

10.6.4. Multicomponent analytes may be quantitated if there is a valid 5 point initial calibration on the instrument for the multicomponent analyte and a mid level standard of the multicomponent is analyzed within 24 hours and prior to the sample. The mid level standard must meet the 15% calibration criteria for quantitation.

10.6.5. The retention time windows for any analytes included in the daily calibration are updated.

10.7. Continuing Calibration

The AB calibration mix is analyzed as the continuing calibration standard. This is analyzed after every 10 samples, including matrix spikes, LCS, and method blanks. The continuing calibration standard need not include multicomponent analytes.

10.7.1. The level 3 calibration standard is used for the continuing calibration.

10.7.2. If only Aroclors are requested, the continuing calibration standard will consist of the mid level 1016/1260 Aroclor standard with the surrogates added.

11. PROCEDURE

11.1. Refer to the method 8000A section of this SOP for general procedural requirements.

11.2. Extraction

The extraction procedure is described in SOP No. CORP-OP-0001.

11.3. Cleanup

Cleanup procedures are described in SOP No. CORP-OP-0001.

11.4. Suggested gas chromatographic conditions are given in Table B-2.

11.5. Allow extracts to warm to ambient temperature before injection.

11.6. The suggested analytical sequence is given in Table B-8.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Refer to the 8000A section of this SOP for identification and quantitation of single component analytes.

12.2. Identification of Multicomponent Analytes

Retention time windows are also used for identification of multi-component analytes, but the "fingerprint" produced by major peaks of those compounds in the standard is used in tandem with the retention times to identify the compounds. The ratios of the areas of the major peaks are also taken into consideration. Identification of these compounds may be made even if the retention times of the peaks in the sample fall outside of the retention time windows of the standard, if in the analyst's judgment the fingerprint (retention time and peak ratios) resembles the standard chromatogram.

12.2.1. The chromatogram is evaluated for technical chlordane if alpha and gamma chlordane are present. If technical chlordane is present it must be quantitated against a 5 point technical chlordane curve.

12.3. Quantitation of Multicomponent Analytes

Use 3-10 major peaks or total area for quantitation as described in section 10.5.4, initial calibration of multicomponent analytes.

If the analyst believes that a combination of Aroclor 1254 and 1260, or a combination of 1242, 1248 and 1232 is present, then only the predominant aroclor is quantitated and reported, but the suspicion of multiple aroclors is discussed in the narrative. If well separated Aroclor patterns are present, then both aroclors are quantitated and reported.

12.3.1. If there are no interfering peaks within the envelope of the multicomponent analyte, the total area of the standards and samples may be used for quantitation. Any surrogate or extraneous peaks within the envelope must be subtracted from the total area.

12.4. Second column confirmation of Aroclors and other multi-component analytes will only be performed when requested by the client, because the appearance of the multiple peaks in the sample usually serves as a confirmation of Aroclor presence.

12.5. Surrogate recovery results are calculated and reported for decachlorobiphenyl (DCB) unless it is determined that sample interference has adversely affected the quantitation of that surrogate. Tetrachloro-m-xylene (TCMX) recovery is reported in lieu of DCB in samples having the interference, and also may be used in samples in which DCB recovery is low. Corrective action is only necessary if DCB and TCMX are both outside of acceptance limits.

12.6. Calculation of Column Degradation/% Breakdown (%B)

Equation 15

$$DDT\,\%B = \frac{A_{DDD} + A_{DDE}}{A_{DDD} + A_{DDE} + A_{DDT}} \times 100$$

where:
A_{DDD}, A_{DDE}, and A_{DDT} = the response of the peaks for 4,4'-DDD, 4,4'-DDE, and 4,4'-DDT in the column degradation evaluation mix.

Equation 16

$$Endrin\,\%B = \frac{A_{EK} + A_{EA}}{A_{EK} + A_{EA} + A_{E}} \times 100$$

where:
A_{EK}, A_{EA}, and A_{E} = the response of endrin ketone, endrin aldehyde, and endrin in the column degradation evaluation mix.

13. METHOD PERFORMANCE

13.1. Performance limits for the four replicate initial demonstration of capability required under Section 13.1 of the main body of this SOP are presented in Table B-9. The spiking level should be equivalent to a mid level calibration.

14. POLLUTION PREVENTION

Refer to section 14 of the 8000A section of this SOP.

15. WASTE MANAGEMENT

15.1. Waste generated in this procedure will be segregated and disposed according to the facility hazardous waste procedures. The Environmental Health and Safety Director should be contacted if additional information is required.

16. REFERENCES

SW846, Update II, September 1994, Method 8080A

17. MISCELLANEOUS

17.1. Modifications from Reference Method

17.1.1. Standards are made up in hexane, not isooctane. Use of standards in the same solvent as the sample extracts (hexane) ensures that analysis of the standard is consistent with analysis of the sample.

17.1.2. Only a single point initial calibration is required for multicomponent analytes (Aroclors, toxaphene and technical chlordane). However, if any of these analytes are found, they must be quantitated against a valid 5 point initial calibration.

17.1.3. Endrin ketone, alpha-chlordane and gamma-chlordane are included in the calibration standards. These are not standard 8080A analytes.

17.2. Modifications from Previous Revisions

None

17.3. Tables

Table B-1
Standard Analyte list and Reporting Limits

Compound	Reporting Limit, ug/L or ug/kg		
	water	soil	waste
Aldrin	0.05	1.7	50
a-BHC	0.05	1.7	50
b-BHC	0.05	1.7	50
d-BHC	0.05	1.7	50
g-BHC (Lindane)	0.05	1.7	50
Chlordane (technical)	0.5	17	500
4,4'-DDD	0.05	1.7	50
4,4'-DDE	0.05	1.7	50
4,4'-DDT	0.05	1.7	50
Dieldrin	0.05	1.7	50
Endosulfan I	0.05	1.7	50
Endosulfan II	0.05	1.7	50
Endosulfan Sulfate	0.05	1.7	50
Endrin	0.05	1.7	50
Endrin Aldehyde	0.05	1.7	50
Heptachlor	0.05	1.7	50
Heptachlor Epoxide	0.05	1.7	50
Methoxychlor	0.1	3.3	100
Toxaphene	2.0	67	2000
Aroclor-1016	1.0	33	1000
Aroclor-1221	1.0	33	1000
Aroclor-1232	1.0	33	1000
Aroclor 1242	1.0	33	1000
Aroclor-1248	1.0	33	1000
Aroclor-1254	1.0	33	1000
Aroclor-1260	1.0	33	1000
APPENDIX IX ADD ONs			
Diallate	1.0	33	1000
Isodrin	0.1	3.3	100
Chlorobenzillate	0.1	3.3	100
Kepone	1.0	33	1000

Note: alpha chlordane, gamma chlordane, and endrin ketone are not 8080A compounds.

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CORP-GC-0001
Addendum 1
Reporting Limits For
Additional Pesticides

Compound	Reporting Limits		
	Water (ug/L)	Soil (ug/kg)	Waste (ug/kg)
Alpha Chlordane	0.05	1.7	50
gamma Chlordane	0.05	1.7	50
Endrin Ketone	0.05	3.3	50

Quanterra
Environmental Services

CORP-GC-0001
Addendum 2

Retention Times

Compound		Retention Time (units = minutes)
Aldrin		16.768
a-BHC		9.670
b-BHC		20.587
d-BHC		21.552
g-BHC (Lindane)		12.978
Chlordane (technical)	(1)	13.080
	(2)	14.578
	(3)	23.940
	(4)	24.311
	(5)	25.705
4,4'-DDD		29.327
4,4'-DDE		25.178
4,4'-DDT		29.977
Dieldrin		25.390
Endosulfan I		23.316
Endosulfan II		29.031
Endosulfan Sulfate		32.572
Endrin		26.387
Endrin Aldehyde		31.069
Heptachlor		14.581
Heptachlor Epoxide		21.931
Methoxychlor		33.100
Toxaphene	(1)	25.153
	(2)	26.477
	(3)	30.257
	(4)	30.947
Aroclor-1016	(1)	7.688
	(2)	10.263
	(3)	14.250
	(4)	15.522
	(5)	17.528
Aroclor-1221	(1)	6.621
	(2)	7.405
	(3)	7.700

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CORP-GC-0001
Addendum 2
Continued

Compound		Retention Time (units = minutes)
Aroclor-1232	(1)	7.642
	(2)	10.197
	(3)	11.088
	(4)	11.722
	(5)	14.161
Aroclor-1248	(1)	10.159
	(2)	14.105
	(3)	17.426
	(4)	19.190
	(5)	19.828
Aroclor-1254	(1)	17.457
	(2)	24.955
	(3)	25.561
	(4)	26.184
	(5)	29.223
Aroclor-1260	(1)	26.409
	(2)	27.573
	(3)	29.208
	(4)	30.903
	(5)	32.218
Diallate	(1)	7.590
	(2)	8.481
Isodrin		19.675
Chlorobenzillate		29.921
Kepone		36.363

The following concentration factors are assumed in calculating the Reporting Limits:

	Extraction Vol.	Final Vol.
Ground water	1000 mL	10 mL
Low-level Soil	30 g	10 mL
High-level soil / waste	1 g	10 mL

Table B-2

Parameter	Recommended Conditions
Injection port temp	220°C
Detector temp	325°C
Temperature program	70°C for 0.5min, 30°C/min to 190°C, 2.5°C/min to 225, 18°C/min to 280°C, 3 min hold
Column 1	DB-5 or Rtx-5 30m x 0.32mm id, 0.5µm
Column 2	DB-1701 or Rtx 1701 30m x 0.32 mm id, 0.25µm
Column 3	DB-608, 30m X 0.32 mm, 0.25µm
Injection	2µL
Carrier gas	Helium or Hydrogen
Make up gas	Nitrogen
Y splitter	Restek or J&W or Supelco glass tee

Table B-4	
Column Degradation Evaluation Mix ng/mL	
Component	Concentration
4,4'-DDT	25
Endrin	25
Tetrachloro-m-xylene (Surrogate)	20
Decachlorobiphenyl (Surrogate)	20

Table B-5			
LCS/Matrix Spike and Surrogate Spike levels ug/L or ug/kg			
	Aqueous	Soil	Waste
gamma BHC (Lindane)	0.20	6.67	200
Aldrin	0.20	6.67	200
Heptachlor	0.20	6.67	200
Dieldrin	0.50	16.7	500
Endrin	0.50	16.7	500
4,4'DDT	0.50	16.7	500
Tetrachloro-m-xylene (Surrogate)	0.20	6.67	200
Decachlorobiphenyl (Surrogate)	0.20	6.67	200

Table B-6			
LCS/Matrix Spike and Surrogate Spike levels for Aroclor analysis with Acid Cleanup ug/L or ug/kg			
	Aqueous	Soil	Waste
Aroclor 1016/1260	10	333	10,000
Tetrachloro-m-xylene (Surrogate)	0.20	6.67	200
Decachlorobiphenyl (Surrogate)	0.20	6.67	200

Table B-7		
LCS/Matrix Spike and Surrogate Spike levels for TCLP ug/L or ug/kg		
	Aqueous	Waste
Heptachlor	5	500
Heptachlor epoxide	5	500
Lindane	5	500
Endrin	5	500
Methoxychlor	10	1000

Table B-9		
Performance limits, four replicate initial demonstration of capability		
Compound	Initial demonstration, mean recovery limits	Initial demonstration, RSD limits
Aldrin	46-112	21
alpha-BHC	51-122	24
beta-BHC	61-120	32
delta-BHC	49.5-118.5	36
gamma-BHC	57-116	23
Chlordane	44.8-108.6	20
4,4'-DDD	52-126	28
4,4'-DDE	46-120	27.5
4,4'-DDT	54-137	36
Dieldrin	42.5-124.5	38
Endosulfan I	43-141	24.5
Endosulfan II	78-171	61
Endosulfan Sulfate	62-132	27
Endrin	49-126	37
Heptachlor	57-100	20
Heptachlor Epoxide	43.5-131.5	25.4
Toxaphene	44.4-111.2	20
Aroclor 1016 + 1260	62.5-110	20

Table C-4			
LCS/Matrix Spike and Surrogate Spike levels ug/L or ug/kg[1]			
	Aqueous	Soil	Waste
2,4-D	16	800	16000
Silvex	4	200	4000
2,4,5-T	4	200	4000
2,4-DB	16	800	16000
Dalapon	8	400	8000
DCAA (surrogate)	16	800	16000

[1] LCS, MS and SS spikes are as the free acid.

Table C-5		
Performance limits, four replicate initial demonstration of capability		
Compound	Initial demonstration, mean recovery limits	Initial demonstration, RSD limits
2,4-D	50-150	25
2,4-DB	50-150	25
2,4,5-TP (Silvex)	50-150	25
2,4,5-T	50-150	25
Dalapon	50-150	25
Dicamba	50-150	25
Dichloroprop	50-150	25
Dinoseb	25-120	40
MCPA	50-150	25
MCPP	50-150	25

5. SAFETY

5.1. Refer to section 5 of the Method 8000A SOP for general safety requirements.

5.2. Aroclors have been classified as a potential carcinogen under OSHA. Concentrated solutions of Aroclors must be handled with extreme care to avoid excess exposure. Contaminated gloves and clothing must be removed immediately. Contaminated skin surfaces must be washed thoroughly.

6. EQUIPMENT AND SUPPLIES

6.1. Refer to Section 6 of the 8000A section of this SOP. A ^{63}Ni electron capture detector is required.

6.2. Refer to Table D-2 for analytical columns.

6.3. Microsyringes, various sizes, for standards preparation, sample injection, and extract dilution.

7. REAGENTS AND STANDARDS

7.1. Refer to the method 8000A section of this SOP for general requirements for reagents and supplies. All standards for this method must be replaced

7.2. Refer to Table D-3 for details of calibration standards.

7.3. Surrogate Standards

Tetrachloro-m-xylene and decachlorobiphenyl are the surrogate standards. Other surrogates may be used at client request. Refer to tables D-5, D-6, and D-7 for details of surrogate standards.

7.4. Column Degradation Evaluation Mix

A mid-level standard containing 4,4'-DDT and Endrin and not containing any of their breakdown products must be prepared for evaluation of degradation of these compounds by the GC column and injection port. This mix must be replaced after one year, or whenever corrective action to columns fails to eliminate the breakdown of the compounds, whichever is shorter. This solution also contains the surrogates. Refer to Table D-4 for details of the column degradation evaluation mix.

10.5.2. The response for each single-peak analyte will be calculated by the external standard procedure described in the general method for GC analysis.

10.5.3. The surrogate calibration curve is calculated from the Individual AB mix (or from the Aroclor 1016/1260 mix if the analysis is for acid cleaned Aroclor only). Surrogates in the other calibration standards are used only as retention time markers.

10.5.4. For multi-component pesticides and Aroclors:

Two options are possible for quantitation of multicomponent pesticides and Aroclors. The same quantitation option must be used for standards and samples.

10.5.4.1. Multiple peak option

Select 3-10 major peaks in the analyte pattern. Calculate the response using the total area or total height of these peaks. Alternatively, find the response of each of the 3-10 peaks per multi-peak pesticide or Aroclor, and use these responses independently, averaging the resultant concentrations found in samples for a final concentration result. When using this option, it is appropriate to remove peaks that appear to be coeluting with contaminant peaks from the quantitation. (i.e. peaks which are significantly larger than would be expected from the rest of the pattern.)

10.5.4.2. Total area option

The total area of the standards and samples may be used for quantitation of multicomponent analytes. Any surrogate or extraneous peaks within the envelope must be subtracted from the total area. This option should not be used if there are significant interference peaks within the multicomponent pattern in the samples. The retention time window for total area measurement must contain at least 90% of the area of the analyte.

10.5.5. For multicomponent analytes, the low level standard must be analyzed as part of the initial calibration. If multicomponent analytes are present above half the reporting limit in any of the samples, these samples must be reanalyzed and quantitated against a valid five point calibration (unless a 5 point calibration for multicomponent was included as part of the initial calibration).

10.6.4. Multicomponent analytes may be quantitated if there is a valid 5 point initial calibration on the instrument for the multicomponent analyte and a mid level standard of the multicomponent is analyzed within 12 hours and prior to the sample. The mid level standard must meet the 15% calibration criteria for quantitation.

10.6.5. The retention time windows for any analytes included in the daily calibration are updated.

10.7. Continuing Calibration

The AB calibration mix is analyzed as the continuing calibration standard. This is analyzed after every 20 samples, including matrix spikes, LCS, and method blanks. (Depending on the type of samples, it may be advisable to analyze continuing calibrations more frequently in order to minimize reruns.)The continuing calibration standard need not include multicomponent analytes.

10.7.1. The level 3 calibration standard is used for the continuing calibration.

10.7.2. If only Aroclors are requested, the continuing calibration standard will consist of the mid level 1016/1260 Aroclor standard with the surrogates added.

10.7.3. For method 8081, if the bracketing standard is out of control, all samples injected after the last standard that met the continuing calibration criteria must be re-injected.

11. PROCEDURE

11.1. Refer to the method 8000A section of this SOP for general procedural requirements.

11.2. Extraction

The extraction procedure is described in SOP No. CORP-OP-0001.

11.3. Cleanup

Cleanup procedures are described in SOP No. CORP-OP-0001.

11.4. Suggested gas chromatographic conditions are given in Table D-2.

11.5. Allow extracts to warm to ambient temperature before injection.

in samples in which DCB recovery is low. Corrective action is only necessary if DCB and TCMX are both outside of acceptance limits.

12.6. Calculation of Column Degradation/% Breakdown (%B)

Equation 17

$$DDT\ \%B = \frac{A_{DDD} + A_{DDE}}{A_{DDD} + A_{DDE} + A_{DDT}} \times 100$$

where:
A_{DDD}, A_{DDE}, and A_{DDT} = the response of the peaks for 4,4'-DDD, 4,4'-DDE, and 4,4'-DDT in the column degradation evaluation mix.

Equation 18

$$Endrin\ \%B = \frac{A_{EK} + A_{EA}}{A_{EK} + A_{EA} + A_{E}} \times 100$$

where:
A_{EK}, A_{EA}, and A_{E} = the response of endrin ketone, endrin aldehyde, and endrin in the column degradation evaluation mix.

13. METHOD PERFORMANCE

13.1. Performance limits for the four replicate initial demonstration of capability required under Section 13.1 of the main body of this SOP are recovery of 80-120% for standard analytes. These limits may not be achievable for certain analytes such as kepone and dichlone. The laboratory must develop internal performance limits for these analytes. The spiking level should be equivalent to a mid level calibration.

14. POLLUTION PREVENTION

Refer to section 14 of the 8000A section of this SOP.

15. WASTE MANAGEMENT

15.1. Waste generated in this procedure will be segregated and disposed according to the facility hazardous waste procedures. The Environmental Health and Safety Director should be contacted if additional information is required.

16. REFERENCES

SW846, Update II, September 1994, Method 8081

17.3. Tables

Table D-1
Standard Analyte list and Reporting Limits

Compound	Reporting Limit, ug/L or ug/kg		
	water	soil	waste
Aldrin	0.05	1.7	50
a-BHC	0.05	1.7	50
b-BHC	0.05	1.7	50
d-BHC	0.05	1.7	50
g-BHC (Lindane)	0.05	1.7	50
αChlordane (technical)	0.05	1.7	50
γChlordane (technical)	0.05	1.7	50
4,4'-DDD	0.05	1.7	50
4,4'-DDE	0.05	1.7	50
4,4'-DDT	0.05	1.7	50
Dieldrin	0.05	1.7	50
Endosulfan I	0.05	1.7	50
Endosulfan II	0.05	1.7	50
Endosulfan Sulfate	0.05	1.7	50
Endrin	0.05	1.7	50
Endrin Aldehyde	0.05	1.7	50
Heptachlor	0.05	1.7	50
Heptachlor Epoxide	0.05	1.7	50
Methoxychlor	0.1	3.3	100
Toxaphene	2.0	67	2000
Aroclor-1016	1.0	33	1000
Aroclor-1221	1.0	33	1000
Aroclor-1232	1.0	33	1000
Aroclor 1242	1.0	33	1000
Aroclor-1248	1.0	33	1000
Aroclor-1254	1.0	33	1000
Aroclor-1260	1.0	33	1000
APPENDIX IX ADD ONs			
Diallate	1.0	33	1000
Isodrin	0.1	3.3	100
Chlorobenzillate	0.1	3.3	100
Kepone	1.0	33	1000

Table D-3

Calibration Levels ng/mL

	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6[2]
Individual Mix AB[1]						
Aldrin	5	10	25	50	100	200
g-BHC (Lindane)	5	10	25	50	100	200
Heptachlor	5	10	25	50	100	200
Methoxychlor	10	20	50	100	200	400
Dieldrin	5	10	25	50	100	200
Endosulfan I	5	10	25	50	100	200
Endosulfan II	5	10	25	50	100	200
4,4'-DDT	5	10	25	50	100	200
Endrin Aldehyde	5	10	25	50	100	200
Endrin Ketone	5	10	25	50	100	200
b-BHC	5	10	25	50	100	200
d-BHC	5	10	25	50	100	200
a-BHC	5	10	25	50	100	200
4,4'-DDD	5	10	25	50	100	200
4,4'-DDE	5	10	25	50	100	200
Endosulfan Sulfate	5	10	25	50	100	200
Endrin	5	10	25	50	100	200
a-Chlordane	5	10	25	50	100	200
g-Chlordane	5	10	25	50	100	200
Multicomponent Standards						
Chlordane (Technical)	50	100	250	500	1000	2000
Toxaphene	200	400	1000	2000	4000	8000
Aroclor 1016/1260	100	200	500	1000	2000	4000
Aroclor 1242	100	200	500	1000	2000	4000
Aroclor 1221 +1254	100	200	500	1000	2000	4000
Aroclor 1232	100	200	500	1000	2000	4000
Aroclor 1248	100	200	500	1000	2000	4000
Surrogates are included with all the calibration mixes at the following levels:						
Tetrachloro-m-xylene	5	10	25	50	100	200
Decachlorobiphenyl	5	10	25	50	100	200

[1] Standards may be split into an A and B mix if resolution of all compounds on both columns is not obtained.

[2] Level 6 is optional and should only be used if linearity can be maintained on the instrument to this level.

Table D-8
Suggested Analytical Sequence

Initial Calibration

Injection #		
1	Solvent blank (optional)	
2	Breakdown Mix	
3-7	Individual mix AB	All levels
8	Aroclor 1016/1260	Level 1[1]
9	Aroclor 1232	Level 1[1]
10	Aroclor 1242	Level 1[1]
11	Aroclor 1248	Level 1[1]
12	Aroclor 1221/1254	Level 1[1]
13	Technical Chlordane	Level 1[1]
14	Toxaphene	Level 1[1]
15	Solvent blank	
16-35	Sample 1-20	
	Solvent blank (optional)	
36	Individual mix AB	Mid level (Continuing calibration)
etc	Samples	
	After 24 hours:	
	Breakdown mix	
	Individual mix AB	
	Any other single component analytes	
	Any multicomponent analytes for quantitation	

[1] A five point curve for any of the multicomponent analytes may be included, and is required for quantitation.

Daily Calibration

At least every 12 hours, counting from the start of the initial calibration, or from the start of the last daily calibration, the retention time windows must be updated using the Individual mix AB, and the breakdown mix must be run before the continuing calibration.

- All samples that have a positive hit for a multicomponent must be run after and within 24 hours of the standard that contains that multicomponent. The standard mix that contains this multicomponent must meet all the calibration criteria.

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Quanterra
Environmental Services

SOP No. CORP-IP-0003
Revision No. 0
Revision Date: 12-09-95

QUANTERRA STANDARD OPERATING PROCEDURE

TITLE: ACID DIGESTION OF AQUEOUS SAMPLES BY SW846 AND MCAWW 200 SERIES METHODS

(SUPERSEDES: NONE)

Prepared by: _____
Technology Standardization Committee

Approved by: _____
Director, Quality Assurance

Approved by: _____
Director, Environmental Health and Safety

Approved by: _____
Management

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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 Graphite Furnace Atomic Absorption (GFAA), Flame Atomic Absorption (FLAA) and Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP) using the MCAWW 200 series methods (NPDES) and SW846 Methods 3005A, 3010A, 3020A and 7060A/7740 (RCRA).

1.2. The applicability of each of these preparation protocols to specific analytes is detailed in Tables I and II (Appendix A) and the applicable determinative methods are illustrated by Figures 6 and 7 (Section 17). 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, solids, sludges, wastes, sediments, air sampling media, biological tissue 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 FLAA, ICP and GFAA (antimony only).

1.5. MCAWW Method 200.7 Section 9.4 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, EP and mobility-procedure extracts, and wastes that contain suspended solids for total metals analysis by FLAA or ICP.

1.7. MCAWW Method 200.7 Section 9.3 is used to prepare surface water and wastes that contain suspended solids for total metals analysis by ICP.

1.8. SW-846 Method 3020A is used to prepare aqueous samples, EP and mobility-procedure extracts, and wastes that contain suspended solids for total metals by GFAA.

1.9. MCAWW Method 200.0 Section 4.1.3 is used to prepare surface water and wastes that contain suspended solids for total metals analysis by GFAA.

1.10. MCAWW Method 200.0 Section 4.1.4 is used to surface water, domestic and industrial waste samples for total recoverable and dissolved metals determination by GFAA.

1.11. SW-846 Methods 7060A and 7740, respectively, contain the procedure for the preparation of aqueous samples for arsenic and selenium.

1.12. MCAWW Methods 206.2 and 270.2, respectively, contain the procedure for the preparation of aqueous samples for arsenic and selenium.

1.13. 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.

2. SUMMARY OF METHOD

2.1. Method 3005A / Method 200.7 Section 9.4 - Preparation for Total Recoverable or Dissolved Metals Analysis by FLAA or ICP Spectroscopy

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 Section 9.3 - Preparation for Total Metals Analysis by FLAA or ICP Spectroscopy

A representative aliquot of sample is refluxed with nitric acid. This step is repeated until the digestate is light in color or until its color has stabilized. 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 200.0 Section 4.1.3 - Preparation for Total Metals for Analysis by GFAA Spectroscopy

A representative aliquot of sample is refluxed with nitric acid. This step is repeated until the digestate is light in color or until its color has stabilized. After the digestate has been reduced to a low volume, it is cooled, filtered (if necessary) and brought up to volume.

2.4. Methods 7060A/206.2 and Methods 7740/270.2 - Preparation for Arsenic/Selenium Analysis by GFAA

A representative aliquot of sample is heated with nitric acid and peroxide until the digestion is complete or until the volume is reduced by one-half. The sample is cooled, filtered (if necessary) and brought up to volume.

2.5. Method 200.0 Section 4.1.4 - Total Recoverable GFAA Preparation (NPDES)

A representative aliquot of sample is heated with nitric acid until the volume is reduced to 15 - 20 mL. 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 QAMP.

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

5.2. Eye protection that satisfies ANSI Z87.1 (as per the Chemical Hygiene Plan), 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 health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the Material Safety Data Sheets (MSDS) maintained in the laboratory. The following specific hazards are known:

5.3.1. The following materials are known to be **corrosive:**

hydrochloric acid and nitric acid.

5.3.2. The following materials are known to be **oxidizing agents**:

nitric acid and hydrogen peroxide.

5.3.3. All sample digestions, including cooling of digestates, must be carried out in a fume hood.

5.4. 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.

5.5. 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 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 or under other means of mechanical ventilation.

5.7. All work must be stopped in the event of a known or potential compromise to the health and safety of a Quanterra associate. The situation must be reported **immediately** to a 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.

5.11. Any and all accidents and spills must be reported to the lab supervisor or EH&S coordinator.

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. 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 pipet 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 Quanterra 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: The ICP LCS/MS working spike solution is provided directly by the vendor, no further standard preparation is necessary.

7.4. Working GFAA LCS/MS spike solution: Prepare the GFAA working LCS spike solution by diluting the custom stock solution (7.2) 100x. The working spike solution 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 GFAA LCS solution must be made fresh every three months.

7.5. The TCLP MS working spike solution is provided directly by the vendor, no further standard preparation is necessary.

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 Quanterra 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 II and III (Appendix A) for details regarding the stock, working standard and final digestate spike concentrations for ICP and GFAA 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 <u>always</u> add acid to water. If the water is added to the acid a violent reaction may occur.

7.12. 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. 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 or within ~~24 hours~~ 15 minutes of collection.

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 Quanterra QA Policy QA-005. 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 Quanterra 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 SOPs (CORP-MT-0001, CORP-MT-0003).

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) 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 or 50 g of reagent water through the appropriate procedure as described in Section 11.

9.4.2. TCLP method blanks are prepared by taking 50 mL or 50 g 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 0.5 mL of the working LCS/MS spike solution (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 0.5 mL of the working LCS/MS spike solution (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 (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.

9.7. Quality Assurance Summaries - Certain clients may require specific project or program QC which may supersede the SOP requirements. Quality Assurance Summaries (QAS) should be developed to address these requirements.

10. CALIBRATION AND STANDARDIZATION

10.1 Hotplate temperature must be verified daily for each hotplate used and must be recorded on either the metals preparation log or in a hotplate temperature logbook. The hotplate temperature should be verified by measuring the temperature of a beaker of reagent water placed on each hotplate.

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. All preparation procedures must be carried out in a properly functioning hood.

11.4. All samples are to be checked out of sample control with the chain of custody documentation filled out completely.

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. In most cases, both AA and ICP digests are required on each sample. It is recommended that both aliquots be measured 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. The following procedure must be followed for all aqueous sample preparations:

11.10.1. Measure and record sample pH with pH paper on a separate aliquot of sample.

Note: If the sample pH is > 2 pH units, the client must be notified of the anomaly.

Note: If sample pH has already been verified and documented in sample receipt this step may be omitted.

11.10.2. Mix sample by shaking the container.

11.10.3. Measure and transfer 50 mL or 50 g of the sample into a beaker.

Note: This SOP allows for samples to be weighed instead of measured volumetrically (See Section 17.1.1.2).

11.10.4. Measure two extra aliquots of sample selected for the MS/MSD analysis. Spike each aliquot with 0.5 mL of spiking solution (7.3 or 7.4).

11.10.5. Measure and transfer 50 mL of reagent water into a beaker for the method blank.

11.10.6. Measure and transfer 50 mL of reagent water into a beaker for the LCS and add 0.5 mL of spiking solution (7.3 or 7.4)

11.11. Proceed to the appropriate Section for the desired method as follows:

Method 3005A or Method 200.7 Section 9.4	11.12
Method 3010A or Method 200.7 Section 9.3	11.13
Method 3020A or Method 200.0 Section 4.1.3	11.14
Method 7060A/7740 or Method 206.2/270.2	11.15
Method 200.0 Section 4.1.4	11.16

11.12. **Method 3005A / Method 200.7 Section 9.4 - Preparation for Total Recoverable or Dissolved Metals Analysis by FLAA or ICP (See Figures 1, 6 and 7)**

11.12.1. To the sample beaker, add 1 mL of concentrated HNO_3 and 2.5 mL of concentrated HCl.

11.12.2. Cover with ribbed watch glass.

11.12.3. 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.

11.12.4. Cool the beaker in a fume hood.

11.12.5. Wash down beaker walls and watch glass with reagent water.

11.12.6. Filter sample, if insoluble materials are present, though Whatman 41 filter paper that has been pre-rinsed with dilute nitric acid.

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.

11.12.7. Rinse beaker and filter paper with reagent water to ensure complete sample transfer.

11.12.8. Add 1.5 mL concentrated HNO_3 and adjust the final volume/mass to 50 mL or 50 g with reagent water. The sample is now ready for analysis

11.13. **Method 3010A / Method 200.7 Section 9.3 - Preparation for Total Metals Analysis by FLAA or ICP Spectroscopy (See Figures 2, 6 and 7)**

11.13.1. To the sample beaker, add 1.5 mL of concentrated HNO_3.

11.13.2. Cover with ribbed watch glass.

11.13.3. Place beaker on hotplate (90-95 °C) and evaporate to low volume of 5 - 10 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 reprepared.

11.13.4. Cool the beaker in a fume hood.

11.13.5. Add another 1.5 mL portion of concentrated HNO_3 and re-cover the beaker.

11.13.6. Continue refluxing until the digestion is complete.

Note: Digestion is complete when the digestate is light in color or does not change in appearance. For most samples the addition of two nitric acid aliquots is sufficient, additional aliquots of nitric acid may be added if necessary.

11.13.7. Evaporate to low volume of 5 - 10 mL while ensuring that no portion of the bottom of the beaker is allowed to go dry.

11.13.8. Cool the beaker in a fume hood.

11.13.9. Add 5 mL of 1:1 HCl.

11.13.10. Cover and reflux for an additional 15 minutes to dissolve precipitate or residue.

11.13.11. Wash down beaker walls and watch glass with reagent water.

11.13.12. Filter sample, if insoluble materials are present, through Whatman 41 filter paper that has been pre-rinsed with dilute nitric acid (1%).

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.

11.13.13. Rinse beaker and filter paper with reagent water to ensure complete sample transfer.

11.13.14. Adjust final volume/mass to 50 mL or 50 g with reagent water. The sample is now ready for analysis.

11.14. **Method 3020A / Method 200.0 Section 4.1.3 - Preparation for Total Metals Analysis by GFAA (See Figures 3, 6 and 7)**

11.14.1. To the sample beaker, add 1.5 mL of concentrated HNO_3.

11.14.2. Cover with ribbed watch glass.

11.14.3. Place beaker on hotplate (90-95 °C) and evaporate to low volume of 5 - 10 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 reprepared.

11.14.4. Cool the beaker in the fume hood.

11.14.5. Add another 1.5 mL portion of concentrated HNO_3.

11.14.6. Recover with watch glass.

11.14.7. Continue refluxing and adding acid as necessary until digestion is complete.

Note: Digestion is complete when the digestate is light in color or does not change in appearance. For most samples the addition of two nitric acid aliquots is sufficient, additional aliquots of nitric acid may be added if necessary.

11.14.8. After the digestion is complete evaporate to low volume of 5 - 10 mL while ensuring that no portion of the bottom of the beaker is allowed to go dry.

11.14.9. Cool the beaker in the fume hood.

11.14.10. Add 10 mL of reagent water and mix sample.

11.14.11. Heat sample for 10 to 15 minutes more to dissolve any residue.

11.14.12. Cool the beaker in the fume hood.

11.14.13. Wash down beaker walls and watch glass with reagent water.

11.14.14. Filter sample, if insoluble materials are present, though Whatman 41 filter paper that has been pre-rinsed with dilute nitric acid (1%).

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.

11.14.15. Rinse beaker and filter paper with reagent water to ensure complete sample transfer.

11.14.16. Adjust final volume to 50 mL with reagent water. The sample is now ready for analysis.

11.15. **Method 7060A/7740 and Method 206.2/270.2 - Preparation for Arsenic and Selenium Analysis by GFAA (See Figures 4, 6 and 7)**

11.15.1. To the sample beaker, add 1 mL of 30 % H_2O_2 and 0.5 mL of concentrated HNO_3.

11.15.2. Heat, until the digestion is complete, at 90 - 95°C or until the volume has been reduced to slightly less than 25 mL.

11.15.3. Cool beaker.

11.15.4. Filter sample, if insoluble materials are present, though Whatman 41 filter paper that has been pre-rinsed with dilute nitric acid.

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.

11.15.5. Rinse beaker and filter paper with reagent water to ensure complete sample transfer.

11.15.6. Adjust final volume to 50 mL with reagent water. The sample is now ready for analysis.

11.16. **Method 200.0 Section 4.1.4 - Preparation for Total Recoverable GFAA Analyses. (See Figures 5 and 7)**

11.16.1. To the sample beaker, add 0.5 mL of concentrated HNO_3.

11.16.2. Heat, until the digestion is complete, at 90 - 95°C or until the volume has been reduced to 15 - 20 mL.

11.16.3. Cool beaker.

11.16.4. Filter sample, if insoluble materials are present, though Whatman 41 filter paper that has been pre-rinsed with dilute nitric acid.

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.

11.16.5. Rinse beaker and filter paper with reagent water to ensure complete sample transfer.

11.16.6. Adjust final volume to 50 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. 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. Waste generated in the procedure must be segregated and disposed according to the facility hazardous waste procedures. The facility EH & S coordinator should be contacted if additional information is required.

15.2. 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. Test Methods for Evaluating Solid Waste , Physical/Chemical Methods, SW-846, 3rd Edition, Final Update I, Revision 1, July 1992. Methods 3005A, 3010A, 3020A, 7060A and 7740A.

16.2. Methods for the Chemical Analysis of Water and Waste (MCAWW), 1983.

16.3. CORP-MT-0001, Inductively Coupled Plasma-Atomic Emission Spectroscopy, Spectrometric Method for Trace Element Analysis of Water and Wastes, Method 6010A and Method 200.7.

16.4. CORP-MT-0003, Graphite Furnace Atomic Absorption Spectroscopy, SW846 Method 7000A and MCAWW 200 Series Methods.

16.5. QA-003, Quanterra QC Program.

16.6. QA-004, Rounding and Significant Figures.

16.7. QA-005, Method Detection Limits.

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 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.

17.1.1.2. This SOP allows for aqueous samples to be weighed instead of measured volumetrically. This assumes the density of the sample is close to 1.0 g/mL. Samples with large amounts of sediment or suspended solids, sludges, non-aqueous liquids must be processed volumetrically. Weighing samples directly into the digestion vessel

minimizes the potential for cross contamination, offers improved accuracy over the use of graduated cylinders (comparable to volumetric flask accuracy), uses less glassware and is more efficient.

17.1.1.3. 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, Olliver 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 3005A

17.1.2.1. In order to matrix match the digestate to the ICP calibration standards, Section 11.12.8 requires the addition of 1.5 mL of concentrated nitric acid to the digestate prior to dilution to final volume. This step ensures that bias due to differences in acid matrix will not be a factor in the analytical determination. Since this step is performed post-digestion it does not impact the digestion recoveries. This approach to matrix matching was discussed with Olliver Fordham of OSW who indicated that it was an acceptable practice.

17.1.3. Modifications Specific to Method 3010A

17.1.3.1. Section 11.13.7 of this SOP requires the sample be reduced to a volume of 5 - 10 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.

17.1.3.2. 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.

17.1.4. Modifications Specific to Method 3020A

17.1.4.1. Section 11.14.8 of this SOP requires the sample be reduced to a volume of 5 - 10 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.

17.1.5. Modifications Specific to Method 7060A/7740

17.1.5.1. Methods 7060A and 7740A incorporate the use of a two step dilution to accommodate the addition of a nickel nitrate modifier. This SOP performs the dilution directly in one step and omits the addition of the modifier. The modifier is added automatically at the instrument by direct injection into the furnace.

17.1.6. 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. Modifications from previous SOP

None.

17.3. Facility Specific SOPs

Each facility shall attach a list of facility specific SOPs or approved attachments (if applicable) which are required to implement this SOP or which are used in conjunction

with this SOP. If no facility specific SOPs or amendments are to be attached, a statement must be attached specifying that there are none. Refer to the Appendices for any facility specific information required to support this SOP.

17.4. Documentation and Record Management

The preparation benchsheet should, at a minimum, include the following information:

- Preparation date, analyst name, matrix, prep type (ICP or GFAA), SOP reference.
- Sample ID, initial weight/volume and final weight/volume.
- Standards Documentation (source, lot, prep date, volume added).
- Analyst Signature.
- Reviewer's Signature and date.

Figure 1. Method 3005A / Method 200.7 Section 9.4 (Section 11.12)

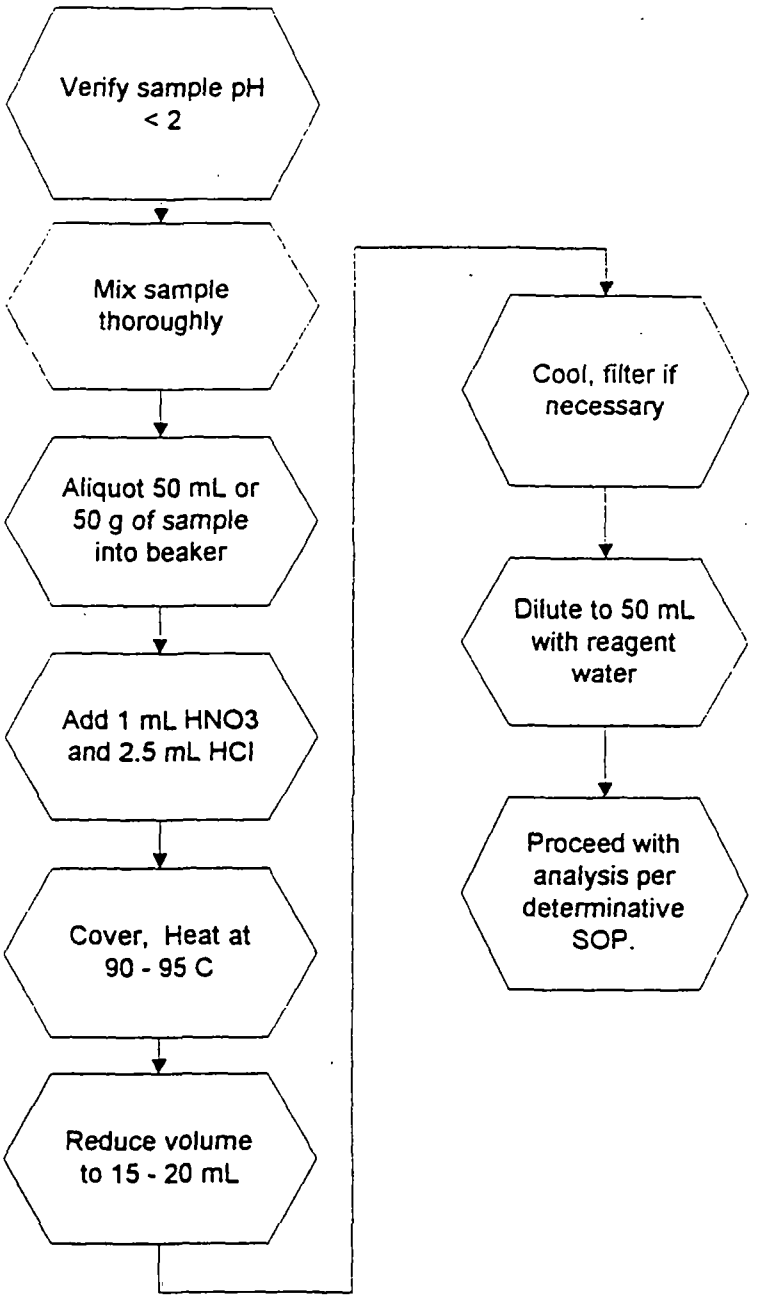


Figure 2. Method 3010A / Method 200.7 Section 9.3 (Section 11.13)

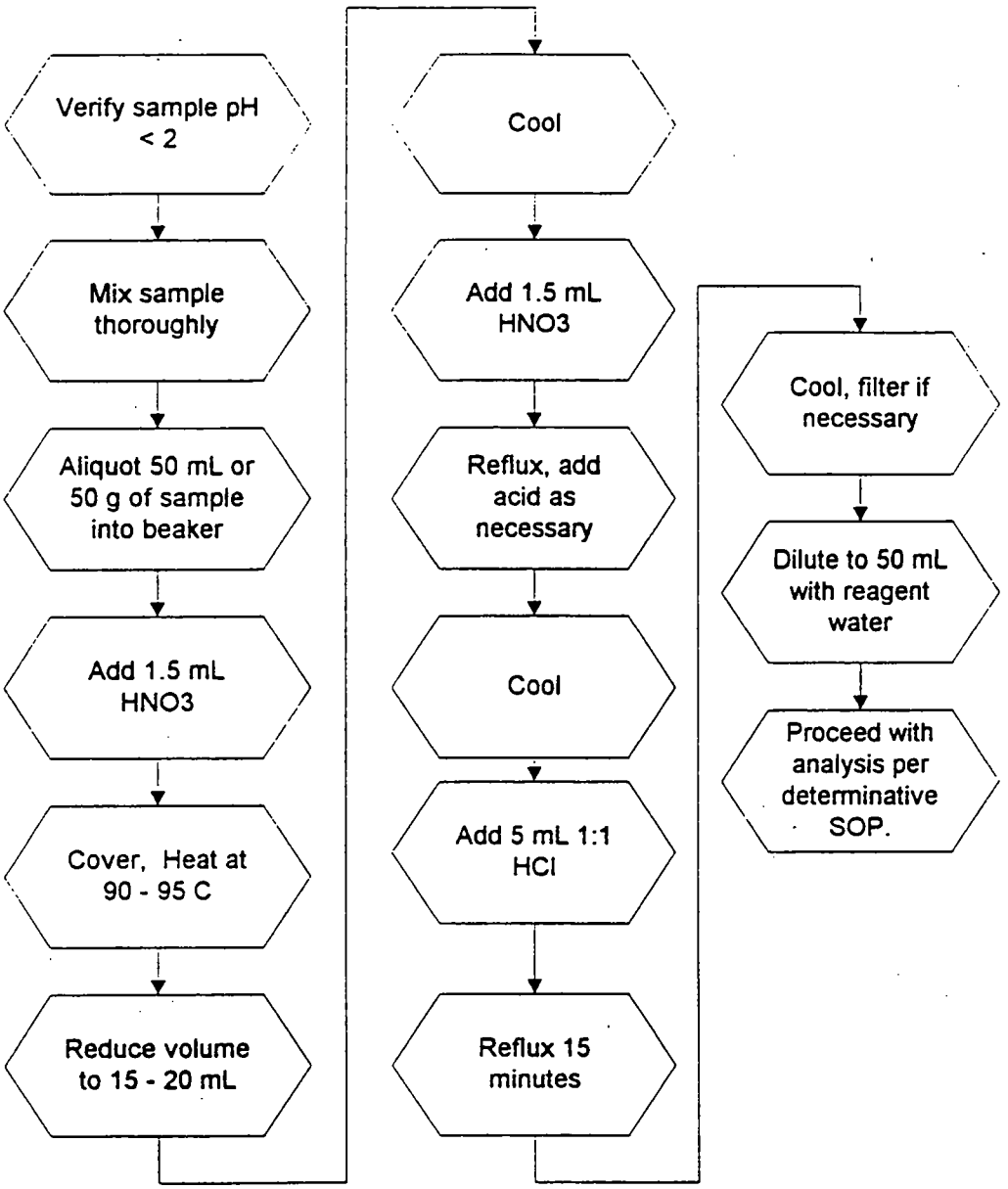


Figure 3. Method 3020A / Method 200.0 Section 4.1.3 (Section 11.14)

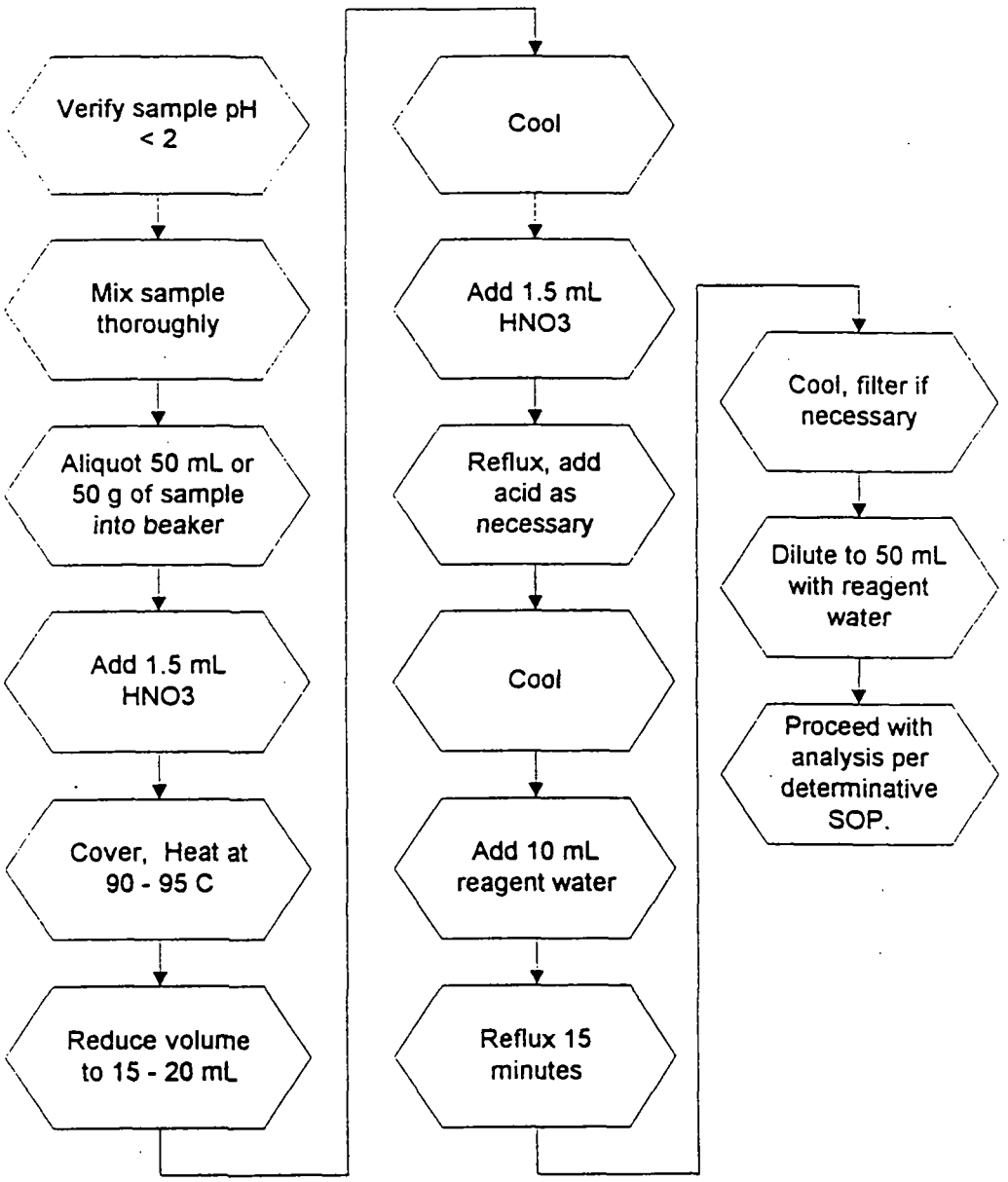


Figure 4. Method 7060A/7740A and Method 206.2/270.2 (Section 11.15)

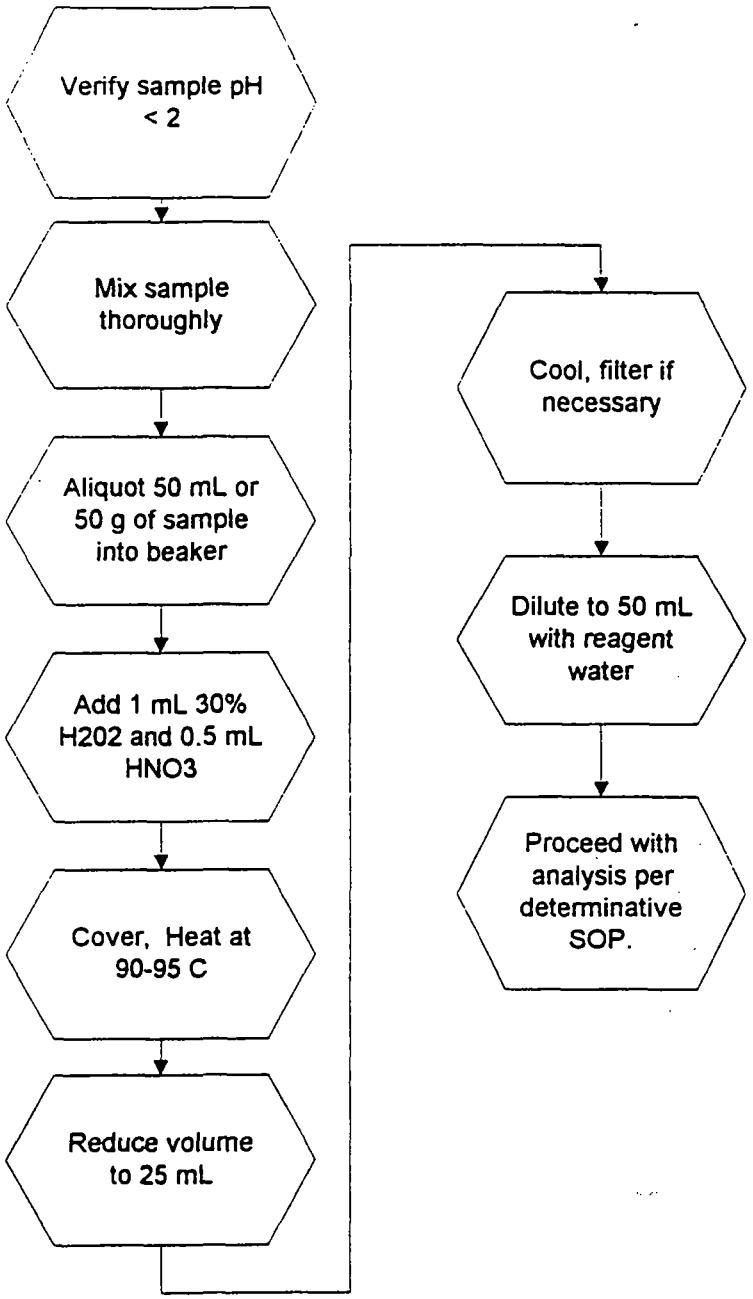


Figure 5. Method 200.0 Section 4.1.4 (Section 11.16)

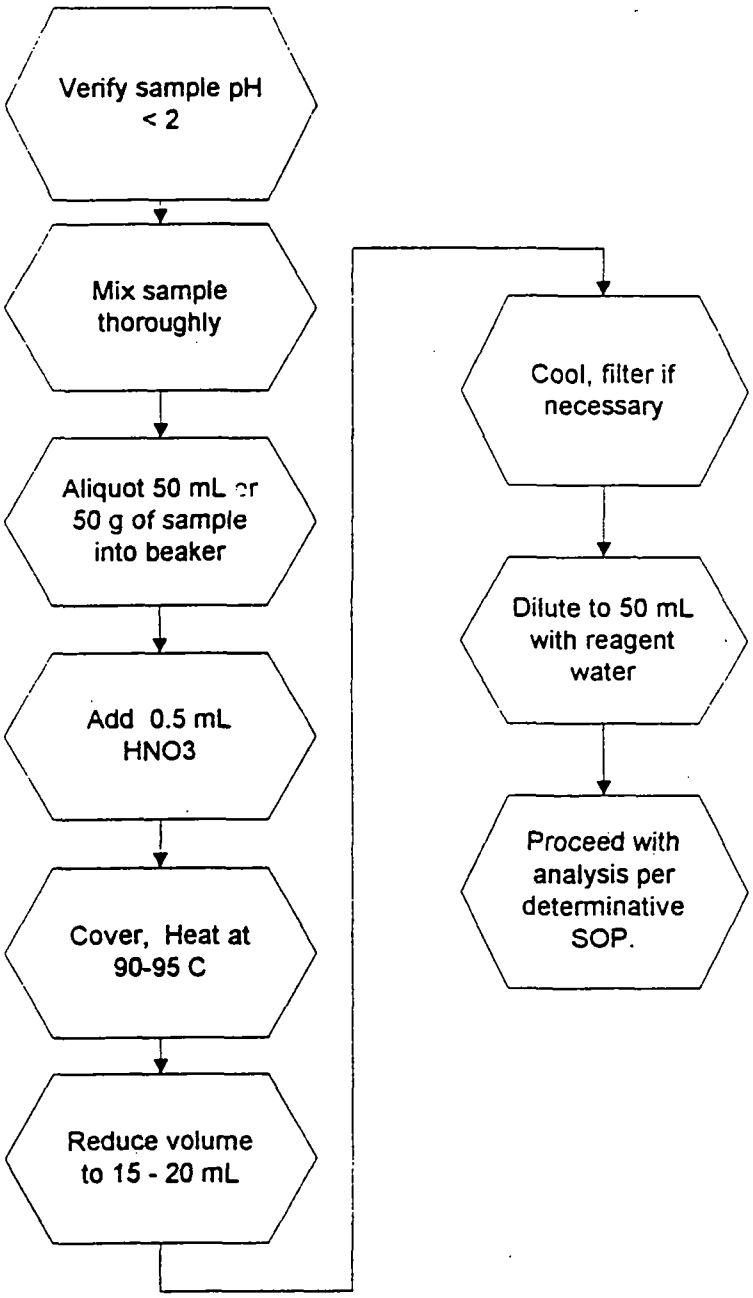
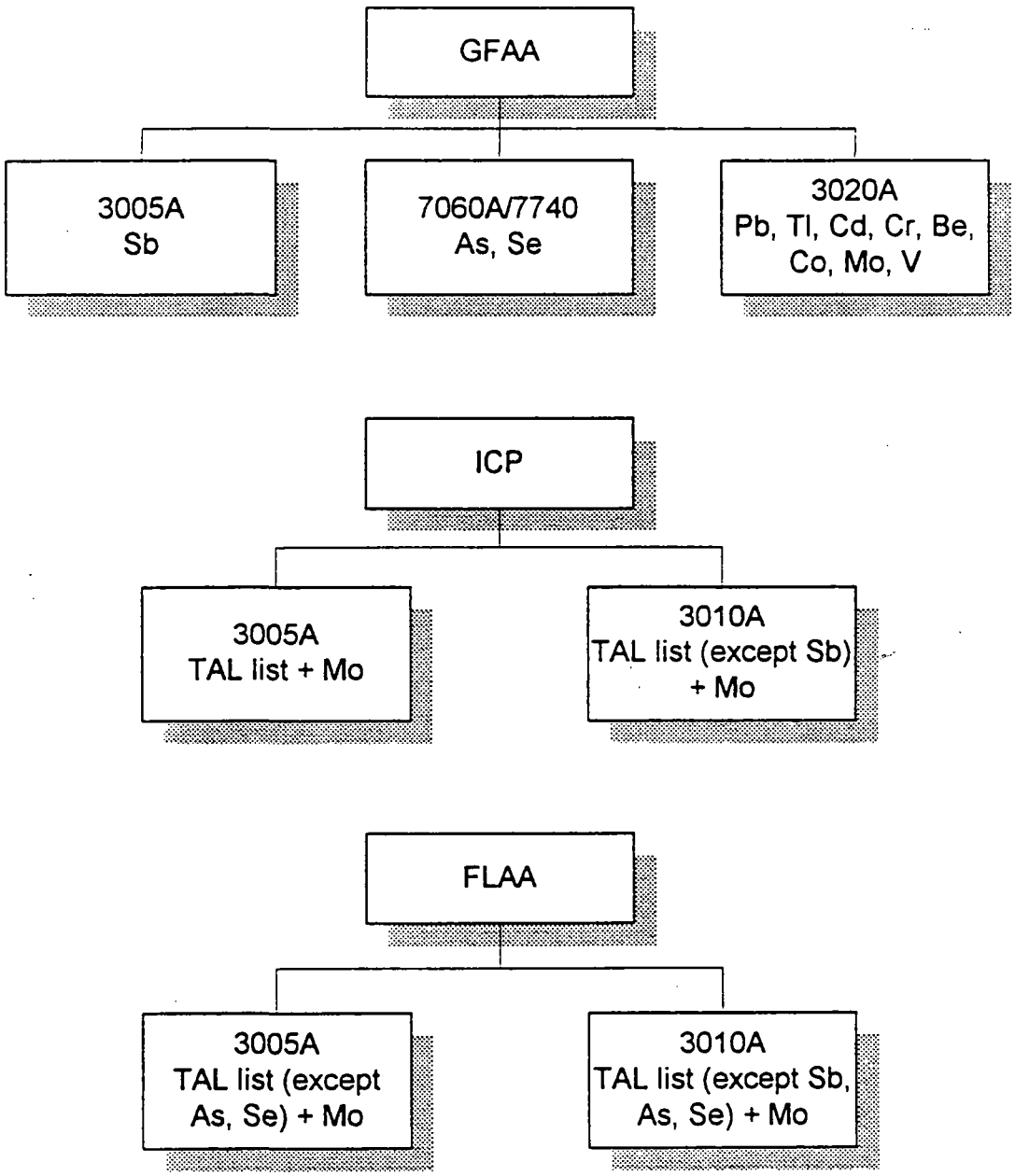
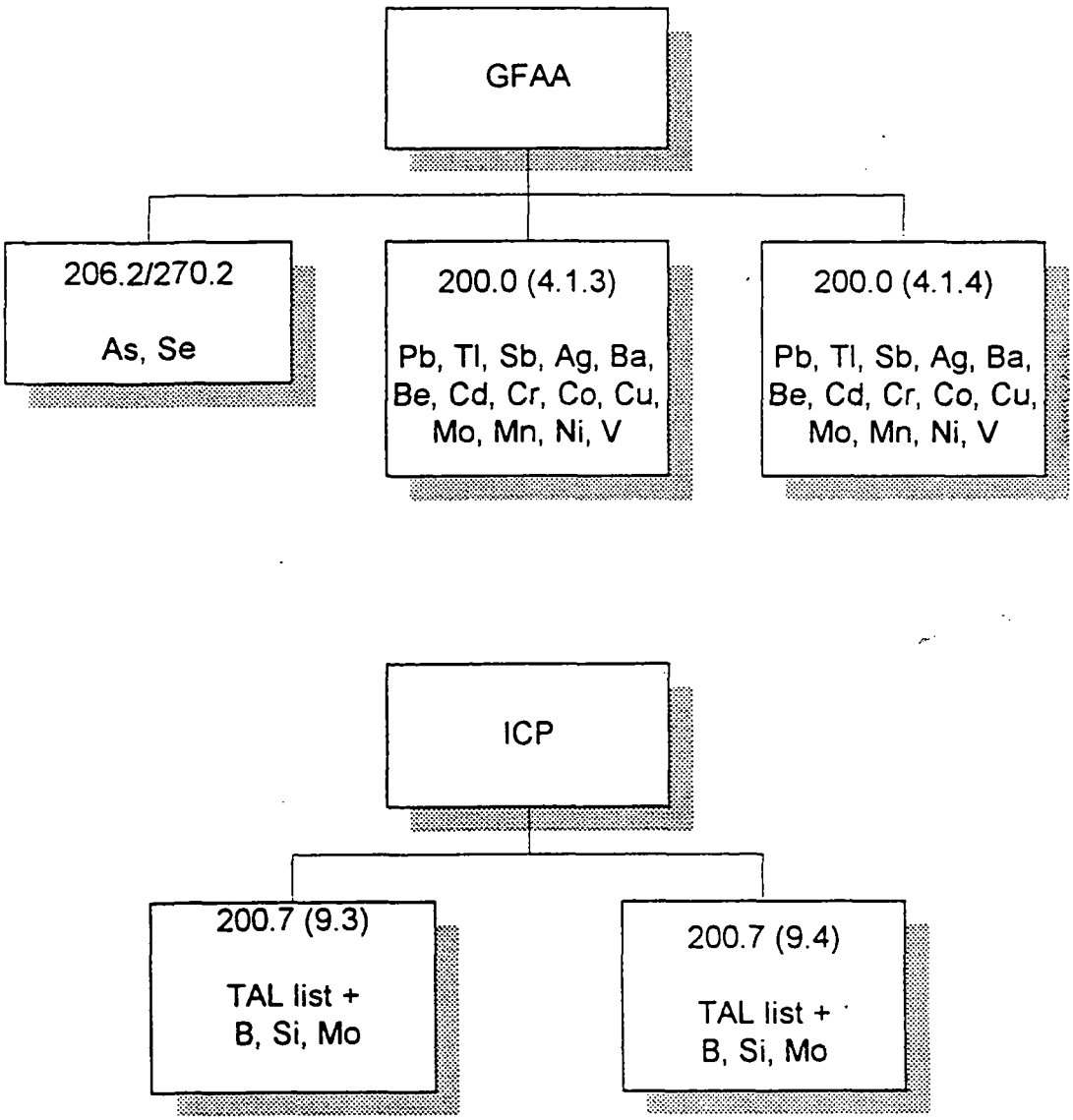


Figure 6. Overview of SW846 Aqueous Preparation Methods by Determinative Method



TAL list : Al, Sb, As, Ba, Be, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Ni, K, Se, Ag, Na, Tl, V, Zn

Figure 7. Overview of MCAWW Aqueous Preparation Methods By Determinative Technique



TAL list : Al, Sb, As, Ba, Be, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Ni, K, Se, Ag, Na, Tl, V, Zn

APPENDIX A

TABLES

TABLE I. Approved Preparation Method Analytes - SW846

ELEMENT	Symbol	CAS Number	3005A	3010A	3020A	7060A 7740
Aluminum	Al	7429-90-5	X	X		
Antimony	Sb	7440-36-0	X			
Arsenic	As	7440-38-2	X	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	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		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)	200.0 (4.1.4)	200.0 (4.1.3)	206.2 270.2
Aluminum	Al	7429-90-5	X	X			
Antimony	Sb	7440-36-0	X	X	X	X	
Arsenic	As	7440-38-2	X	X			X
Boron	B	7440-42-8	X	X			
Barium	Ba	7440-39-3	X	X	X	X	
Beryllium	Be	7440-41-7	X	X	X	X	
Cadmium	Cd	7440-43-9	X	X	X	X	
Calcium	Ca	7440-70-2	X	X			
Chromium	Cr	7440-47-3	X	X	X	X	
Cobalt	Co	7440-48-4	X	X	X	X	
Copper	Cu	7440-50-8	X	X	X	X	
Iron	Fe	7439-89-6	X	X	X	X	
Lead	Pb	7439-92-1	X	X	X	X	
Magnesium	Mg	7439-95-4	X	X			
Manganese	Mn	7439-96-5	X	X	X	X	
Molybdenum	Mo	7439-98-7	X	X	X	X	
Nickel	Ni	7440-02-0	X	X	X	X	
Potassium	K	7440-09-7	X	X			
Selenium	Se	7782-49-2	X	X			X
Silicon	Si	7631-86-9	X	X			
Silver	Ag	7440-22-4	X	X	X	X	
Sodium	Na	7440-23-5	X	X			
Thallium	Tl	7440-28-0	X	X	X	X	
Vanadium	V	7440-62-2	X	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 III. ICP and FLAA Matrix Spike and Aqueous Laboratory Control Sample Levels

ELEMENT	Working LCS/MS Standard (mg/L)	Aqueous LCS/ MS Level * (ug/l)
Aluminum	200	2000
Antimony	50	500
Arsenic	200	2000
Barium	200	2000
Beryllium	5	50
Cadmium	5	50
Calcium	5000	50000
Chromium	20	200
Cobalt	50	500
Copper	25	250
Iron	100	1000
Lead	50	500
Lithium	100	1000
Magnesium	5000	50000
Manganese	50	500
Molybdenum	100	1000
Nickel	50	500
Phosphorous	1000	10000
Potassium	5000	50000
Selenium	200	2000
Silver	5	50
Sodium	5000	50000
Strontium	100	1000
Thallium	200	2000
Vanadium	50	500
Zinc	50	500
Boron	100	1000
Silica	1000	10000
Tin	200	2000
Titanium	100	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 (7.3) to 50 mL of sample.

TABLE IV. GFAA Matrix Spike and Aqueous LCS Spike Levels

ELEMENT	Stock LCS/MS Standard (mg/L)	Working LCS/MS Standard (ug/L)	Aqueous LCS/ MS Level * (ug/l)
Arsenic	400	4000	40
Selenium	400	4000	40
Lead	400	4000	40
Thallium	400	4000	40
Antimony	400	4000	40
Cadmium	40	400	4
Chromium	100	1000	10
Silver	50	500	5

* 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

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: CORP-MT-0001 CORP-MT-0003	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: CORP-MT-0001 CORP-MT-0003	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: CORP-MT-0001 CORP-MT-0003	Reprep not required unless preparation error suspected.
Matrix Spike Duplicate	See Matrix Spike	Refer to determinative SOPs: CORP-MT-0001 CORP-MT-0003	See Corrective Action for Matrix Spike.

APPENDIX B

QUANTERRA METALS PREP BENCHSHEET

Quanterra Metals Preparation Log

Prep Date : _____ Matrix : _____ QC Batch: _____ SOP (circle) : CORP-IP-0001 Rev 0
Analyst : _____ Prep Type (circle): ICP GFAA Method #: _____ CORP-IP-0002 Rev 0
CORP-IP-0003 Rev 0
Other _____

SPIKE	ID	LOT #	Prep Date	Vol. Added	Custom Spike/Comments
LCS					
MS/MSD					

#	Sample ID	Initial Wt (g)/Vol(mL)	Final Wt (g)/Vol(mL)	Comments
BLK				
LCS				
1				
2				
3				
4				
5				
6				
7				
8				
9				
10				
11				
12				
13				
14				
15				
16				
17				
18				
19				
20				
MS				
MSD				

Analyst Signature: _____ Date: _____ Reviewed by: _____ Date: _____

CHAIN-OF-CUSTODY INFORMATION FOR DIGESTATES:
Relinquished By: Date: Received By: Date:

APPENDIX C

CONTAMINATION CONTROL GUIDELINES

APPENDIX C. 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.

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Environmental Services

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QUANTERRA 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 0)

Prepared by: _____
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Reviewed by: _____
Technology Standardization Committee

Approved by: _____
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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. 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.

1.3. Method 7470A is applicable to the preparation and analysis of mercury in ground water, aqueous samples, wastes, wipes, TCLP, EP and other leachates/extracts. Certain solid and sludge type wastes may also be analyzed, however Method 7471A (see CORP-MT-0007) is usually the method of choice. All matrices require sample preparation prior to analysis.

1.4. Method 245.1 is applicable to the determination of mercury in drinking, surface and saline waters, domestic and industrial wastes. All matrices require sample preparation prior to analysis.

1.5. The Quanterra reporting limit for mercury in aqueous matrices is 0.0002 mg/L except for TCLP, SPLP or EPTOX leachates for which the reporting limit is 0.002 mg/L.

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.

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. Seawaters, brines and industrial effluents high in chlorides require additional permanganate (as much as 25 mL) because, during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation 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 head space 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. Procedures shall be carried out in a manner that protects the health and safety of all Quanterra associates.

5.2. Eye protection that satisfies ANSI Z87.1 (as per the Chemical Hygiene Plan), 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 health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the Material Safety Data Sheets (MSDS) maintained in the laboratory. The following specific hazards are known:

5.3.1. The following materials are known to be **corrosive:**

hydrochloric acid, nitric acid and sulfuric acid.

5.3.2. The following materials are known to be **oxidizing agents**:

nitric acid, potassium permanganate, potassium persulfate and magnesium perchlorate.

5.3.3. Mercury is a highly toxic element that must be handled with care. The analyst must be aware of the handling and clean-up techniques before working with mercury. Since mercury vapor is toxic, precaution must be taken to avoid its inhalation, ingestion or absorption through skin. All lines should be checked

for leakage and the mercury vapor must be vented into a hood or passed through a mercury absorbing media such as:

5.3.3.1. Equal volumes of 0.1 M $KMnO_4$ and 10% H_2SO_4, or

5.3.3.2. Iodine, 0.25%, in a 3% KI solution.

5.3.4. Magnesium sulfate is known to be a reproductive toxin (mutagen).

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.

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 Quanterra associate. The situation must be reported **immediately** to a 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 a temperature of 90-95 °C) or autoclave that is able to obtain conditions of 15 lbs., 120 °C for 15 minutes.

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 achieve 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. 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 (1000 ppm) mercury standards (in 10% HNO_3) are purchased as custom Quanterra 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. Intermediate mercury standard (10 ppm): Take 1 mL of the stock mercury standard (7.2) and dilute to 100 mL with reagent water. The intermediate standard must be made monthly and must be prepared in a matrix of 2% HNO_3. This acid (2 mL of concentrated HNO_3) must be added to the flask/bottle before the addition of the stock standard aliquot.

7.4. Working mercury standard (0.1 ppm): Take 1 mL of the intermediate mercury standard (7.3) 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.

7.5. The calibration standards listed in Table I must be prepared fresh daily from the working standard (7.4) by transferring 0, 0.2, 0.5, 1.0, 2.0, 5.0 and 10.0 mL aliquots of the working mercury standard into 100 mL flasks and diluting to volume with reagent water.

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.

7.6. The initial calibration verification standard must be made from a different stock solution than that of the calibration standards.

7.7. 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.

7.8. 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.

7.9. Sulfuric acid (H_2SO_4), concentrated, trace metal grade or better.

7.9.1. Sulfuric acid, 0.5 N: Dilute 14.0 mL of concentrated H_2SO_4 to 1 liter with reagent water.

7.10. Stannous sulfate solution: Add 25 g of stannous sulfate to 250 mL of 0.5 N sulfuric acid. This mixture is a suspension and should appear cloudy. This solution should be made daily and should be stirred continuously during use.

Note: Stannous chloride may be used in place of stannous sulfate. Prepare the stannous chloride solution according to the recommendations provided by the instrument manufacturer.

7.11. 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.

7.12. Potassium permanganate, 5% solution (w/v): Dissolve 5 g of potassium permanganate for every 100 mL of reagent water.

7.13. Potassium persulfate, 5% solution (w/v): Dissolve 5 g of potassium persulfate 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 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

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 7470A or the 245.1, 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 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 Quanterra 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) 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. 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).

- 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 taken in consultation with the client and 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 and the client must be notified.**

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. The CCV results can be reported as LCS results since all CCVs (as well as all other standards) are processed through the sample preparation step with the field samples. No more than 20 samples can be associated with one CCV used for the purpose of reporting LCS data.

- 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 80 - 120% recovery must be applied.

- In the instance where the LCS recovery is > 120% and the sample results are < RL, the data may be reported with qualifiers. Such action must be taken in consultation with the client and must be addressed in the case 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 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 20% 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 11.2.11 and Section 11.2.12 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 associated samples.

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 11.2.11 and 11.2.12 *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. Sample results may only be reported when bracketed by valid ICV/CCV and ICB/CCB pairs. If a mid-run CCV or CCB fails, the analysis must be terminated, the problem corrected, the instrument recalibrated, the calibration verified and the affected samples reanalyzed. If the cause of the CCV or CCB failure was not directly instrument related the corrective action will include repreparation of the associated samples.

9.9. 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 11.2.13 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 Quanterra reporting limit. Analyze standards in ascending order beginning with the blank. Refer to Section 7.5 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.

10.7. 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.

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.

11.1.3. Add 5 mL of concentrated H_2SO_4 and 2.5 mL of concentrated HNO_3 mixing after each addition.

Note: All spiking should be done after the initial addition of acids.

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.

NOTE: Alternatively, for RCRA analyses using 7470A, samples may be digested using an autoclave for 15 minutes at 120 °C and 15 lbs.

11.1.6. Cool samples.

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. 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). Add this solution in 6 mL increments until the permanganate is completely reduced.

11.2.4. Manual determination:

11.2.4.1. Treating each sample individually, purge the head space of the sample bottle for at least one minute.

11.2.4.2. Add 5 mL of stannous chloride solution and immediately attach the bottle to the aeration apparatus.

11.2.4.3. 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.

11.2.4.4. Place the aeration device into 100 mL of 1% HNO_3 and allow to bubble rinse until the next sample is analyzed.

11.2.5. Automated determination: Follow instructions provided by instrument manufacturer.

11.2.6. 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.

11.2.7. 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.

11.2.8. 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.

11.2.9. The samples must be allowed to cool to room temperature prior to analysis or a decrease in the response signal can occur.

11.2.10. 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.

11.2.11. The following analytical sequence must be used with 7470A and 245.1:

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 Methods 7470A and 245.1.

Note: Samples include the method blank, LCS, MS, MSD, duplicate, field samples and sample dilutions.

11.2.12. The following run sequence is consistent with 7470A, CLP and 245.1 and may be used as an alternate to the sequence in 11.2.11. 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

Refer to the appropriate CLP SOP (CORP-MT-0006) for quality control requirements for QC samples.

* Refer to the CLP SOP for information on the CRA.

11.2.13. 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 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 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.

11.6. 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. 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 Quanterra 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:

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. Waste generated in the procedure must be segregated and disposed according to the facility hazardous waste procedures. The Environmental Health and Safety Director should be contacted if additional information is required.

16. REFERENCES

16.1. Test Methods for Evaluating Solid Waste , Physical/Chemical Methods, SW-846, 3rd Edition, Final Update II, Revision I, September 1994, Method 7470A (Mercury).

16.2. "Methods for the Chemical Analysis of Water and Wastes", EPA-600/4-79-020, U.S.EPA, August 1983, Method 245.1.

16.3. U.S.EPA Statement of Work for Inorganics Analysis, ILMO3.0.

16.4. QA-003, Quanterra QC Program.

16.5. QA-004, Rounding and Significant Figures.

16.6. QA-005, Method Detection Limits.

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."

17.1.1.3. The alternate run sequence presented in Section 11.2.12 is consistent with method requirements. An additional QC analysis (CRA) was added to accommodate the CLP protocol requirements.

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.

17.1.2.2. Documentation is on file from EPA's Office of Solid Waste (Olliver Fordham 11/28/95) regarding the acceptance of the autoclave as an equivalent heating device to the water bath. In his letter, Mr. Fordham cited the CLP water protocol 245.1 CLP-M and therefore the operating parameters from that method were adopted for 7470A (15 minutes at 120 °C and 15 lbs.).

17.1.2.3. Method 7470A does not state control criteria within the text of the method. The QC section of 7470A refers the analyst to Section 8.0 of Method 7000A, the generic atomic absorption method, which discusses flame and furnace methods. The ICV criteria stated in Method 7000A is ± 10%. This SOP requires ICV control limits of ± 20% based on the fact that the mercury ICV, unlike the ICV for the flame and furnace analytes, is digested and therefore is equivalent to a LCS. The CLP protocol 245.1 CLP-M recognizes this factor and requires control limits of ± 20%.

17.1.3. Modifications from 245.1

17.1.3.1. Method 245.1 Section 9.3 states concentrations should be reported as follows: Between 1 and 10 ug/L, one decimal; above 10 ug/L, to the nearest whole number. Quanterra reports all Hg results under this SOP to two significant figures.

17.2. Modifications from previous SOP

None.

17.3. Facility Specific SOPs

Each facility shall attach a list of facility specific SOPs or approved attachments (if applicable) which are required to implement this SOP or which are used in conjunction with this SOP. If no facility specific SOPs or amendments are to be attached, a statement must be attached specifying that there are none. Refer to the Appendices for any facility specific information required to support this SOP.

17.4. 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.
- Non-conformance summary (if applicable).

Figure 1. Aqueous Sample Preparation - Mercury

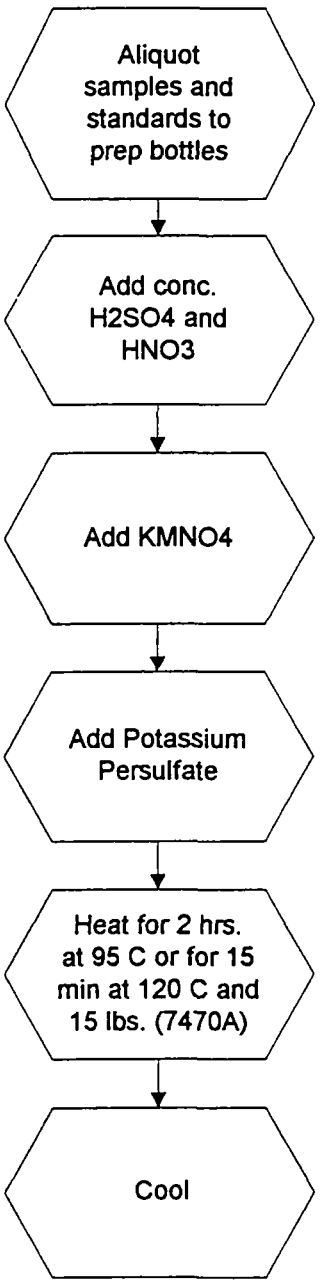
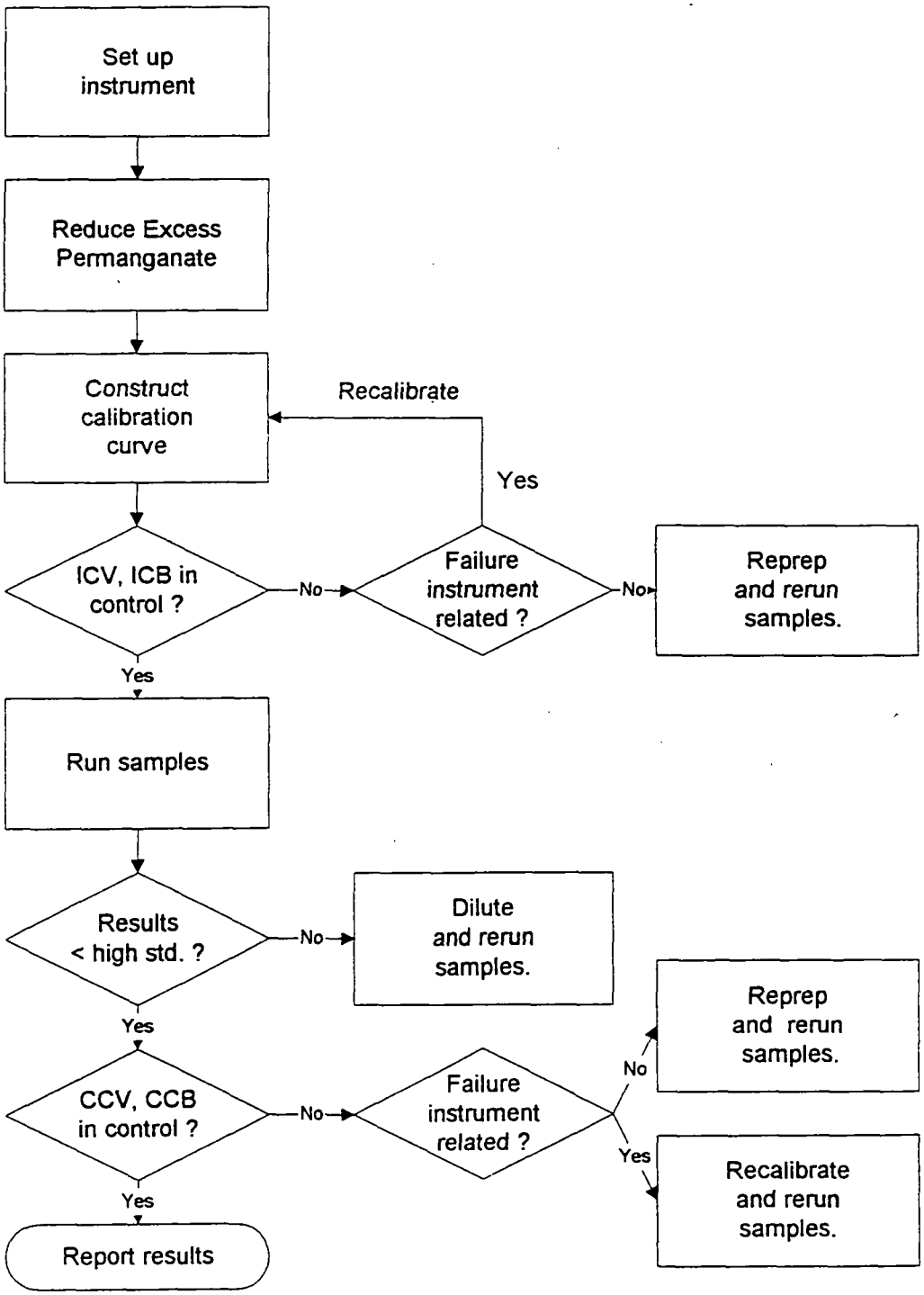


Figure 2. CVAA Mercury Analysis



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	0.0002
Std 2	0.0005
Std 3	0.001
Std 4	0.002
Std 5	0.005
Std 6 **	0.010
ICV	0.001 or 0.0025 ***
LCS/CCV	0.0025 or 0.005 ***
Aqueous MS	0.001
TCLP MS	0.005

* **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 high standard concentration and ICV must be 20-25% of high standard concentration.**

TABLE II. Summary Of Quality Control Requirements

QC PARAMETER	FREQUENCY *	ACCEPTANCE CRITERIA	CORRECTIVE ACTION
ICV	Beginning of every analytical run.	80 - 120 % recovery.	Terminate analysis; Correct the problem; Recalibrate or reprep batch (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 batch (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 batch (see Section 9.8).
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 batch (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 11.2.11 and 11.2.12 for exact run sequence to be followed.

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.	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 11.2.13
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
QUANTERRA Hg DATA REVIEW CHECKLIST

Quanterra 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 / 245.5** : CORP-MT-0007 Rev 1
CLP - AQ : CORP-MT-0006 Rev 0 **CLP - SOL** : CORP-MT-0008 Rev 0

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

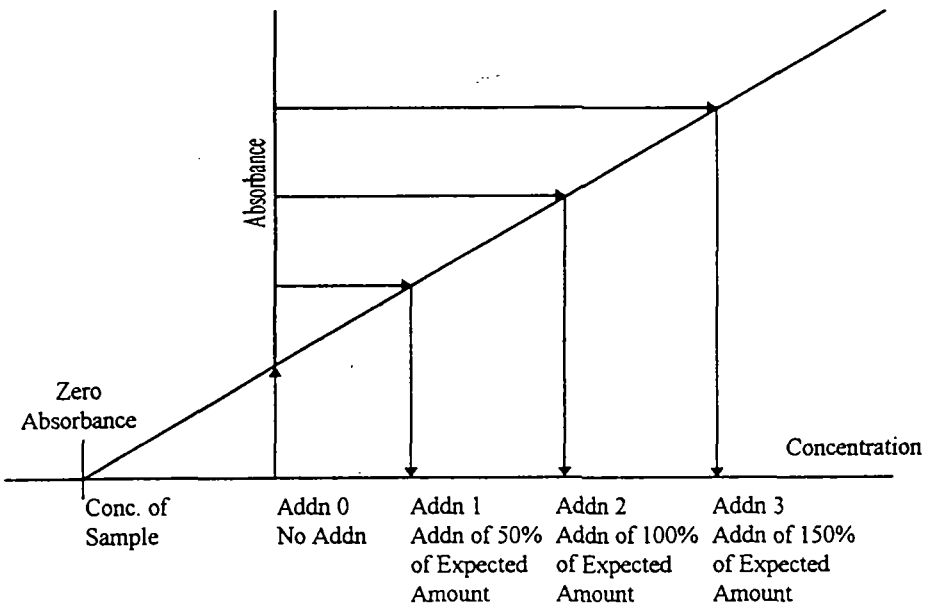
APPENDIX C. MSA GUIDANCE

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.	

QUANTERRA STANDARD OPERATING PROCEDURE

TITLE: INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROSCOPY, SPECTROMETRIC METHOD FOR TRACE ELEMENT ANALYSIS, METHOD 6010A AND METHOD 200.7

(SUPERSEDES: REVISION 0)

Prepared by: _____
Principal Scientist, Inorganics

Reviewed by: _____
Technology Standardization Committee,

Approved by: _____
Director, Quality Assurance,

Approved by: _____
Director, Environmental Health and Safety,

Approved by: _____
Management,

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1. SCOPE AND APPLICATION

1.1. This procedure describes the analysis of certain metals by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP) using SW-846 protocol Method 6010A and Methods for Chemical Analysis of Waters and Wastes protocol, Method 200.7 as published in 40 CFR Part 136, Appendix C. Table I of Appendix A lists the elements approved for analysis by Methods 6010A and 200.7. Additional elements may be analyzed under Methods 6010A and 200.7 provided 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 6010A is applicable to the determination of dissolved, suspended, total recoverable and total elements in ground water, aqueous samples, soils, sludges, wastes, sediments, 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 do require digestion of dissolved samples and this must be clarified before project initiation.

1.4. Method 200.7 is applicable to the determination of dissolved, suspended, total recoverable and total elements in surface water, domestic and industrial waste waters. 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.

1.5. This SOP is not applicable to the analysis of drinking water samples due to the wide array of state specific requirements which must be accommodated. Refer to facility specific SOPs for guidance on performing drinking water analyses.

2. SUMMARY OF METHOD

2.1. This method describes a technique for the determination of elements in solution. 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 a radio frequency inductively coupled plasma (ICP). The spectra are dispersed by a grating spectrometer and the intensities of the 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 where a background corrective measurement would actually degrade the analytical result. The possibility of additional interferences should also be recognized and appropriate actions taken.

2.2. Consult the appropriate SOP's 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. Interelement correction factors (IEC's) are necessary to compensate for spectral overlap. Interelement 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. Interelement corrections (IEC's) must be applied to the analyte to remove the effects of these unwanted emissions. To calculate an IEC, divide the observed concentration of the analyte by the observed concentration of the "interfering element."

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

5.2. Eye protection that satisfies ANSI Z87.1 (as per the Chemical Hygiene Plan), 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 health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the Material Safety Data Sheets (MSDS) maintained in the laboratory.

5.3.1. The following materials are known to be **corrosive**:

sulfuric acid, hydrochloric acid, nitric acid and hydrofluoric acid. (NOTE: sulfuric and hydrofluoric acids are used in cleaning the ICP torch and hydrofluoric acid is also commonly used in air toxics preparations.)

5.3.2. The following materials are known to be **oxidizing agents**:

nitric acid and hydrogen peroxide.

5.3.3. The plasma emits strong UV light and is harmful to vision. AVOID looking directly at the plasma.

5.3.4. 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.

5.4. 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. 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. 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 Quanterra associate. The situation must be reported **immediately** to a laboratory supervisor.

5.7. The use of hydrofluoric acid requires special safety precautions. Consult the facility EH&S Manager and laboratory supervisor for guidance.

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. Nitrogen or 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.

6.7. Class A volumetric flasks.

6.8. Autosampler tubes.

7. REAGENTS AND STANDARDS

7.1. Intermediate standards are purchased as custom Quanterra 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.

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. An exception to this is in the event the Trace ICP is utilized without the internal standard. In this case, the standard acid matrix must be matched to the final preparation matrix as listed in Section 11.10.

7.3. 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.

7.4. Concentrated nitric acid (HNO_3), trace metal grade or better.

7.5. Concentrated hydrochloric acid (HCl), trace metal grade or better.

7.6. 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 analysis.

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

Prior to analysis of any analyte using either Method 200.7 or Method 6010A, the following requirements must be met.

9.1.1. Instrument Detection Limit (IDL) - The IDL for each analyte must be determined for each analyte wavelength used on each instrument. The IDL must be determined annually. If the instrument is adjusted in any way 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 standard solution (each analyte in reagent water) at a concentration 3x - 5x the previously determined IDL, 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 Quanterra reporting limit. The CLP IDL procedure can be used for this method.

9.1.2. 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 Quanterra QA Policy QA-005. 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 Quanterra reporting limit.

9.1.3. Linear Range Verification (LR) - The linear range must be determined on an annual basis for each analyte wavelength used on each instrument. The standards used to define the linear range limit must be analyzed during a routine analytical run. The determined concentration of the linear range standard must be within 5% of the true value. The linear range is the

concentration above which results cannot be reported without dilution of the sample. If the instrument is adjusted in any way that may affect the LR's, the LR's must be redetermined.

9.1.4. 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. Background correction points must be set prior to determining IEC's. Refer to the facility specific instrument operation SOP and ICP instrument manual for specific procedures to be used in setting background correction points.

9.1.5. Interelement Corrections (IEC) - ICP interelement correction factors must be determined prior to the analysis of samples and annually thereafter. If the instrument is adjusted in any way that may affect the IEC's, the IEC's must be redetermined. When initially determining IEC's 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., GFAA or 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 IEC's. Refer to the facility specific instrument operation SOP and 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.

Note: Trace ICP IEC's are more sensitive to small changes in the plasma and instrument setup conditions. Adjustments in the IEC's will be required on a more frequent basis for the Trace as reflected by the ICSA response.

9.1.6. Rinse Time Determination - Rinse times must be determined annually. To determine the appropriate rinse time for a particular ICP system, the linear range verification standard (see 9.1.3) 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). 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).

- If the analyte is a common laboratory contaminant (copper, iron, lead (Trace only) 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 taken in consultation with the client and 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 taken in consultation with the client and 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 and the client must be notified.**

- 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.

9.3. 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. Until 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 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 120% and the sample results are < RL, the data may be reported with qualifiers. **Such action must be taken in consultation with the client and must be addressed in the case 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 (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 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. Control limits of 80 - 120 % 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 4x 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.

- 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. Serial Dilution (L) - Serial dilution analysis 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 serial dilution sample. The serial dilution is performed by running a sample at a 4x dilution. Samples identified as field blanks cannot be used for serial dilution analyses. 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 40x the IDL. If the results are not within 10%, narrate the possibility of chemical or physical interference.

9.6. High Calibration Standard (HCAL) - At the beginning of the run, prior to the analysis of samples, the high standard must be rerun and recovered within 95 - 105%. If any analyte of interest falls outside the acceptance criteria corrective action must occur. The analysis should be terminated, the problem resolved and the instrument recalibrated. (See Section 11.11 or 11.12 for required run sequence.)

9.7. 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. For Method 6010A, the ICV 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, the instrument recalibrated and the calibration reverified. (See Section 11.11 or 11.12 for required run sequence).

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 made from a 2x dilution of the calibration standard. For analyses that require Method 200.7, the CCV result must fall within 5% of the true value for that solution. For Method 6010A, the CCV must fall within 10% of the true value for that solution. A CCB is analyzed immediately following each CCV. (See Section 11.11 or 11.12 for required run sequence.) The CCB result must fall within +/- RL from zero. Sample results may only be reported

when bracketed by valid ICV/CCV and ICB/CCB pairs. If a mid-run CCV or CCB fails, the analysis for the affected element must be terminated, the problem corrected, the instrument recalibrated, the calibration verified and the affected samples reanalyzed. (Refer to Section 11.13 for an illustration of the appropriate rerun sequence).

9.9. 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 Quanterra multielement ICS solutions must be used. All analytes must be spiked into the ICSAB solution, therefore, if a non-routine analyte is required then it must be manually spiked into the ICSAB using a certified ultra high purity single element solution or custom lab-specific mix. 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.

9.9.1. The ICSA and ICSAB solutions must be run at the beginning and end of the run or every 8 hours, whichever is more frequent. (See Section 11.11 or 11.12 for required run sequence.)

9.9.2. 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.

9.9.3. The ICSAB analytes must be recovered within 80 - 120% of the true value. If the ICSAB analytes do not meet criteria the analysis must be terminated, the problem corrected, the instrument recalibrated and the samples rerun for the affected analytes.

9.9.4. ICSA results for the non-interfering elements with reporting limits ≤ 10 ug/L must fall within the Quanterra guidelines of +/- 2x RL from zero. If the ICSA results for the non-interfering elements do not fall within +/- 2x RL 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 IEC's 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.

9.10. CRI - To verify linearity near the RL for ICP analysis, a CRI standard is run at the beginning of each sample analysis run following the ICB. The CRI standard must contain all analytes at two times the RL. The CRI results must fall within 50% of the true value or the run must be terminated, the problem corrected and the instrument recalibrated.

9.11. 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 D for specific MSA requirements.

9.12. Quality Assurance Summaries - Certain clients may require specific project or program QC which may supersede the SOP requirements. Quality Assurance Summaries (QAS) should be developed to address these 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).

10.2. Calibrate the instrument according to the instrument manufacturer's recommendations. Refer to the facility specific instrument SOP and ICP instrument manual for detailed set up and operation protocols.

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 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 samples must be digested unless it can be documented that the sample meets all of the following criteria:

A. COD is < 20 ppm.
B. Visibly transparent with a turbidity measurement of 1 NTU or less.
C. Colorless with no perceptible order.
D. Is of one liquid phase and free of particulate or suspended matter following acidification.

11.2. A minimum of two exposures 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 9.1.6 it can be demonstrated that a shorter rinse time may be used. Triton-X can be added to the rinse solution to facilitate the rinse process.

11.4. The use of an autosampler for all runs is strongly recommended.

11.5. 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.

11.6. 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.

11.7. To facilitate the data review and reporting processes it is strongly recommended that all necessary dilutions and post digestion spikes be performed before closing out the instrument run.

11.8. For unattended overnight auto-runs it is strongly recommended that the frequency of ICSA/ICSAB analysis be increased to every 4 hours.

11.9. The use of an internal standard is recommended on the non-Trace ICP's.

11.10. The use of an internal standard is required 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
CLP Aqueous	1	5
CLP Soil	5	2.5
SW846 3050	5	5
SW846 3005	2	5
SW846 3010	3	5

The following procedural guidelines must be followed when using an internal standard:

11.10.1. Recommended internal standards are yttrium or scandium. (Note: Any element can be used that is not typically found in environmental samples at a high rate of occurrence.)

11.10.2. 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 should be added to blanks, samples and standards in a like manner, so that dilution effects resulting from the addition may be disregarded.

11.10.3. The concentration of the internal standard should 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.

11.10.4. The internal standard raw intensity counts must be printed on the raw data.

11.10.5. 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).

11.10.5.1. If the internal standard counts fall within 30% of the counts observed in the ICB then the data is acceptable.

11.10.5.2. If the internal standard counts in the field samples are more than 30% higher than the expected level, the field samples must then be screened without the addition of the internal standard.

11.10.5.3. If the internal standard element is not identified in the unspiked field sample at a level exceeding 10% of the level spiked, the data may be accepted.

11.10.5.4. If the IS analyte is detected in the unspiked field sample at a concentration greater than 10% of the spiked level then either:

- A different internal standard must be used.
- The IS concentration must be raised.
- The sample must be diluted and rerun.
- The analysis must be run without an internal standard (matrix matching must be substituted.)

11.11. The following analytical sequence must be used for Methods 6010A and 200.7:

Instrument Calibration
ICV
ICB
CRI
HCAL
ICSA
ICSAB
6 samples
CCV
CCB
10 samples
CCV
CCB
Repeat sequence of up to 10 samples between CCV/CCB pairs as required to complete run
CCV
CCB

ICSA
ICSAB
CCV
CCB

Refer to Quality Control Section 9.0 and Table VII (Appendix A) for Method 6010A and 200.7 quality control criteria.

11.12. The following run sequence is consistent with 200.7, 6010A and CLP requirements and may be used as an alternate to the sequence specified in 11.11 if multiple methods must be accommodated in the same analytical run:

Instrument Calibration
ICV
ICB
CRI
HCAL
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
CCV
CCB
CRI
ICSA
ICSAB
CCV
CCB

Refer to the CLP SOP (CORP-MT-0002) for additional quality control requirements.

11.13. 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 9.8:

Original Run: Instrument Calibration
ICV
ICB
CRI
HCAL
ICSA
ICSAB
6 samples
CCV1
CCB1
10 samples
CCV2
CCB2
10 samples **
CCV3 *
CCB3 *
10 samples **
CCV4
CCB4
10 samples
CCV5
CCB5
ICSA
ICSAB
CCV6
CCB6

* Failure occurs at CCV3/CCB3
**Samples requiring rerun for affected analytes

Reanalysis: Recalibrate
ICV
ICB
CRI
HCAL
CCV2
CCB2
10 samples
CCV3
CCB3
10 samples
CCV4
CCB4
ICSA
ICSAB
CCV6
CCB6

Notes: If the reanalysis is conducted under the same instrument setup conditions then it is not necessary to rerun the ICSA/ICSAB at the start of the reanalysis sequence as long as the 8 hour criteria are met. If reanalysis can't be initiated immediately or under the same run conditions then reanalysis must be conducted using the full analysis sequence as detailed in Section 11.11.

Samples between CCV4 and CCV5 do not require reanalysis as they were bracketed by compliant QC samples.

See CORP-MT-0002 for the appropriate reanalysis sequence if CLP requirements must also be met.

11.14. Full method required QC must be available for each wavelength used in determining reported analyte results.

11.15. Guidelines are provided in the appendices on procedures to minimize contamination of samples and standards, preventive maintenance and troubleshooting.

11.16. 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 is established. If an interelement 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.

11.17. 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 E provides guidance on performing MSA analyses.

11.18. 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.

11.19. 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 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
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
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 serial dilution percent difference for each component is calculated as follows:

$$\%Difference = \frac{|I - S|}{I} \times 100$$

Where:
I = Sample result (Instrument reading)
S = Serial dilution result (Instrument reading × 4)

12.9. Appropriate factors must be applied to sample values if dilutions are performed.

12.10. Sample results should be reported with up to three significant figures in accordance with the Quanterra 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. Refer to Tables I, IA & II in Appendix A for the list of Method 6010A 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 matrix spike and matrix spike duplicate samples as well as method blanks and laboratory control samples. 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 Section 9.2. The laboratory control samples should recover within 20% of the true value until in house control limits are established.

13.4. 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. Waste generated in the procedure must be segregated and disposed according to the facility hazardous waste procedures. The Environmental Health and Safety Director should be contacted if additional information is required.

15.2. 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. 40 CFR Part 136, Appendix C, 7-1-92, Method 200.7.

16.2. 40 CFR Part 136, Table IB, 7-1-92.

16.3. Test Methods for Evaluating Solid Waste , Physical/Chemical Methods, SW-846, 3rd Edition, Final Update I, July 1992. Method 6010A.

16.4. CORP-MT-0002, Inductively Coupled Plasma-Atomic Emission Spectroscopy, Method 200.7 CLP-M, SOW ILMO3.0.

16.5. QA-003, Quanterra QC Program.

16.6. QA-004, Rounding and Significant Figures.

16.7. QA-005, Method Detection Limits.

17. MISCELLANEOUS (TABLES, APPENDICES, ETC.)

17.1. Modifications/Interpretations from reference method

17.1.1. Modifications from both Method 6010A and 200.7.

17.1.1.1. Method 200.7 and Chapter 1 of SW846 specify the use of reagent water with a purity equivalent to ASTM Type II 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. The alternate run sequence presented in Section 11.12 is consistent with method requirements. Additional QC analyses were added to accommodate the CLP protocol requirements.

17.1.2. Modifications from Method 200.7.

17.1.2.1. Blank subtraction is not performed as per Quanterra QC policy. Method blank results are provided in the analytical report.

17.1.2.2. 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 a reagent blank signal. Quanterra labs utilize the CLP IDL definition as defined in Section 9.1.1 of this SOP.

17.1.2.3. 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.

17.1.2.4. Section 7.6.3 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.

17.1.2.5. The ICS criteria applied by this SOP differ from those stated in the method. 200.7 states that results should fall within the established control limits of 1.5 times the standard deviation of the mean value. These control criteria were based on a specific solution made available by EMSL-Cincinnati to labs several years ago. Since this solution is no longer available, Quanterra has modeled their ICSA/ICSAB solutions on the design of the ICSA/ICSAB solution provided by EPA directly to EPA contract laboratories. The control limits listed in this SOP are those which EPA states applicable to the EPA designed solution.

17.1.2.6. Method 200.7 states the CCB should be within 2x the standard deviation of the average blank reading. The intent of this requirement is to ensure that the calibration is not drifting at the low end. In the absence of guidance on how to determine the mean blank level from EPA, Quanterra has adopted an absolute control limit of +/- RL from zero for calibration blank criteria.

17.1.3. Modifications from Method 6010A.

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. Calibration is performed according to instrument manufacturer's recommendations. Method 6010A provides contradictory instructions for instrument calibration by stating to calibrate both according to instrument manufacturer's recommendations as well as to use a blank and three standards. TJA has stated that the use of multiple standards may be detrimental to determinations near the detection limit due to the inability of the linear equation to force-fit through the origin (see Appendix C) and recommends the calibration be performed using a blank and one standard. Leeman recommends a blank and three standards. EPA has stated that manufacturer's recommendations should take precedence and that the next version of the method, 6010B, will clear up the issue by stating "The calibration curve should consist of a minimum of a blank and a standard." This SOP requires verification of the initial instrument calibration using a CRI at two times the RL, an ICV at 5 - 25% of the calibration level, a CCV at 50% of the calibration level and by rerunning the high calibration standard (HCAL) post calibration to demonstrate linearity (See Tables I, IA and II).

17.1.3.3. Section 5.6 of 6010A states that the instrument check standard (CCV) should be prepared from a second source standard. This SOP states that the CCV will be from the same source as the calibration standards. The purpose of the second source standard is to verify the accuracy of the calibration standards. The intent of this requirement is met through the analysis of a second source ICV standard prior to the analysis of samples. The use of a same source CCV provides for a more accurate and consistent measure of instrument drift from initial calibration.

17.1.3.4. Section 5.7 states that spiking of the ICS solution with analytes is not required if the ICP will display overcorrection as a negative number. All Quanterra instrumentation has this capability and therefore the spike analysis is not required. Quanterra does run a spiked ICSAB but the analytes are not spiked at the 10x IDL level referenced in 6010A. The ICSAB solution run by Quanterra is based on the design of the ICSA/ICSAB solution provided by EPA directly to contract environmental labs.

17.1.3.5. Method 6010A uses a Quality Control Standard (QCS) on a weekly basis to verify calibration standard accuracy. Quanterra refers to the QCS as an ICV and the accuracy verification is performed on a daily basis. The QCS described in Method 6010A is made to contain analytes at 10x the IDL. The Quanterra ICV solution is not made at 10x IDL for all elements as this concentration is not appropriate relative to the standard reporting limits. Quanterra designed the ICV to be a reliable indicator of calibration standard accuracy by raising the analyte concentrations to a level where the analytical determination is not impacted by low level curve bias.

17.1.3.6. Method 6010A states the CCB should be within 3x the standard deviations of the average blank reading. The intent of this requirement is to ensure that the calibration is not drifting at the low end. In the absence of guidance on how to determine the mean blank level from EPA, Quanterra has adopted an absolute control limit of +/- RL from zero for calibration blank criteria.

17.2. Modifications from previous SOP

None.

17.3. Facility Specific SOP's

Each facility shall attach a list of facility specific SOPs or approved attachments (if applicable) which are required to implement this SOP or which are used in conjunction with this SOP. If no facility specific SOPs or amendments are to be attached, a statement must be attached specifying that there are none. Refer to the appendices for any facility specific information required to support this SOP.

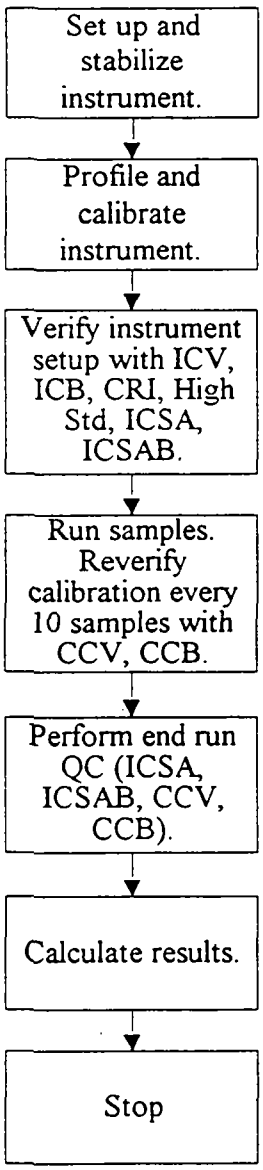
17.4. Documentation and Record Management

The following documentation comprises a complete ICP raw data package:

- Raw data (direct instrument printout signed by analyst).
- Relevant sample preparation benchsheets.
- Run log printout from instrument software where this option is available (TJA) or manually generated run log (i.e., Ward WSL printout).
- Data review checklist - See Appendix B.
- Standards documentation (including prep date, source and lot #).

- Non-conformance summary (if applicable).

17.5. Flow Diagram



APPENDIX A

TABLES

TABLE I. Method 200.7 and 6010A Analyte List

ELEMENT	Symbol	CAS #	6010A 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	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
Lithium	Li	7439-93-1	X		50	5
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
Phosphorus	P	7723-14-0	X		300	30
Potassium	K	7440-09-7	X	X	5000	500
Selenium	Se	7782-49-2	X	X	250	25
Silicon	Si	7631-86-9		X	500	50
Silver	Ag	7440-22-4	X	X	10	1
Sodium	Na	7440-23-5	X	X	5000	500
Strontium	Sr	7440-28-0	X		50	5
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 6010A Trace ICP 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	7440-03-26	50	5
Bismuth	Bi	7440-06-99	200	20
Zirconium	Zr	7440-06-77	100	10
Tungsten	W	7440-03-37	500	50
Tellurium	Te	1349-48-09	500	50
Thorium	Th	7440-02-91	500	50
Uranium	U	7440-06-11	500	50
Palladium	Pd	7440-00-53	100	10

NOTE: Analysis of all elements listed may not be available at all Quanterra facilities.

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
Lithium	1000	1000
Magnesium	50000	50000
Manganese	500	500
Molybdenum	1000	1000
Nickel	500	500
Phosphorous	10000	10000
Potassium	50000	50000
Selenium	2000	2000
Silver	50	50
Sodium	50000	50000
Strontium	1000	1000
Thallium	2000	2000
Vanadium	500	500
Zinc	500	500
Boron	1000	1000
Silicon	10000	10000
Tin	2000	2000
Titanium	1000	1000
Bismuth	1000	1000
Zirconium	1000	1000
Tellurium	1000	1000
Thorium	1000	1000
Uranium	1000	1000
Tungsten	1000	1000
Palladium	1000	1000

TABLE IV. ICP Calibration and Calibration Verification Standards

Element	Calibration Level	RL (ug/L)	CRI (ug/L)	ICV (ug/L)	CCV (ug/L)
Aluminum	100000	200	400	25000	50000
Antimony	10000	60	120	1000	5000
Arsenic	10000	300	600	1000	5000
Barium	10000	200	400	1000	5000
Beryllium	10000	5	10	1000	5000
Cadmium	10000	5	10	1000	5000
Calcium	100000	5000	10000	25000	50000
Chromium	10000	10	20	1000	5000
Cobalt	10000	50	100	1000	5000
Copper	10000	25	50	1000	5000
Iron	100000	100	200	25000	50000
Lead	10000	100	200	1000	5000
Lithium	10000	50	100	1000	5000
Magnesium	100000	5000	10000	25000	50000
Manganese	10000	15	30	1000	5000
Molybdenum	10000	40	80	1000	5000
Nickel	10000	40	80	1000	5000
Phosphorous	10000	300	600	1000	5000
Potassium	100000	5000	10000	25000	50000
Selenium	10000	250	500	1000	5000
Silver	2000	10	20	500	1000
Sodium	100000	5000	10000	25000	50000
Strontium	10000	50	100	1000	5000
Thallium	20000	2000	4000	5000	10000
Vanadium	10000	50	100	1000	5000
Zinc	10000	20	40	1000	5000
Boron	10000	200	400	1000	5000
Silicon	10000	500	1000	1000	5000
Tin	10000	100	200	1000	5000
Titanium	10000	50	100	1000	5000
Bismuth	10000	200	400	1000	5000
Zirconium	10000	100	200	1000	5000
Tellurium	10000	500	1000	1000	5000
Thorium	10000	500	1000	1000	5000
Uranium	10000	500	1000	1000	5000
Tungsten	10000	500	1000	1000	5000
Palladium	10000	100	200	1000	5000

TABLE IVA. Trace Calibration and Calibration Verification Standards

Element	Calibration Level	RL (ug/L)	CRI (ug/L)	ICV (ug/L)	CCV (ug/L)
Aluminum	50000	200	400	12500	25000
Antimony	1000	10	20	250	500
Arsenic	1000	10	20	250	500
Barium	4000	10	20	1000	2000
Beryllium	4000	5	10	1000	2000
Cadmium	1000	2	4	250	500
Calcium	100000	5000	10000	25000	50000
Chromium	4000	5	10	1000	2000
Cobalt	4000	50	100	1000	2000
Copper	4000	25	50	1000	2000
Iron	50000	100	200	12500	25000
Lead	1000	3	6	250	500
Magnesium	100000	5000	10000	25000	50000
Manganese	4000	15	30	1000	2000
Molybdenum	4000	40	80	1000	2000
Nickel	4000	40	80	1000	2000
Potassium	100000	5000	10000	25000	50000
Selenium	1000	5	10	250	500
Silver	2000	5	10	500	1000
Sodium	100000	5000	10000	25000	50000
Thallium	2000	10	20	500	1000
Vanadium	4000	50	100	1000	2000
Zinc	4000	20	40	1000	2000

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

* Custom Quanterra solutions contain analytes common to all Quanterra facilities. Non-routine elements not listed above must be spiked into the ICSAB at 1000 ug/L.

TABLE VI. 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

TABLE VII. Summary Of Quality Control Requirements

QC PARAMETER	FREQUENCY *	ACCEPTANCE CRITERIA	CORRECTIVE ACTION
Reanalysis of High Standard (HCAL)	Beginning of every analytical run, after CRI.	95 - 105 % recovery.	Terminate analysis; Correct the problem; Recalibrate.
ICV	Beginning of every analytical run.	Method 200.7: 95 - 105 % recovery. Method 6010A: 90 - 110 % recovery.	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: 95 - 105 % recovery. Method 6010A: 90 - 110 % recovery.	Terminate analysis; Correct the problem; Recalibrate and rerun all samples not bracketed by acceptable CCV.
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.
ICSA	Beginning and end of every run and every 8 hours.	Analyte results must be within +/- 2x RL from zero for analytes with RL ≤ 10 ug/L.	See Section 9.9.
ICSAB	Immediately following each ICSA.	Results must be within 80 - 120% recovery.	See Section 9.9.
CRI	Immediately following ICB.	Results must be within 50 - 150% recovery.	Terminate analysis; Correct the problem; Recalibrate.

* See Sections 11.11 and 11.12 for exact run sequence to be followed.

TABLE VII. Summary of Quality Control Requirements (Continued)

QC PARAMETER	FREQUENCY	ACCEPTANCE CRITERIA	CORRECTIVE ACTION
Serial Dilution	One per prep batch.	For samples > 40x IDL, dilutions must agree within 10%.	Narrate the possibility of physical or chemical interference.
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 after consultation with the client (See 9.2). Sample results greater than 20x the blank concentration are acceptable. Samples for which the contaminant is < RL may not require redigestion or reanalysis (see Section 9.2).	Redigest 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 redigestion or reanalysis (see Section 9.3)	Terminate analysis; Correct the problem; Redigest and reanalyze all samples associated with the LCS.
Matrix Spike	One per sample preparation batch of up to 20 samples.	80 - 120 % recovery. If the MS/MSD is out for an analyte, it must be in control in the LCS. For TCLP See Section 11.17.	In the absence of client specific requirements, flag the data; no flag required if the sample level is > 4x the spike added. For TCLP see Section 11.17.
Matrix Spike Duplicate	See Matrix Spike	80 - 120 % recovery; RPD ≤ 20% (See MS).	See Corrective Action for Matrix Spike.

APPENDIX B

QUANTERRA ICP DATA REVIEW CHECKLIST

Quanterra ICP Data Review Checklist

Run/Project Information:

Run Date: _____ **Analyst:** _____ **Instrument:** _____
Prep Batches Run: _____

Circle Methods used: **6010A / 200.7: CORP-MT-0001 Rev 0**
CLP : CORP-MT-0002 Rev 0

Review Items

A. Calibration/Instrument Run QC	Yes	No	N/A	2nd Level
1. Instrument calibrated per manufacturer's instructions and at SOP specified levels ?				
2. ICV/CCV analyzed at appropriate frequency and within control limits ? (6010A, CLP = 90 - 110%, 200.7 = 95 -105%)				
3. ICB/CCB analyzed at appropriate frequency and within +/- RL or +/- CRDL (CLP) ?				
4. High Std. (HCAL) reanalyzed before samples and recovered within QC limits ? (6010A/200.7 95-105%, CLP- N/A)				
5. CRI run and recovered within QC limits ? (+/- 50% for non-CLP)				
6. ICSA/ICSAB run at required frequency and within SOP limits ?				
B. Sample Results				
1. Were samples with concentrations > the linear range for any parameter 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 ?				
5. Serial dilution done per prep batch (or per SDG for CLP) ?				
6. Post digest spike analyzed if required (CLP only) ?				
D. Other				
1. Are all nonconformances documented appropriately ?				
2. Current IDL/LR/IEC data on file ?				
3. Calculations checked for error ?				
4. Transcriptions checked for error ?				
5. All client/project specific requirements met ?				
6. Date/time of analysis verified as correct ?				

Analyst: _____ **Date:** _____
Comments: _____

2nd Level Reviewer : _____ **Date:** _____
Comments: _____

APPENDIX C

TJA CALIBRATION RECOMMENDATION

Thermo Jarrell Ash Corporation

85 Forge Parkway
Franklin, MA 02038-3148

(508) 520-1880
Fax: (508) 520-1732
Telex: 174230 TJA UT

Ms. Ruth Wolfe
Enseco, RMAL
4955 Yarrow St.
Arvada, CO 8002

Dear Ruth,

I would like to respond to your question concerning the recommended standardization procedure for the ICP instrument you own. As the manufacturer, we recommend a 2-point standardization verified by an independent standard which is normally done with every analytical run when using EPA protocols. Since the instrument is known to be linear for at least five orders of magnitude of concentration, using multiple standards is unnecessary and may be detrimental to determinations near the detection limit. This is due to the inability of the linear equation to force-fit through the origin. Therefore, if the multiple standards are not made to exact specifications, there may be a bias near the origin.
Most EPA methods recognize this and follow the procedure I've recommended above, verifying the upper linear range on a quarterly basis.
If you need additional information concerning the standardization procedure please let me know.

Regards,

Bob Foster

Bob Foster

A subsidiary of
Thermo Instrument
Systems Inc.

APPENDIX D

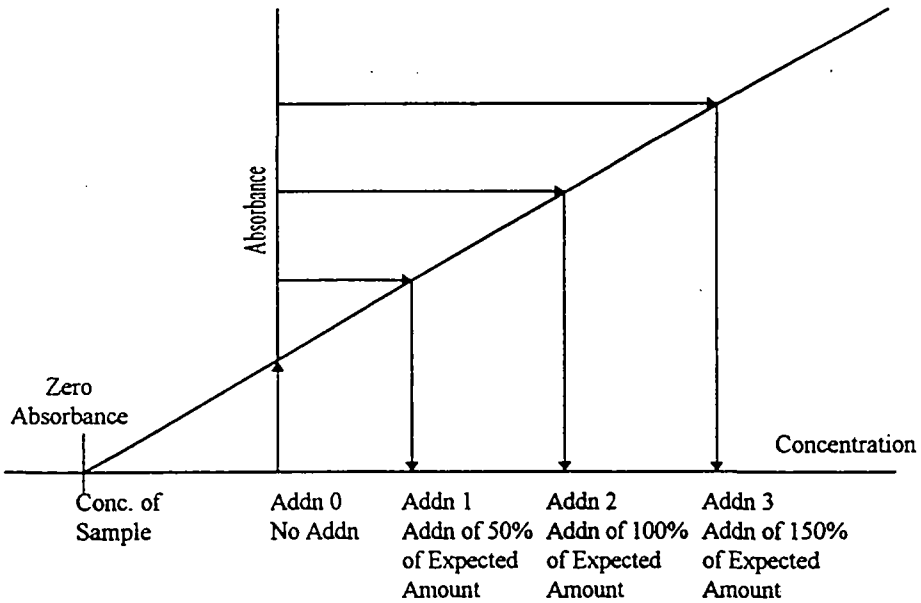
MSA GUIDANCE

Appendix D. 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 E

TROUBLESHOOTING GUIDE

APPENDIX E. 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
Cu/Mn Ratio Outside Limits or Low Sensitivity	Plasma conditions changed Clean nebulizer, torch or spray chamber Replace tubing (clogged) Realign torch Check IEC's
Standards reading twice normal absorbance or concentration	Incorrect standard used Incorrect dilution performed

APPENDIX F

CONTAMINATION CONTROL GUIDELINES

APPENDIX F. 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 G

PREVENTIVE MAINTENANCE

APPENDIX G. 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 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 droplet size to verify nebulizer is not clogged.
- Check sample flow for cross flow nebulizer
- Check Cu/Mn ratio-should be 30% of value at date that IECs were performed
- 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 autosamper sipper probe

Weekly
- Apply silicon spray on autosampler tracks
- Check water level in coolflow

Monthly
- Clean air filters on back of power unit to remove dust
- Check D mirror for air instruments

Bi-yearly
- Change oil for vacuum systems
- Replace coolant water filter (may require more or less frequently depending on quality of cooling water)

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SOP No. CORP-MT-0003
Revision No. 1
Revision Date: 08-22-95
Page: 1 of 48

QUANTERRA STANDARD OPERATING PROCEDURE

TITLE: GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROSCOPY, SW-846 METHOD 7000A AND MCAWW 200 SERIES METHODS

(SUPERSEDES: REV. 0)

Prepared by: _____
Principal Inorganic Scientist

Reviewed by: _____
Technology Standardization Committee

Approved by: _____
Director, Quality Assurance

Approved by: _____
Director, Environmental Health and Safety

Approved by: _____
Management

Proprietary Information Statement:

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1. SCOPE AND APPLICATION

1.1. This procedure describes the analysis of certain metals by Graphite Furnace Atomic Absorption Spectroscopy (GFAA) using SW-846 protocol, Method 7000A and the MCAWW 200 series methods. Table I (Appendix A) lists the routine elements approved for analysis by Method 7000A and the 200 series methods. Table IA (Appendix A) lists non-routine elements that may be analyzed under Method 7000A and the 200 series methods, provided the method performance criteria presented in Section 13.0 are met.

1.2. GFAA analysis provides for the determination of metal concentrations in the parts per billion range. Detection limits, sensitivity and optimum concentration ranges of the metals will vary with the matrices and instrumentation used. The sensitivity and limited linear dynamic range of GFAA often implies the need to dilute a sample prior to analysis. The actual magnitude of the dilution can dramatically influence the quality of the analytical results. Therefore, sample types requiring large dilutions (>50:1) should be analyzed by another client approved test procedure that has a larger linear dynamic range or that is inherently less sensitive than GFAA.

1.3. Method 7000A is applicable to the determination of dissolved, suspended, total recoverable and total elements in ground water, aqueous samples, solids, sludges, wastes, sediments, air sampling media, biological tissue, wipes 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 do require digestion of dissolved samples and this must be clarified before project initiation.

1.4. 200 series methods are applicable to the determination of dissolved, suspended, total recoverable and total elements in ground water, aqueous samples, solids, sludges, wastes, and sediments. 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 11.2 are met. 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.

1.5. This method is not applicable to drinking water samples due to the wide array of state specific requirements which must be accommodated. Refer to facility specific SOPs for guidance on performing drinking water analyses.

2. SUMMARY OF METHOD

2.1. This method describes a technique for the determination of elements in solution. The basis of the method is the measurement of atomic absorption by an optical spectroscopic technique. A representative aliquot of a sample is placed in a graphite tube in the furnace, evaporated to dryness, charred and atomized, causing the atoms to be vaporized and dissociated within the graphite tube. A light beam from a hollow cathode lamp (HCL) or electrodeless discharge lamp (EDL) is directed through the graphite tube. The intensity of the transmitted radiation decreases in proportion to the amount of the ground state atoms in the vapor contained within the graphite tube. Because the wavelength of the light beam is characteristic of the metal being determined, the light energy absorbed by the sample in the tube is a measure of the concentration of that metal in the sample. Concentration of the analyte in the sample is determined by comparison of the sample absorbance to the calibration curve (absorbance vs. concentration).

2.2. Consult the appropriate SOP's 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

Chemical and physical interferences are prevalent when analyzing samples using these methods.

4.1. The problem of oxide formation is greatly reduced with furnace procedures because atomization occurs in an inert atmosphere. The technique, however, is still subject to chemical interferences. The composition of the sample matrix can have a major effect on the analysis and must be taken into consideration in the analysis of each different matrix encountered. The effects of the sample matrix are evaluated by following the spike recovery check procedure described in Section 9.7.

4.2. Matrix modifiers are added to the samples prior to the determination of most analytes. The modifier prevents premature loss of the analytes as volatile salts and/or helps prevent signal suppression during atomization due to the formation of high temperature stable complexes.

4.3. Background interferences must be compensated for by the use of background correction. Background correction is especially important below 350 nm. Certain samples, when atomized, may absorb or scatter light from the lamp. This can be caused by the presence of gaseous molecular species, salt particles, or smoke in the sample beam. If no correction is made, sample absorbance will be greater than it should be, and the analytical result will be erroneously high. Continuum background correction cannot correct for all types of background interference. When the background interference cannot be compensated for, chemically remove the analyte or use an alternate form of background correction (e.g., Zeeman). Zeeman background correction is effective in overcoming composition or structured background interferences. It is particularly useful when analyzing for As in the presence of Al and when analyzing for Se in the presence of Fe.

4.4. Interference from a smoke-producing sample matrix can sometimes be reduced by extending the charring time at a higher temperature or utilizing an ashing cycle in the presence of air, or by diluting the sample. Care must be taken, however, to prevent the loss of the analyte.

4.5. The mixing of hydrogen with the inert purge gas has also been used to suppress chemical interference. The hydrogen acts as a reducing agent and aids in molecular dissociation, also it facilitates the binding of the Pd matrix modifier with the element of interest.

4.6. Samples containing large amounts of organic materials should be oxidized by acid digestion before being placed in the furnace. In this way, broad band absorption will be minimized.

4.7. Carbide formation, resulting from the chemical environment of the furnace, has been observed in certain elements that form carbides at higher temperatures (e.g., Mo, V). When carbides form, the metal is released very slowly from the resulting metal carbide during the atomization cycle. For example, molybdenum may require 30 sec or more atomization time for the signal to return to the baseline level. Carbide formation is greatly reduced and sensitivity increased with the use of pyrolytically coated graphite.

4.8. Based on anion interference studies in the graphite furnace, it is generally accepted that nitrate is the preferred anion to combine with metal cations. Therefore, nitric acid is preferable for any digestion or solubilization step. If another acid in addition to

nitric acid is required, a minimum amount should be used. This applies particularly to hydrochloric acid and, to a lesser extent, to sulfuric and phosphoric acids.

4.9. Memory effects occur when the analyte is not totally volatilized during atomization. The analyte which remains in the furnace can produce false positive signals on subsequent samples. This condition depends on several factors: volatility of the element and its chemical form, whether pyrolytic graphite is used, the rate of atomization and furnace design. The analyst should establish the analyte concentration which can be injected into the furnace and adequately removed in one complete set of furnace cycles. This concentration represents the maximum concentration of analyte within a sample which will not cause a memory effect on the subsequent samples. If during a sample analysis run this concentration is exceeded, the tube should be cleaned by performing blank tube burns , as needed, to assure the memory interference has been eliminated before continuing sample analysis.

4.10. Specific element interferences

- High lead concentrations cause spectral interferences for **antimony** on the 217.6-nm line. The interference is eliminated by the use of Zeeman background correction or the use of the secondary wavelength. Antimony also suffers from an interference produced by K_2SO_4. In the absence of hydrogen in the char cycle, K_2SO_4 produces a relatively high background absorbance, which can produce a false signal, even with Zeeman background correction. However, this background level can be dramatically reduced by the use of a hydrogen/argon gas mixture in the char step.

- **Arsenic** and **selenium** analyses are subject to many interferences. Elemental arsenic and selenium and their compounds are volatile and are subject to losses during sample preparation. Verify that the analyte is not volatilized using spike samples. A matrix modifier must be added to minimize volatilization during drying and ashing. Caution must be employed in selecting temperatures and times for the dry and char steps. In addition to the normal interferences, arsenic and selenium can suffer from severe nonspecific absorption and light scattering caused by matrix components during atomization. Arsenic analysis is particularly susceptible to these problems because of its low analytical wavelength (193.7 nm). Zeeman background correction is strongly recommended to avoid erroneous high results for arsenic from aluminum interferences and low bias for selenium from iron interferences. The use of hydrogen as a purge gas during the dry and char steps can cause a suppression in selenium response if not purged from the furnace before atomization.

- **Cadmium** can be affected by severe nonspecific absorption and light scattering caused by matrix during atomization. To minimize this, simultaneous background

correction is required. A matrix modifier solution can reduce the effects of premature volatilization from excess chlorides.

- Due to interferences from nonspecific absorption and scattering, background correction should be used when analyzing for **chromium**. Low concentrations of calcium and/or phosphate may also cause interferences. Chromium is very susceptible to carbide formation and memory effects (see Sections 4.7 and 4.9). Nitrogen should not be used as the purge gas because of a possible CN band interference.

- For **lead**, matrix modification should be used to suppress sulfate interferences.

- The use of hydrochloric acid should be avoided for **silver** analysis since silver chloride is insoluble. Storage of silver standards in brown bottles may prevent silver nitrates from plating on the container walls.

- Hydrochloric acid or excessive chlorides will cause volatilization of **thallium** at low temperatures. The use of spike samples helps to verify that losses are not occurring. If analyses are being done using continuum background correction in combination with the use of a palladium modifier an over-correction of the background signal may result. This over-correction only occurs at atomization temperatures high enough to volatilize palladium. Since thallium is very volatile, it is possible to fully volatilize the thallium (at 1600 C) without volatilizing palladium.

5. SAFETY

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

5.2. Eye protection that satisfies ANSI Z87.1 (as per the Chemical Hygiene Plan), 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 health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the Material Safety Data Sheets (MSDS) maintained in the laboratory. The following specific hazards are known:

5.3.1. The following materials are known to be **corrosive:**

hydrochloric acid, nitric acid, sulfuric acid, phosphoric and hydrofluoric acid.

5.3.2. The following materials are known to be **oxidizing agents**:

nitric acid and hydrogen peroxide.

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. 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. 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. The use of hydrofluoric acid requires special safety precautions. Consult the facility EH&S manager and laboratory supervisor for guidance.

5.7. All work must be stopped in the event of a known or potential compromise to the health and safety of a Quanterra associate. The situation must be reported **immediately** to a laboratory supervisor.

5.8. The Zeeman background correction technique utilizes a strong magnet. People with electronic cardiac pacemakers or similar devices that are affected by strong magnetic fields should not be near the instruments during operation.

5.9. Do not look directly into the beam of a HCL or EDL. The UV light that these lamps radiate is harmful to the eyes.

5.10. Do not look directly at the graphite tube when it is heated to incandescence to avoid possible injury to the eyes from the intense radiation.

5.11. The furnace heats to approximately 3000°C during atomization. Therefore, to avoid burns, be cautious not to touch the furnace housing until the furnace has cooled sufficiently.

5.12. 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.

5.13. The furnace must be properly vented with an exhaust hood directly over the furnace chamber to remove potentially harmful fumes generated when samples are heated.

6. EQUIPMENT AND SUPPLIES

6.1. Atomic Absorption Spectrophotometer equipped with graphite furnace, autosampler and background correction.

6.2. Hollow cathode (HCL) or electrodeless discharge lamp (EDL) with EDL power supply.

6.3. Argon gas supply, welding grade or equivalent. A premixed 5% hydrogen/95% argon gas is strongly recommended to enhance matrix modifier performance when using palladium in combination with magnesium nitrate.

6.4. Graphite tubes and platforms.

6.5. Coolflow or appropriate water cooling device.

6.6. Calibrated automatic pipettes or Class A glass volumetric pipettes.

6.7. Class A volumetric flasks.

6.8. Autosampler cups.

6.9. Disposable cups or tubes.

7. REAGENTS AND STANDARDS

7.1. Stock standards are purchased as custom Quanterra multi-element mixes or as single element 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.

7.2. Working calibration and calibration verification solutions must be made daily. Standards must be prepared in a matrix of 2% HNO_3 per 100 mL for all analytes except antimony. Antimony standards must be made in a matrix of 2% HNO_3 and 5% HCl.

7.3. Refer to Tables III, IV, and V (Appendix A) for details regarding the working standard concentrations for calibration, calibration verification and spiking solutions.

7.4. Concentrated nitric acid (HNO_3), trace metal grade or better.

7.5. Concentrated hydrochloric acid (HCl), trace metal grade or better.

7.6. Hydrogen peroxide (H_2O_2), 30%.

7.7. 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.

7.8. Matrix modifiers as recommended by instrument manufacturers. The use of a palladium modifier is strongly recommended for the determination of all analytes. This will correct for general chemical interferences as well as allow for higher char and atomization temperatures without allowing the premature liberation of analyte. EPA has recommended a combination modifier of palladium, magnesium nitrate and a hydrogen (5%)/argon (95%) gas mixture in their most recent method releases.

7.8.1. Dissolve 300 mg palladium powder in concentrated HNO_3 (1 mL of HNO_3, adding 0.1 mL of concentrated HCl, if necessary). Dissolve 200 mg of $Mg(NO_3)_2$ in reagent water. Pour the two solutions together and dilute to 100 mL with reagent water.

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. 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 analysis.

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 the analysis of any analyte using 7000A or the 200 series methods, the following requirements must be met.

9.1.1. Instrument Detection Limit (IDL) -The IDL for each analyte must be determined for each analyte wavelength used on each instrument. The IDL must be determined annually. If the instrument is adjusted in any way that may affect the IDL, the IDL for that instrument must be redetermined. For example, the IDL must be redetermined after the instrument is moved or the internal optics cleaned. The IDL shall be determined by multiplying by 3, the standard deviation obtained from the analysis of a standard solution (each analyte in reagent water) at a concentration 3 - 5 times the previously determined IDL, 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). Analytical spikes are not required for IDL determinations by 7000A and 200 series methods. IDLs determined by the CLP procedure can be used for this method. The result of the IDL determination must be below the Quanterra reporting limit.

9.1.2. 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 as detailed in Quanterra QA Policy QA-005. 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 Quanterra reporting limit.

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 20 times higher than the blank contamination level).

- 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 taken in consultation with the client and 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 taken in consultation with the client and 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 and the client must be notified.**

- For dissolved metals samples which have not been digested, a continuing calibration blank (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. The LCS is used to monitor the accuracy of the analytical process. Aqueous LCS spike levels are provided in Table III (Appendix A). 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. Until 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 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 120% and the sample results are < RL, the data may be reported with qualifiers. **Such action must be taken in consultation with the client and must be addressed in the case 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 continuing calibration verification (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 (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 III (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. Until in-house control limits are established, a control limit of 80 - 120 % 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.

- 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. 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 11.14 for required run sequence).

9.6. 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 analyses that require 200 series methods the CCV result must fall within 10% of the true value. For Method 7000A, the CCV result must fall within 20% of the true value for that solution. A CCB is analyzed immediately following each CCV. (See Section 11.14 and 11.15 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. Sample results may only be reported when bracketed by valid ICV/CCV and ICB/CCB pairs. If a mid-run CCV or CCB fails, the analysis must be terminated, the problem corrected, the instrument recalibrated, the calibration verified and the affected samples reanalyzed.

9.7. Spike Recovery Check (AS) - In order to verify the presence or absence of matrix interferences, a post digest analytical spike is analyzed for each sample, including the method blank. A post digest spike is not required on the LCS or matrix spike sample. The analytical spike of a sample must be run immediately after that sample. See Table III (Appendix A) for spiking levels. The percent recovery of the spike will then determine how the sample will be quantitated and reported as follows:

- If the spike recovery is less than 40%, the sample must be diluted and rerun with another spike (recommended dilution 5-10X). If the spike recovery still falls less than 40% the client should be contacted and an alternate method of analysis recommended (i.e., Trace or ICP).

- If the spike recovery is greater than or equal to 40% and less than 85%, report the data with the following flag: "Post digestion spike recovery fell between 40-85% due to matrix interference."

- If the spike recovery is greater than or equal to 85% and less than or equal to 115%, report the data unflagged.

- If the spike recovery is greater than 115% and less than 150% and the sample result is less than the Quanterra reporting limit, then report the data unflagged.

- If the spike recovery is greater than 115% and less than 150% and the sample result is greater than the Quanterra reporting limit, then report the data with the

following flag: "Post digestion spike recovery fell between 115-150% due to matrix interference."

- If the spike recovery is greater than 150% and the sample result is less than the Quanterra reporting limit, then report the data unflagged.
- If the spike recovery is greater than 150% and the sample result is greater than the Quanterra reporting limit then dilute the sample and rerun with another spike. Until the spike recovery falls less than 150%, this dilution step must be repeated.
- If the method blank (MB) analytical spike recovery is less than 85% or greater than 115%, the spiking solution must be verified by respiking and rerunning the MB once. If the MB analytical spike is still out of control, correct the problem and reanalyze all analytical samples associated with that blank.

9.8. 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. By definition, the recovery check procedure defined in Section 9.7 is a single point MSA. Sample results are not biased corrected based on the single point MSA result unless this is specifically requested by the client. Refer to Section 11.16 for additional information on when full 4 point MSA is required as well as Appendix C for specific MSA requirements.

9.9. Quality Assurance Summaries - Certain clients may require specific project or program QC which may supersede the SOP requirements. Quality Assurance Summaries (QAS) should be developed to address these 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 facility specific instrument SOP and GFAA instrument manual for detailed setup and operation protocols.

10.2. Calibrate the instrument according to instrument manufacturer's instructions, using a minimum of three standards and a blank. See Table V (Appendix A) for calibration standard details. One standard must be at the Quanterra reporting limit as defined in Tables I and IA (Appendix A). Calibration standards must be prepared fresh daily.

10.3. Calibration must be performed daily (every 24 hours) and each time the instrument is set up for an element. The instrument calibration date and time must be included in the raw data.

10.4. Refer to Section 9.0 for calibration verification procedures, acceptance criteria and corrective actions.

11. PROCEDURE

11.1. Because of differences between various makes and models of GFAA instrumentation, no detailed operating instructions can be provided. Refer to the facility specific instrument operating SOP and the GFAA instrument manual for detailed setup and operation protocols.

- Table II (Appendix A) provides recommended GFAA analytical guidelines for wavelength, char and atomization temperatures, and tube type.
- All labs are required to detail the furnace conditions/programs utilized for each analyte/instrument within the facility specific instrument operation SOP.

11.2. For 200 series analyses, dissolved samples must be digested unless it can be documented that the sample meets all of the following criteria:

A. COD is < 20 ppm.
B. Visibly transparent with a turbidity measurement of 1 NTU or less.
C. Colorless with no perceptible odor.
D. Is of one liquid phase and free of particulate or suspended matter following acidification.

11.3. The use of an autosampler for all runs is required. The use of an autosampler for the addition of matrix modifier and analytical post digestion spikes is strongly recommended if the instrument in use is capable of the automated additions.

11.4. To reduce the number of reruns due to dilutions it is recommended that whenever possible the samples be run by ICP first to "screen" the samples prior to GFAA analysis. The information obtained from the ICP run will enable the analyst to either eliminate the GFAA analysis completely (i.e., if sufficiently high report ICP result with client approval) or dilute the samples appropriately. Screening also may prevent potential contamination of the analytical system as well as other samples during the instrument run.

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 and post digestion spikes be performed before closing out the instrument run.

11.7. Daily, prior to the analysis of samples, a sensitivity check must be performed and recorded. The sensitivity of the instrument may be checked by either comparing the absorbance of the mid level calibration standard to the absorbance of the same standard used during the IDL determination or by calculating the characteristic mass. If the daily results do not compare within +/- 30% of the reference sensitivity the instrument may need adjustment. Refer to Appendix D for assistance if the criterion is not met.

11.8. At a minimum, single burn analyses will be performed. When double burns are performed, the CV or RSD must be less than or equal to 20% if the sample results are greater than the reporting limit.

11.9. 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. Acid strength must be maintained in the dilution of samples through the use of acidified dilution water (2% HNO_3).

11.10. 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.

11.11. Samples requiring large dilutions due to the presence of high concentrations of analyte may be reported using alternate techniques (i.e., ICP, flame) **with the approval of the client**. Whenever possible, samples should be processed by ICP, prior to GFAA, to facilitate in determining appropriate dilution factors or eliminate the GFAA analysis altogether.

11.12. Baseline correction or cleanout burns are 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. Cleanout burns must be counted as injections when determining instrument QC frequency.

11.13. Graphite tubes may be changed during an analytical run, providing the last samples analyzed on the tube are a compliant CCV and CCB, and the first samples analyzed on the new tube are a compliant CCV and CCB.

11.14. The following analytical sequence must be used with 7000A and 200 series methods:

Instrument Calibration (Blank and three standards)
ICV
ICB
Maximum 10 samples
CCV
CCB
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 VI (Appendix A) for quality control criteria to apply to Methods 7000A and the 200 series methods.

Note: Samples include the method blank, LCS, MS, MSD, duplicate, field samples and sample dilutions. Spike recovery check (AS) injections are not considered as independent samples for the purpose of determining instrument QC frequency.

11.15. The following run sequence is consistent with 7000A, CLP and 200 series, and may be used as an alternate to the sequence in 11.14. This run sequence is recommended if multiple method requirements must be accommodated in one analytical run:

Instrument Calibration (Blank and three standards)
ICV
ICB
CRA**
CCV
CCB
5* samples with AS (maximum 20 burns)
CCV
CCB
5* samples with AS (maximum 20 burns)
CCV
CCB
Repeat sequence of 5* samples between CCV/CCB pairs as required to complete run.
CCV
CCB

Refer to the appropriate CLP SOP (CORP-MT-0004) for quality control requirements for QC samples.

* Note- Only 5 samples can be analyzed between CCV/CCB because double burn analyses are performed as required by CLP protocols.

**Note- Refer to the CLP SOP for information on the CRA.

11.16. 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 IV (Appendix A). Appendix C provides guidance on performing MSA analyses.

11.17. Guidelines are provided in the appendices on procedures to minimize contamination of samples and standards, preventive maintenance and troubleshooting.

11.18. 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.

11.19. 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. Analytical spike and 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

NOTE: When the sample concentration is less than the IDL, use SR = 0 for purposes of calculating analytical spike recovery.

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 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
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
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 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. Appropriate factors must be applied to sample values if dilutions are performed.

12.9. Sample results should be reported with up to three significant figures in accordance with the Quanterra 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. Refer to Tables I & IA in Appendix A for the list of routine as well as non-routine analytes that may be analyzed using this SOP.

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 +/- 20 % and the matrix spike duplicates should compare within 20% RPD. Method blanks must meet the criteria specified in Section 9.2. The laboratory control samples should recover within 20% of the true value until in house control limits are established.

13.4. 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. Waste generated in the procedure must be segregated and disposed according to the facility hazardous waste procedures. The Environmental Health and Safety Director should be contacted if additional information is required.

15.2. 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. Test Methods for Evaluating Solid Waste , Physical/Chemical Methods, SW-846, 3rd Edition, Final Update I, July 1992. Methods 7000A, 7060A, 7740, 7421, 7841, 7041, 7131A, 7191, 7211 and 7761.

16.2. Methods for the Chemical Analysis of Water and Waste, 1983.

16.3. 40 CFR Part 136, Table IB, 7-1-92.

16.4. CORP-MT-0004, Graphite Furnace Atomic Absorption Spectroscopy Method, 2XX.X - CLP-M, SOW ILMO3.0.

16.5. QA-003, Quanterra QC Program.

16.6. QA-004, Rounding and Significant Figures.

16.7. QA-005, Method Detection Limits.

17. MISCELLANEOUS (TABLES, APPENDICES, ETC. . .)

17.1. Modifications/Interpretations from reference method.

17.1.1. Modifications from both 7000A and 200 series methods.

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. The alternate run sequence presented in Section 11.15 is consistent with method requirements. Additional QC analyses were added to accommodate the CLP protocol requirements.

17.1.2. Modifications from Method 7000A.

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. Common lab contaminants are allowed up to two times the reporting limit in the blank following consultation with the client.

17.1.2.2. The SW846 methods contain contradictory statements regarding the frequency of CCV analysis. Section 7.3.6 of Method 7000A states a check standard should be run after approximately every 10 sample injections. Section 8.3 (Quality Control) states a check sample must be run every 10 samples. Since Quanterra defines an

analytical sample as a sample with its corresponding interference test and the SW846 document contains discrepancies in the frequency requirements for CCV analysis, this SOP requires that a CCV be analyzed every 10 analytical samples or 20 burns, whichever is more frequent.

17.1.2.3. Section 1.2 of Method 7000A states "To ensure valid data with furnace techniques, the analyst must examine each matrix for interference effects and, if detected, treat them accordingly, using either successive dilution, matrix modification, or method of standard addition." Quanterra utilizes matrix modifiers for all GFAA analyses and has also elected to run all samples using single point MSA rather than spike one "representative" sample per matrix type. The serial dilution test is presented in Method 7000A as a means to determine if interferences are present. Since the Quanterra SOP proceeds directly to single point MSA on all samples the use of the serial dilution test is not incorporated in this SOP. Sample results are not biased corrected based on the single point MSA result unless this is specifically requested by the client.

17.1.2.4. The SW846 methods contain contradictory statements regarding the acid matrix for calibration standards. Section 5.7 of Method 7000A states that the calibration standards should be prepared using the same type of acid or combination of acids and at the same concentration as will result in the samples following processing. Section 5.0 in each of the 7000 series methods states differing specific concentrations of acids in each method (i.e., Method 7421 states a 0.5% HNO_3 matrix). Since the addition of nitric acid to samples acts as a modifier (i.e., improves the recovery of the analyte) and the digestion procedures used incorporate higher nitric acid concentrations than specified in the individual methods, this SOP requires a 2% HNO_3 matrix for all standards.

17.1.3. Modifications from 200 series methods.

17.1.3.1. Method 200.0 section 9.3.7 states that a check standard should be run after approximately every 10 sample injections. Method 200.0 section 10.2.2 states that the curve must be verified every 20 samples. Since Quanterra defines an analytical sample as a sample with its corresponding interference test and Method 200.0 contains discrepancies in the frequency requirements for CCV analysis, this

SOP requires that a CCV be analyzed every 10 analytical samples or 20 burns whichever is more frequent.

17.1.3.2. The 200 series methods contain contradictory statements regarding the number of calibration standards to be used for calibration. Section 8.3 of the introductory method states to "Prepare a blank and at least four calibration standards using the same type of acid or combination of acids and at the same concentration as will result in the samples following processing. Section 10.2.1 of the same document states that a calibration curve is composed of a minimum of a reagent blank and three standards. This SOP requires the use of a blank and three standards.

17.1.3.3. Each analyte specific 200 series method specifies matrix modifiers. EPA recognizes that there have been many improvements in matrix modifier technology since these methods were originally written. In order to minimize interferences due to sample matrix, Quanterra has adopted the use of a palladium matrix modifier and/or currently recommended manufacturer modifiers.

17.2. Modifications from previous SOP

None.

17.3. Facility Specific SOPs

Each facility shall attach a list of facility specific SOPs or approved attachments (if applicable) which are required to implement this SOP or which are used in conjunction with this SOP. If no facility specific SOPs or amendments are to be attached, a statement must be attached specifying that there are none. Refer to the Appendices for any facility specific information required to support this SOP.

17.4. Documentation and Record Management

The following documentation comprises a complete GFAA raw data package:

- Raw data (direct instrument printout signed by analyst)
- Relevant sample preparation benchsheets.
- 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 and sufficient date and time information to verify that the QC time criteria were met).

Note: The Ward CVT benchsheet option is recommended as an efficient way to generate a benchsheet and run log.

- Data review checklist - See Appendix B
- Standards Documentation (including prep date, source and lot number).

17.5. Non-conformance summary (if applicable).

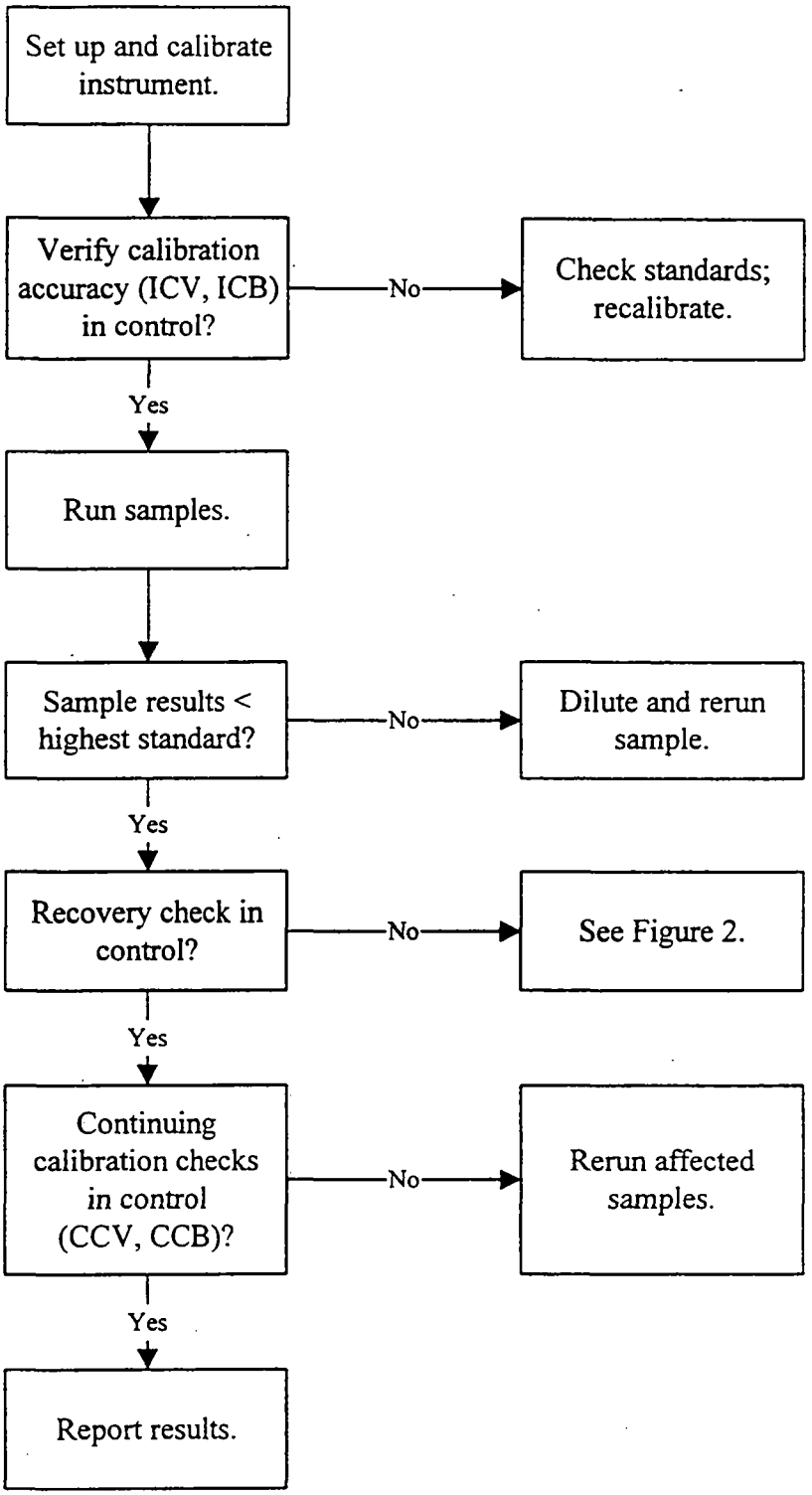


Figure 1. GFAA Analysis Flow Diagram

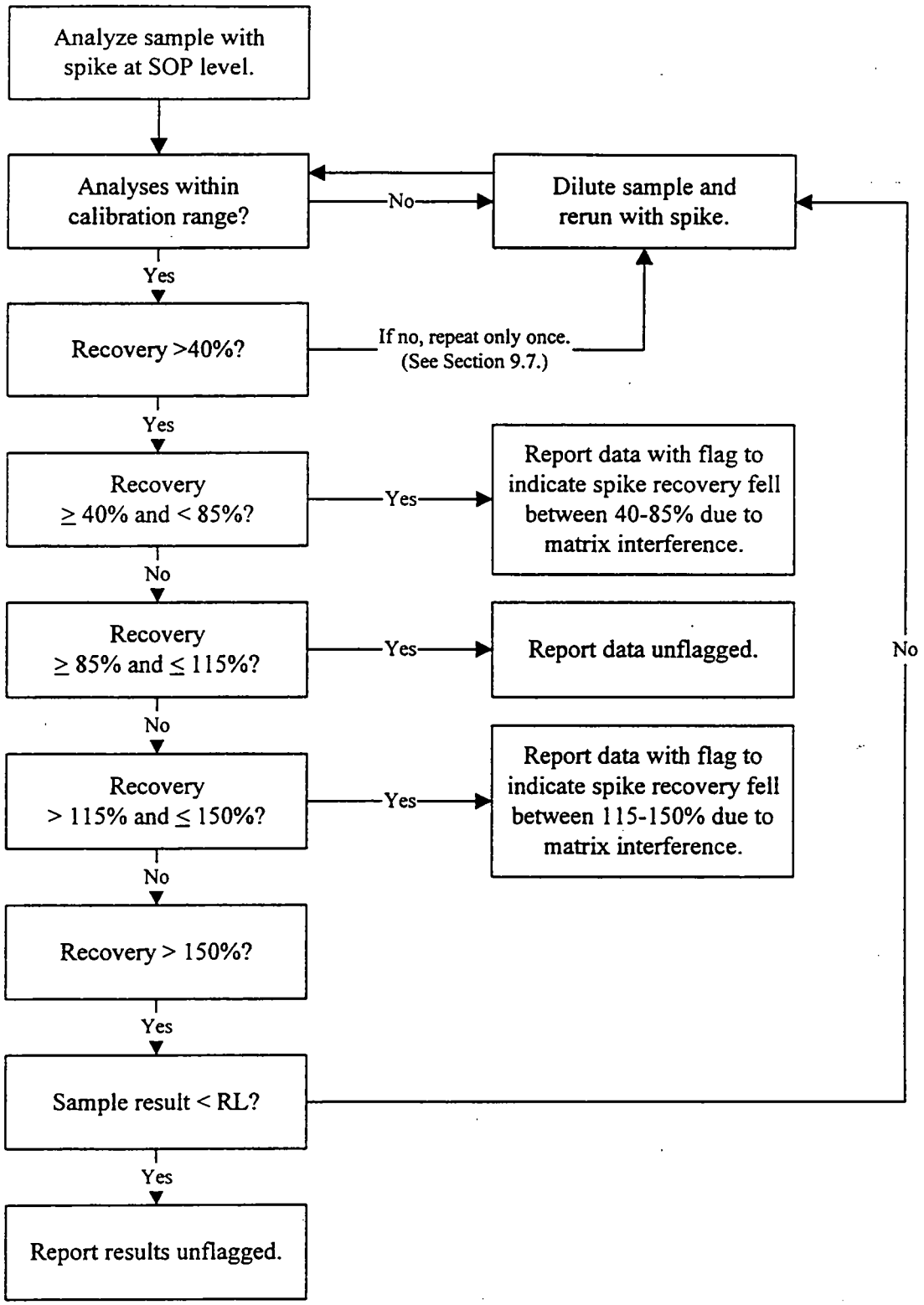


Figure 2. Recovery Check Protocol

APPENDIX A

TABLES

TABLE I. 7000 and 200 Series Routine Analyte List

ELEMENT	Symbol	CAS #	SW-846 Method	MCAWW Method	Aqueous RL (ug/L)	Solid RL (mg/Kg)
Arsenic	As	7440-38-2	7060A	206.2	10	1.0
Selenium	Se	7782-49-2	7740	270.2	5	0.5
Lead	Pb	7439-92-1	7421	239.2	3	0.3
Thallium	Tl	7440-28-0	7841	279.2	10	1.0
Antimony	Sb	7440-36-0	7041	204.2	10	1.0
Cadmium	Cd	7440-43-9	7131A	213.2	1	0.1
Chromium	Cr	7440-47-3	7191	218.2	5	0.5
Copper	Cu	7440-50-8	7211	220.2	5	0.5
Silver	Ag	7440-22-4	7761	272.2	1	0.1

TABLE IA. Non-routine GFAA Analytes *

ELEMENT	Symbol	CAS #	SW846 Method	MCAWW Method
Barium	Ba	7440-39-3	7081	208.2
Beryllium	Be	7440-41-7	7091	210.2
Cobalt	Co	7440-48-4	7201	219.2
Iron	Fe	7439-89-6	7381	236.2
Manganese	Mn	7439-96-5	7461	243.2
Nickel	Ni	7440-02-0	NA	249.2
Molybdenum	Mo	7439-98-7	7481	246.2
Vanadium	V	7440-62-2	7911	286.2
Zinc **	Zn	7440-66-6	7951	289.2

Note: Elements are not available at all Quanterra Laboratories.

* Additional elements may be possible by this method. ICP is recommended for all elements listed in Table IA.

**Not recommended by this procedure due to background contamination levels.

NA - Not applicable.

TABLE II. Recommended GFAA Analytical Guidelines

Element	λ (nm)	Char Temp°C	Atom Temp°C	Tube
Arsenic	193.7	1200-1400	2000-2800	Py/Pl
Selenium	196.0	900-1400	1900-2700	Py/Pl
Lead	283.3	700-1100	1500-2300	Py/Pl
Thallium	276.8	400-1100	1400-2600	Py/Pl
Antimony	217.6	400-1400	1900-2800	Py/Pl
Cadmium	228.8	500-1200	1400-2300	Py/Pl
Chromium	357.9	1100-1650	2300-2800	Un/W
Copper	324.8	800-1300	1900-2500	Un/W
Silver	328.1	500-1000	1600-2600	Py/Pl

*Py/Pl refers to a pyrolytically coated platform tube.

*Un/W refers to an uncoated tube without a platform.

TABLE III. Matrix Spike, Analytical Spike and Laboratory Control Sample Levels (ug/L)

ELEMENT	LCS/ Matrix Spike	Analytical Spike
Arsenic	40	20
Selenium	40	20*
Lead	40	20
Thallium	40	20
Antimony	40	20
Cadmium	4	4
Chromium	10	10
Copper	20	10
Silver	5	5

*If running in combined protocol mode (Section 11.15), a spike level of 10ppb is used to accommodate CLP criteria.

TABLE IV. 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

TABLE V. Calibration and Calibration Verification Standards

ELEMENT	Std 1	Std 2	Std 3	ICV	CCV
Arsenic	10	50	100	40	50
Selenium	5	40	80	30	40
Lead	3	40	80	30	40
Thallium	10	40	80	30	40
Antimony	10	40	80	30	40
Cadmium	1	5	10	4	5
Chromium	5	25	50	20	25
Copper	5	20	40	10	20
Silver	1	5	10	4	5

***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.**

TABLE VI. 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.
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 7000A: 80 - 120 % recovery. 200 series: 90 -110 % recovery.	Terminate analysis; Correct the problem; Recalibrate and rerun all samples not bracketed by acceptable CCV.
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.
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 after consultation with the client (See Section 9.2) Sample results greater than 20x the blank concentration are acceptable. Samples for which the contaminant is < RL do not require redigestion (See Section 9.2).	Redigest and reanalyze samples. Note exceptions under criteria section. See Section 9.2 for additional requirements.

*See sections 11.14 and 11.15 for exact run sequence to be followed.

TABLE VI. 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. Samples for which the contaminant is < RL and the LCS results are > 120% may not require redigestion or reanalysis (see Section 9.3)	Terminate analysis; Correct the problem; Redigest and reanalyze all samples associated with the LCS.
Matrix Spike	One per sample preparation batch of up to 20 samples.	80 - 120 % 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. For TCLP see Section 11.16
Matrix Spike Duplicate	See Matrix Spike	80 - 120 % recovery or in-house control limits; RPD ≤ 20%. (See MS)	See Corrective Action for Matrix Spike.
Analytical Spike	One per each sample analyzed including method blank.	85 - 115 % recovery.	See Section 9.7 (Spike Recovery Check).

APPENDIX B
QUANTERRA GFAA DATA REVIEW CHECKLIST

Quanterra GFAA Data Review Checklist

Run/Project Information

Run Date: _____ **Analyst:** _____ **Instrument:** _____
Prep Batches Run: _____

Circle Methods used: **7000A / 2XX.X : CORP-MT-0003 Rev 1**
CLP : CORP-MT-0004 Rev 1

Review Items

A. Calibration/Instrument Run QC	Yes	No	N/A	2nd Level
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. RSD of replicate burns < 20 % when sample results > RL ?				
3. All reported results bracketed by in control QC ?				
4. 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?				
5. Analytical spike within QC limits or appropriate action taken ?				
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/time of analysis verified as correct ?				

Analyst: _____ **Date:** _____
Comments:

_____

_____

2nd Level Reviewer : _____ **Date:** _____

_____

_____

APPENDIX C

MSA GUIDANCE

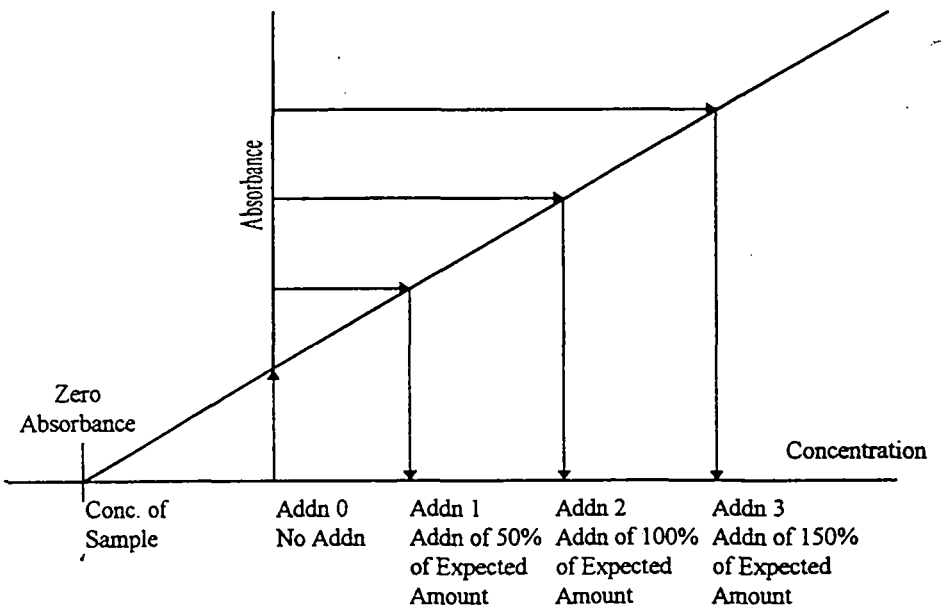
APPENDIX C. MSA GUIDANCE

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 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.

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 (See Section 11.4)	Read time too short Incorrect wavelength Low atomization temperature Char temperature too high Dry temperature too high No read step in program Dirty windows Window loose Etched or dirty optics Wrong lamp Bad lamp Bad graphite tube Bad contact rings Not enough or no sample injected Empty sample cup No modifier in sample Incorrectly made standards Poor injection into tube or on platform Flush solution empty Gas flow during read step Gas leak EDL power supply set on "Continuous"
Tube Impedance Error	Bad tube Bad contact rings Sample matrix Door not tight Argon supply out Cooling system malfunction

Problem	Possible Cause
Erratic Readings or High % RSD	Source lamp not aligned properly Lamp not prewarmed Injection tip partially clogged Rinse bottle empty Water cooling not on Bad lamp Injection tip hitting outside of tube Injection tip coated or not set properly Salt buildup on tip Leak in sample capillary Ruby valve clogged Wrong or no modifier Incomplete dry step Dry temperature too high Bad tube Bad contact rings Unstable power supply Air bubbles in syringe or cylinders(Varian)
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 Lamp driver faulty (EDL2)
Sample Not Drying or Crackling	Incorrect dry temperature Tube is placed incorrectly Tube is bad Platform not seated properly Furnace door not tight Sample matrix Bad contact rings
Standards reading twice normal absorbance or concentration	Incorrect standard used Incorrect dilution perform
Background Correction Light Blinking	Background screen or attenuator faulty D2 lamp and element lamp energy don't match Analyte lamp energy too low (bad lamp) Background screen or attenuator faulty
Preparation blank spike recovery outside recovery limits	Incorrect concentration of nitric acid HCl added to sample in prep lab Injection tip worn or clogged Sample pump worn Contaminated cup or spike solution

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:

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.

The buildup of matrix modifiers in the furnace housing can cause cross contamination. For example: If nickel nitrate is used as a matrix modifier, the furnace housing should be thoroughly cleaned prior to the analysis of nickel.

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.

Pyrolytic tubes can contain contaminants. If suspected, the tube should be cleaned by operating the furnace at full power as required to eliminate the 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	Clean contact rings and windows Check tube and platform, replace if corroded, flaking or sensitivity check fails Check gas lines and supply level Check rinse solution and fill if needed Check drain lines and waste containers, empty if needed Clean outside of capillary tip Adjust autosampler arm as needed Debubble syringe (Varian instruments only) Clean fume extraction tip, replace fume extraction filter and water trap (PE4100ZL)
Weekly	Trim capillary tip as needed Check water level in coolflow Wipe exterior of instrument
Monthly	Clean filters and radiators
Quarterly	Change contact rings (if needed) Clean instrument water system
Annually	Notify manufacturer service engineer to clean optics

To obtain the maximum graphite tube life the following guidelines should be followed.

1. Contact rings should be cleaned when replacing the graphite tube.

2. After insertion, every new tube should be thermally conditioned. It is recommended that for the first heating, a ramp time between 60 and 100 seconds and a temperature range from ambient temperature to 2650°C be applied. After a few seconds at 2650°C and a cool down of 20 seconds, the process should be repeated three times with a ramp time 10 seconds.

3. It is very important to long tube life to always use a ramp time for thermal pretreatment. No higher temperature increase than 50°C per second is recommended.

4. For optimal performance, no higher atomization temperatures should be used than 2650°C for pyrolytically coated tubes and 2700°C for uncoated tubes. For refractory elements, application of higher atomization temperature can initially increase the signal, but will drastically reduce the tube lifetime.

5. When using peak area, atomization time has to be sufficiently long for the signal to come back to the baseline. High atomization and heatout temperatures should be applied as long as required, and not a second longer.

6. To avoid a negative effect of acids on tube lifetime, always keep a check on acid concentrations, use a slow ramp for thermal pretreatment and use pyrolytically coated tubes as specified in Table II.

7. If the temperature of the GFAA cooling water is too low and the flowrate is too high, condensation from atmospheric humidity can occur around the contact rings. A cooling water flowrate of 2 L/min +/-0.5 L/min is specified by Perkin Elmer. The use of a coolflow is strongly recommended since it always provides the same water flow and temperature.

8. Nitrogen gas results in a lower peak sensitivity for several elements. It can also cause the generation of cyanogen above 2300°C, making it potentially dangerous in a poorly ventilated room. Perkin Elmer recommends the use of argon.

QUANTERRA STANDARD OPERATING PROCEDURE

TITLE: CYANIDE DISTILLATION METHOD

(SUPERSEDES: NC-WC-0032 (REVISION 0))

Prepared by: _____

Reviewed by: _____
Technology Specialist

Approved by: _____
Quality Assurance Manager

Approved by: _____
Environmental Health and Safety Coordinator

Approved by: _____
Laboratory Director

Proprietary Information Statement:

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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, SW 846 Method 9012, EPA 335.1 and 335.2, and Standard Method 4500-CN-I. The working linear range is 0.005 - 0.1 mg/L for waters and 0.25 to 5 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 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 Quality Assurance Management Plan (QAMP).

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.

5. SAFETY

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

5.2. Eye protection that satisfies ANSI Z87.1 (per the Chemical Hygiene Plan), 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 health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the

Material Safety Data Sheets (MSDS) maintained in the laboratory. The following specific hazards are known:

5.3.1. The following are known to be **corrosive: sulfamic acid, sodium hydroxide, sulfuric acid, acetic acid.**

5.3.2. Cyanide is a highly toxic compound that must be handled with care. The analyst must be aware of the handling and clean-up techniques before using this material.

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. 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 Quanterra associate. The situation must be reported **immediately** to a 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

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.

7.1.3. Ascorbic Acid: reagent grade

7.1.4. Sodium Hydroxide: (NaOH), reagent 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 to 900 mL reagent water and dilute to 1 liter with reagent water.

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.

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

7.2. Standards

7.2.1. Secondary 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. Prepare fresh every 1 - 3 months.

Note: Cyanide stock standard must be standardized prior to use (See Section 7.2.3)

7.2.2. Working Standards: Add the required amounts of 1.25 N NaOH and cyanide standards to volumetric flasks according to the suggested chart. Dilute to volume using reagent water. See chart below:

Chart 1 Working Standards

Volume 1.25 N NaOH (mL)	Std Volume (mL)	Std Conc. (mg/L)	Final Volume (mL)	Final Conc. (mg/L)	Expiration Time (Days)
20	10	1000	100	100	14
20	10	100	100	10	7
20	10	10	100	1	1

7.2.3. Cyanide Standardization

7.2.3.1. Using a volumetric pipet 10.0 mL of the 1000 ppm stock cyanide standard into an Erlenmeyer flask and add 90 mL of reagent water.

7.2.3.2. Add 10 drops of Rhodanine indicator.

7.2.3.3. Titrate with 0.0192 N Silver nitrate until the color changes from yellow to pink/orange.

7.2.3.4. Calculation:

$$\textit{Cyanide, mg/L} = \frac{(A)\ (1000)}{\textit{mL cyanide solution}\ (10)}$$

Where: ***A = mL Titrant for standard***

7.2.3.5. If the cyanide concentration is not 1000 ppm, adjust concentration accordingly.

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 is fourteen days from sampling to analysis.

NOTE: CLP samples holding time is twelve days from receipt to analysis.

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, MS, MSD, Method Blanks) which are processed similarly, with respect to the procedure. All samples within the batch must be treated with the same lots of reagents and the same processes. All samples within the batch must be treated with the same processes.

9.2. Method Blank (MB)

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. A blank consisting of 50 mL reagent water must be prepared and distilled 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) - One aqueous 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.

9.3.1. A midrange LCS consisting of 50 mL of reagent water and 2.0 mL of the 1.0 mg/L standard (secondary source) must be distilled with each analytical batch of samples.

9.3.2. Corrective Action for Laboratory Control Samples

9.3.2.1. If any analyte is outside established control limits the system is out of control and corrective action must occur.

9.3.2.2. 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. 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.

9.4.2. 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.

9.4.3. 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 reported as DIL (diluted out).

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.

NOTE: MS for CLP samples require 5 mL of 1.0 mg/L standard (true 100 µg/L)

10. CALIBRATION AND STANDARDIZATION

10.1. Not Applicable.

11. PROCEDURE

11.1. Summary

11.1.1. The sample is distilled/refluxed under acidic conditions for one hour and fifteen minutes. The released HCN is trapped in 0.25 N NaOH solution.

11.1.2. The following procedure is applicable for use with the Midi distillation unit.

11.2. Sample Preparation Procedure.

11.2.1. Checking for Interferences

11.2.1.1. Using pH strips paper, check the pH of the sample and record it on the analytical logsheet.

11.2.1.2. Using lead acetate paper, check the sample for excess sulfide. If sulfide is present the test strip will turn silver/brown. Record findings on the analytical logsheet. Using potassium iodide paper, check for chlorine presence. If chlorine is present the test strip will turn dark blue. If chlorine is present add 0.1 - 0.5 grams ascorbic acid to sample until the chlorine is destroyed. Record this on the analytical logsheet.

11.2.1.3. Complex Cyanide Preparation Procedure: 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 11.2.4.1).

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.

11.2.2. The following procedures are applicable for use with the Midi cyanide distillation unit.

11.2.3. Amenable Cyanide (Chlorinated Aliquot)

11.2.3.1. 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 11.2.4). Also set up an unchlorinated aliquot of sample (50 mL or 1.0 g) following the total cyanide method.

11.2.4. Total Cyanide

11.2.4.1. Add 50 or 1.0 g of the sample and 2 - 3 boiling chips to the distillation tube. Bring all volumes 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.

11.2.4.2. 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.

11.2.4.3. In the order stated, add 2.0 mL sulfamic acid solution, 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 on additional 2.5 mL of sulfuric acid. Be sure the pH is < 2.

11.2.4.4.Flip the heater switch to "on" and turn the dial to 10.5 (this represents one hour and fifteen minutes of heated refluxing). Be sure to adjust the air flow and water as necessary. After the heating period, the heater will turn off automatically. Allow to cool for fifteen minutes. Keep the vacuum and cooling water on.

11.2.4.5.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.

11.2.5. Free Cyanide (Weak and Dissociable)

11.2.5.1. 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.

11.2.5.2. 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.

11.2.5.3. Flip on the heater switch and turn the dial to "10.5". Adjust the air flow and water as needed. After the heating period, the heater will shut off automatically. Allow the sample to cool for fifteen minutes with the air and water on.

11.2.5.4. 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.

11.2.6. Cyanide Unit Clean-up

11.2.6.1. Cyanide distillation unit glassware is very fragile and expensive. It must be handled with care at all times.

11.2.6.2. 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.

11.2.6.3. Wash each set-up with soap and hot water, and then rinse with 1:1 HCI. Rinse several times with reagent water

11.2.6.4. Re-assemble the set-up.

11.2.6.5. Be sure to wash each set up as a separate unit and replace in the same position.

11.2.6.6. If a sample of known high cyanide concentration was distilled in a certain position, be sure to change the appropriate tubing on that position.

11.3. Analytical Documentation

11.3.1. 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.

11.3.2. 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.

11.3.3. 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.

11.3.4. 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.

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. Acid waste must be collected in clearly labeled acid waste cans.

15.2. Solid waste materials (soil, gloves, soiled paper products, etc.) are placed in the solid debris container. Do not put liquids in the solid waste container.

15.3. Refer to the Laboratory Sample and Waste Disposal plan

16. REFERENCES

16.1. References.

16.1.1. SW846, Test Methods for Evaluating Solid Waste, Third Edition, Total and Amenable Cyanide, Automated UV; Method 9012

16.1.2. EPA 600; Cyanide, Total and Cyanide, Amenable to Chlorination; Methods 335.1 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

16.2. Associated SOPs

16.2.1. Cyanide, Automated Method NC-WC-0031

17. MISCELLANEOUS (TABLES, APPENDICES, ETC...)

17.1. None

QUANTERRA STANDARD OPERATING PROCEDURE

TITLE: CYANIDE AUTOMATED, PYRIDINE-BARBITURIC ACID METHOD

(SUPERSEDES: ENSECO SOP #LM-WALN-1141 (REVISION 2.0))

Prepared by: _____

Reviewed by: _____
Technology Specialist

Approved by: _____
Quality Assurance Manager

Approved by: _____
Environmental Health and Safety Coordinator

Approved by: _____
Laboratory Director

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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, SW846 Method 9012, EPA 335.1 and 335.2, and Standard Method 4500-CN-I. The working linear range is 0.005 - 0.1 mg/L for waters and 0.25 to 5 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 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.

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 Quality Assurance Management Plan (QAMP).

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 sodium hydroxide distillate with cadmium carbonate prior to analysis.

5. SAFETY

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

5.2. Eye protection that satisfies ANSI Z87.1 (as per the Chemical Hygiene Plan), 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 health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the Material Safety Data Sheets (MSDS) maintained in the laboratory. The following specific hazards are known:

5.3.1. The following materials are known to be **corrosive: Sodium Hydroxide**

5.3.2. Cyanide is a highly toxic compound that must be handled with care. The analyst must be aware of the handling techniques.

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. 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 Quanterra associate. The situation must be reported **immediately** to a laboratory supervisor.

6. EQUIPMENT AND SUPPLIES

6.1. Traacs 800 autoanalyzer

6.2. Probe 0.016"

6.3. Flowcell 10nm

6.4. Wavelength cell 570nm

6.5. Manifold-Multitest cartridge with cyanide tubing

6.6. 125 mL Erlenmeyer flasks

6.7. 100 mL, 250 mL, 1000 mL volumetric flasks

6.8. Volumetric pipets: 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 (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.

7.1.6. 0.25 N sodium hydroxide: Add 200 mL of N NaOH to a 1 liter volumetric flask and dilute to volume with reagent water.

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 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 must be standardized prior to use. See Appendix I.

7.2.3. Calibration Standards (Water and Solid Matrices)

7.2.3.1. Pipet the appropriate amount of cyanide standard into 100 mL volumetric. Add 20 mL 1.25N NaOH to each calibration standard (except the 1.0 mg/L) and bring to volume with reagent water. 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
*0.1 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

NOTE: The 1 ppm CN standard is only good for the day it is prepared and is not preserved with NaOH.

8. SAMPLE COLLECTION, 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 is fourteen days from sampling to analysis.

*NOTE: Holding time for CLP is twelve days from receipt to analysis.

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, 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.

9.2. 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. A reagent water blank consisting of 50 mL reagent water must be distilled and analyzed with each analytical batch of samples. See Method LM-WALN-1142 (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 aqueous 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. 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. See Method LM-WALN-1142 (NC-WC-0032) for distillation instruction.

9.3.3. Corrective Action for LCS

9.3.3.1. If any analyte is outside established control limits the system is out of control and corrective action must occur.

9.3.3.2. 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. 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.

9.4.2. 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 Method LM-WALN-1142 (NC-WC-0032) for distillation instructions..

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 DIL (diluted out).

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.

10. CALIBRATION AND STANDARDIZATION

10.1. Summary

10.1.1. The instrument is calibrated using five cyanide standards at the time of analysis.

10.2. Initial Calibration

10.2.1. 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 correlation coefficient of the original curve must be $\geq$ 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. The CCV is composed of the 0.025 ppm secondary standard.

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 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. Normal Tray Protocol

10.4.1. P,5C>2, H@2, 2L@0, G@2, XS>7, H@2, 2L@0, G@2, E

NOTE: X = number of sample cups minus the six calibration cups.

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. The sample is distilled/refluxed under acidic conditions for one hour and fifteen minutes. The released HCN is trapped in 50 mL of 0.25 N NaOH solution.

11.3.2. Sample Preparation Procedure

11.3.2.1. Add approximately 0.5 g cadmium carbonate to each distillate if it is suspected that the sample contains sulfide. If precipitate remains white, shake distillate vigorously for about 30 seconds. Let precipitate settle out or filter the distillate and transfer to sample cup. If precipitate turns yellow, sulfide interferences are present. Add cadmium carbonate, shaking vigorously after each addition until precipitate turns white. Let

cadmium carbonate settle out or filter and then transfer distillate to sample cup.

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 0.1 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.

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. CCV's and CCB's are analyzed at the beginning, end, and between every 10 samples. CCV's must be prepared from a secondary source.

11.4.3.4. Sample distillates higher than the highest calibration standard (0.1 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. 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. $$\textit{Total Cyanide, mg / L} = \frac{\textit{mg / L } CN^- \textit{ from printout x 50}}{\textit{mL of sample distilled}} \textit{ x D}$$

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:

$$\frac{\textit{Instrument Value}}{\textit{0.04(true)}} \textit{ x 100} = \textit{\% Recovery}$$

12.5. CCV Recovery:

$$\frac{\textit{Instrument Value}}{0.025\ (true)} \times 100 = \%\ Recovery$$

NOTE: CCV recovery must be between 85 - 115% for data to be acceptable. If CCV recovery is not within these limits, reanalysis is required.

12.6. ***MS/MSD Recovery for Waters and solids:***

$$\frac{A - B}{0.040\ (true)} \times 100 = \%\ Recovery$$

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.

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 distillates can be rinsed down the drain with large amounts of water unless they contain high levels of Cyanide. If they are highly concentrated, they must be disposed of in the liquid waste container.

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

15.3. Acid waste must be collected in clearly labeled acid waste containers.

15.4. Solid materials (gloves, soiled paper products, etc.) are placed in the solid debris container. Do not put liquids in the solid waste container.

15.5. Refer to the Laboratory Sample and Waste Disposal plan.

15.6. Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices of Quanterra. 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, Update I; Total and Amenable Cyanide, Automated UV; Method 9012 A

16.1.2. EPA 600; Cyanide, Total and Cyanide, Amenable to Chlorination; Methods 335.1 and 335.2, March 1983

16.1.3. Standard Methods for the Examination of Water and Wastewater, Eighteenth Edition: Weak and Dissociable Cyanide; Method 4500-CN-E

16.1.4. USEPA CLP SOW ILM03.0, Section D - Cyanide Midi Distillation

16.2. Associated SOPs

16.2.1. LM-WALN-1142 (NC-WC-0032), Cyanide Distillation Method

17. MISCELLANEOUS (TABLES, APPENDICES, ETC...)

17.1. Reporting limits

17.1.1. The lower reporting limit (RL) is 0.005 mg/L for waters (50 mL used) and 0.25 mg/kg for solids (1.0 g used).

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.

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 buret) 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.

Quanterra Environmental Services' North Canton
METHOD DETECTION LIMIT STUDY

DATE COMPLETED:	February - 1996	PROG/PROJECT:	NA
METHOD NUMBER:	6010 / 200.7	PROJECT NUMBER:	1996 - MDLs
METHOD DESCRIPTION:	ICP Trace	ANALYST:	Metals
PREP METHOD:	WATER	QUALITY ASSURANCE:	MJL

ANALYTE	SPIKE CONC ug/L	REPLICATE MEASUREMENT 1	2	3	4	5	6	7	AVG ug/L	Recovery of Spike %	PREC. ug/L	MDL ug/L	Report. Limit ug/L	STATUS
Antimony	5	6.2759	6.2455	8.9898	4.8378	7.2036	5.9001	5.9832	6.49	129.82%	1.30	4.10	5	pass
Arsenic	5	7.4219	7.3904	7.2319	5.7102	5.9962	7.8434	6.1263	6.82	136.34%	0.85	2.66	5	pass
Cadmium	1	1.0860	0.9668	1.0710	1.0550	1.1790	1.0010	1.0840	1.06	106.33%	0.07	0.21	1	pass
Chromium	4	5.1270	4.4050	4.2330	4.3980	5.0660	4.1140	4.2070	4.51	112.68%	0.42	1.31	5	pass
Lead	3	4.7436	3.6100	4.1052	4.8612	5.3442	3.8950	4.5029	4.44	147.91%	0.60	1.90	3	pass
Molybdenum	3	4.3610	3.9810	3.6580	4.1410	3.8800	3.8350	3.8690	3.96	132.02%	0.23	0.72	5	pass
Selenium	5	4.8918	5.5536	3.7799	4.8667	4.6797	4.5839	6.4767	4.98	99.52%	0.84	2.65	5	pass
Silver	3	3.0430	2.9000	2.9790	2.9300	2.7030	3.1100	3.2960	2.99	99.81%	0.18	0.58	5	pass
Thallium	6	8.6585	6.7172	6.9404	5.0751	7.3618	5.4750	5.1825	6.49	108.12%	1.32	4.15	10	pass
Cobalt	5	5.418	4.692	5.825	4.923	6.456	4.258	5.412	5.28	105.67%	0.73	2.31	7	pass
Vanadium	2	1.688	2.297	1.813	1.809	2.130	1.770	2.146	1.95	97.52%	0.23	0.74	8	pass

fail => MDL Value is above RL, Accuracy is < 50% or > 150%, or MDL <10% or > 10X spike level

Quanterra Environmental Services' North Canton
METHOD DETECTION LIMIT STUDY

DATE COMPLETED:	FEBRUARY, MARCH	PROG/PROJECT:	NA
METHOD NUMBER:	7000 & 200 Series Atomic Absorption	PROJECT NUMBER:	1996 - MDLs
METHOD DESCRIPTION:	GFAA & CVAA	ANALYST:	Metals
PREP METHOD:	WATER	QUALITY ASSURANCE:	MJL

	SPIKE	REPLICATE MEASUREMENT							AVG	Recovery	PREC.	MDL	Report.	
	CONC									of Spike			Limit	
ANALYTE	ug/L	1	2	3	4	5	6	7	ug/L	%	ug/L	ug/L	ug/L	STATUS
Antimony	5	4.2	6.9	4.3	5.3	4.5	5.7	3.7	4.94	98.86%	1.10	3.45	5	pass
Arsenic	5	5.2	4.8	4.8	4.1	4.2	4.1	4.5	4.53	90.57%	0.42	1.33	5	pass
Cadmium	0.5	0.51	0.51	0.54	0.54	0.54	0.54	0.56	0.53	106.86%	0.02	0.06	0.1	pass
Chromium	5	8.2	5.2	5.5	5.9	5.4	5.4	5.6	5.89	117.71%	1.04	3.28	5	pass
Lead	3	3.3	2.3	2.4	2.8	2.4	2.1	2.2	2.50	83.33%	0.42	1.31	3	pass
Mercury	0.1	0.1540	0.1410	0.1521	0.1409	0.1439	0.1378	0.1495	0.15	145.60%	0.01	0.02	0.2	pass
Selenium	5	5.3	4.4	4.6	4.0	5.0	3.9	5.0	4.60	92.00%	0.53	1.67	5	pass
Silver	1	1.4	1.0	1.1	1.1	1.0	1.0	1.0	1.09	77.55%	0.15	0.46	1	pass
Thallium	4	4.1	4.7	5.0	5.2	4.7	4.8	5.0	4.79	119.64%	0.35	1.11	2	pass

Water

fail => MDL Value is above RL, Accuracy is < 50% or > 150%, or MDL <10% or > 10X spike level

Quanterra Environmental Services' North Canton
METHOD DETECTION LIMIT STUDY

DATE COMPLETED:	March - 1996	PROG/PROJECT:	NA
METHOD NUMBER:	Various	PROJECT NUMBER:	1996 - MDLs
METHOD DESCRIPTION:	Various Wet Chemistry Parameters	ANALYST:	Wetchem
PREP METHOD:	Various	QUALITY ASSURANCE:	MJL

ANALYTE	SPIKE CONC mg/L	REPLICATE MEASUREMENT 1	2	3	4	5	6	7	8	AVG mg/L	Recovery of Spike %	PREC. mg/L	MDL mg/L	Report. Limit mg/L	STATUS
Alkalinity	5.0	5.50	6.50	5.80	5.50	5.60	5.50	5.60	5.50	5.69	113.75%	0.344	1.03	5	pass
Alkalinity-auto	5	7.80	7.50	7.70	7.60	7.20	7.20	7.70		7.53	150.57%	0.24	0.76	5	pass
Ammonia	1	0.78	1.34	1.01	0.90	1.12	0.90	1.01		1.01	100.86%	0.18	0.57	1	pass
Ammonia - ISE	0.20	0.175	0.206	0.207	0.206	0.202	0.204	0.205	0.203	0.20	100.50%	0.0106	0.0319	0.20	pass
Chloride - auto	1.0	0.863	0.759	0.744	0.617	0.686	0.570	0.564	0.730	0.69	69.16%	0.103	0.309	1.0	pass
Chloride - manual	2	3.90	4.06	3.90	3.90	4.06	4.06	3.90	3.90	3.96	197.88%	0.0807	0.242	3.0	pass
COD-Manual	50	51.40	51.40	51.40	51.40	64.00	48.00	48.00		52.23	104.46%	5.43	17.07	50	pass
COD-Spect.	20	29.50	32.00	29.50	27.00	27.00	24.50	32.00		28.79	143.94%	2.78	8.75	10	pass
Cyanide-midi	0.005	0.00300	0.00080	0.00269	0.00147	0.00166	0.00173	0.00063		0.00171	34.20%	0.000883	0.00278	0.010	pass
Ferrous Iron	0.020	0.0415	0.0415	0.0316	0.0415	0.0415	0.0415	0.0515	0.0415	0.0415	207.56%	0.00532	0.0159	0.020	pass
Fluoride	0.10	0.0914	0.0909	0.0942	0.0962	0.0962	0.0967	0.100		0.10	95.09%	0.0032	0.0100	0.1	pass
Formaldehyde	0.050	0.033	0.036	0.033	0.033	0.074	0.036	0.052	0.033	0.041	82.50%	0.0147	0.0441	0.050	pass
Hardness	2.0	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	100.00%	0.000	0.000	2.0	pass
Hexavalent Chromium	0.02	0.02143	0.02006	0.01868	0.0214	0.01868	0.01868	0.02006		0.02	99.30%	0.0012	0.0039	0.02	pass
MBAS	0.10	0.09549	0.09549	0.09549	0.07458	0.07458	0.07981	0.08503		0.09	85.78%	0.00975	0.0306	0.10	pass
Nitrate	0.1	0.06306	0.08481	0.09121	0.08667	0.08449	0.08864	0.08611		0.08	83.57%	0.01	0.03	0.1	pass
Nitrite	0.04	0.03161	0.03172	0.03097	0.03188	0.0321	0.02858	0.03287		0.03	78.48%	0.00136	0.00429	0.04	pass
Nitrite-Nitrate	0.1	0.08804	0.08954	0.07848	0.09976	0.07842	0.0870	0.08035		0.09	85.94%	0.01	0.02	0.1	pass
Orthophosphorus	0.10	0.11	0.11	0.11	0.12	0.12	0.10	0.09		0.11	109.54%	0.00979	0.0308	0.10	pass
Phenol - 10 mm	0.020	0.010	0.010	0.010	0.010	0.010	0.010	0.010		0.01	50.00%	0.000	0.00000	0.020	pass
Phenol - 20 mm	0.01	0.0061	0.0061	0.01005	0.01399	0.01005	0.01399	0.01005		0.01	100.47%	0.00	0.010	0.01	pass
Phenol - 40 mm	0.01	0.00182	0.00182	0.00384	0.00585	0.00585	0.00585	0.00384		0.0041	41.24%	0.00181	0.00570	0.01	pass
Phosphorus	0.100	0.114	0.112	0.110	0.120	0.118	0.128	0.112	0.114	0.12	116.00%	0.00586	0.0176	0.10	pass
Sulfate	5.0	4.50	4.80	4.50	3.50	3.50	3.50	5.00		4.19	83.71%	0.664	2.09	5.0	pass
Sulfide	0.5	0.624	0.448	0.544	0.768	0.608	0.768	0.768		0.65	129.37%	0.13	0.40	0.5	pass
TOC-solid	100	105	103	94	94	95	102	101	101	99.38	99.38%	4.37	13.75	100	pass

Quanterra Environmental Services' North Canton
METHOD DETECTION LIMIT STUDY

DATE COMPLETED:	March - 1996	PROG/PROJECT:	NA
METHOD NUMBER:	Various	PROJECT NUMBER:	1996 - MDLs
METHOD DESCRIPTION:	Various Wet Chemistry Parameters	ANALYST:	Wetchem
PREP METHOD:	Various	QUALITY ASSURANCE:	MJL

ANALYTE	SPIKE CONC mg/L	REPLICATE MEASUREMENT 1	2	3	4	5	6	7	8	AVG mg/L	Recovery of Spike %	PREC. mg/L	MDL mg/L	Report. Limit mg/L	STATUS
Total Dissolved Solid	10	6.00	12.00	6.00	9.00	9.00	9.00	8.00		8.43	84.29%	2.07	6.51	10	pass
Total Organic Carbon	1.0	1.43	1.36	1.26	1.19	1.05	1.19	1.26		1.25	124.86%	0.124	0.389	1.0	pass
Total Organic Halogens	0.010	0.01073	0.01029	0.01002	0.00947	0.01028	0.01054	0.01028	0.01083	0.01	103.05%	0.000430	0.00129	0.030	pass
Total Solids	10	8.00	7.00	10.00	13.00	8.00	7.00	10.00	10.00	9.13	91.25%	2.03	6.09	10	pass
Total Suspended Solids	4.0	3.00	3.00	3.00	3.00	3.00	3.00	3.00	1.00	2.75	68.75%	0.707	2.12	4.0	pass
TOX-solid	5	4.96	4.98	4.69	4.37	4.48	4.54	4.69		4.66	93.16%	0.23	0.73	1	pass

Method Detection Limit Study

Matrix : Water

Analyte	MDL	Units	Date of MDL	Rep 1	Rep 2	Rep 3	Rep 4	Rep 5	Rep 6	Rep 7	Avg	Std Dev	Student t Multiplier
1,2,3,4-Tetrachlorobenzene	1.37	ug/L	04/95	7.93	8.47	8.34	8.05	7.40	7.98	7.31	7.93	.436	3.143
1,2,3,5-Tetrachlorobenzene	.98	ug/L	04/95	8.46	8.92	8.43	8.29	8.17	8.50	7.92	8.38	.311	3.143
1,2,3-Trichlorobenzene	.96	ug/L	04/95	7.18	7.62	7.13	7.25	7.38	7.49	6.68	7.25	.304	3.143
1,2,4,5-Tetrachlorobenzene	1.18	ug/L	04/95	8.11	8.49	8.09	8.13	7.81	7.93	7.27	7.98	.376	3.143
1,2,4-Trichlorobenzene	3.28	ug/L	04/95	8.72	9.13	9.70	10.03	12.00	9.61	9.86	9.86	1.043	3.143
1,2-Dichlorobenzene	4.28	ug/L	04/95	8.98	9.18	10.04	10.86	12.90	9.45	9.67	10.15	1.361	3.143
1,2-Dichlorobenzene-d4	3.90	ug/L	04/95	8.35	8.88	9.76	10.34	12.25	9.86	9.69	9.88	1.240	3.143
1,2-Dinitrobenzene	4.21	ug/L	04/95	9.80	10.54	11.29	12.05	13.95	12.10	12.25	11.71	1.340	3.143
1,2-diphenylhydrazine	3.60	ug/L	04/95	9.44	8.62	10.20	9.86	12.24	10.87	9.96	10.17	1.144	3.143
1,3,5-Trichlorobenzene	.96	ug/L	04/95	6.85	7.25	6.97	7.14	6.83	6.93	6.29	6.89	.307	3.143
1,3,5-Trinitrobenzene	2.15	ug/L	04/95	5.19	5.13	3.71	5.61	5.66	5.57	5.48	5.19	.686	3.143
1,3-Dichloro-2-propano	1.92	ug/L	04/95	2.78	2.63	1.44	3.19	2.98	2.09	2.12	2.46	.609	3.143
1,3-Dichlorobenzene	4.10	ug/L	04/95	8.39	8.07	9.54	9.99	12.05	9.32	9.10	9.49	1.305	3.143
1,3-Dinitrobenzene	3.83	ug/L	04/95	9.32	8.96	9.94	10.13	12.57	11.19	10.11	10.32	1.217	3.143
1,4-Dichlorobenzene	3.68	ug/L	04/95	8.59	9.09	10.03	9.99	12.31	9.71	10.01	9.96	1.171	3.143
1,4-Dinitrobenzene	3.12	ug/L	04/95	7.87	7.98	8.81	10.04	10.48	9.47	8.72	9.05	.992	3.143
1,4-Naphthoquinone	10.25	ug/L	04/95	18.03	20.50	13.23	13.48	21.13	19.28	15.50	17.31	3.260	3.143
1-Methylnaphthalene	3.05	ug/L	04/95	8.73	8.70	9.90	10.17	11.55	10.03	9.64	9.82	.970	3.143
1-Naphthylamine	2.12	ug/L	04/95	5.25	7.12	6.65	6.66	6.67	7.29	6.20	6.55	.673	3.143
2,3,4,6-Tetrachlorophenol	3.09	ug/L	04/95	8.44	8.61	9.67	9.97	11.31	9.97	10.25	9.75	.983	3.143
2,3,5,6-Tetrachlorophenol	2.84	ug/L	04/95	9.82	9.42	10.75	10.85	12.09	11.01	11.39	10.76	.905	3.143
2,4,5-Trichlorophenol	3.21	ug/L	04/95	9.20	9.83	10.35	10.26	12.40	10.90	9.94	10.41	1.020	3.143
2,4,6-Tribromophenol	3.12	ug/L	04/95	11.58	10.39	11.70	12.33	13.68	11.50	11.83	11.86	.994	3.143
2,4,6-Trichlorophenol	3.12	ug/L	04/95	8.72	9.20	9.94	10.37	11.82	10.42	10.25	10.10	.991	3.143
2,4-Dichlorophenol	3.55	ug/L	04/95	7.70	7.92	8.97	9.43	11.09	9.40	8.71	9.03	1.129	3.143
2,4-Dimethylphenol	5.33	ug/L	04/95	4.60	4.97	7.37	7.88	9.55	7.06	7.10	6.93	1.697	3.143
2,4-Dinitrophenol	4.06	ug/L	04/95	5.52	5.33	6.88	7.19	8.61	7.79	8.35	7.10	1.291	3.143
2,4-Dinitrotoluene	3.58	ug/L	04/95	9.93	9.73	10.80	11.74	13.03	11.36	11.64	11.18	1.139	3.143

MDL Study performed according to specifications in:

40 CFR Part 136 Appendix B

Method Detection Limit Study

Matrix : Water

Analyte	MDL	Units	Date of MDL	Rep 1	Rep 2	Rep 3	Rep 4	Rep 5	Rep 6	Rep 7	Avg	Std Dev	Student t Multiplier
2,6-Dichlorophenol	1.45	ug/L	04/95	7.14	7.76	6.29	6.78	7.19	7.15	6.73	7.01	.462	3.143
2,6-Dinitrotoluene	3.81	ug/L	04/95	9.79	10.02	11.40	11.04	13.51	11.18	10.88	11.12	1.214	3.143
2-Acetylaminofluorene	.78	ug/L	04/95	4.69	5.08	4.92	4.80	5.21	5.11	4.52	4.90	.249	3.143
2-Chloronaphthalene	2.83	ug/L	04/95	9.68	9.92	10.68	11.02	12.44	11.09	10.75	10.80	.901	3.143
2-Chlorophenol	3.29	ug/L	04/95	8.37	8.65	8.88	9.93	11.50	9.39	9.37	9.44	1.047	3.143
2-Chlorophenol-d4	3.17	ug/L	04/95	8.64	8.72	9.53	10.32	11.58	9.69	9.43	9.70	1.009	3.143
2-Fluorobiphenyl	3.17	ug/L	04/95	10.31	10.00	10.76	11.53	13.09	11.03	11.17	11.13	1.008	3.143
2-Fluorophenol	3.34	ug/L	04/95	7.81	8.34	8.21	9.77	10.89	8.63	8.91	8.94	1.061	3.143
2-Methylnaphthalene	2.89	ug/L	04/95	8.52	8.81	9.55	9.95	11.38	9.69	9.59	9.64	.920	3.143
2-Methylphenol	3.52	ug/L	04/95	8.23	8.44	9.65	9.97	11.56	9.97	9.14	9.57	1.121	3.143
2-Naphthylamine	2.06	ug/L	04/95	5.67	7.14	7.56	6.50	6.93	7.23	6.22	6.75	.656	3.143
2-Nitroaniline	3.13	ug/L	04/95	9.16	9.38	10.09	10.41	11.88	11.41	10.15	10.35	.994	3.143
2-Nitrophenol	2.56	ug/L	04/95	8.23	8.22	8.81	9.22	10.59	9.37	9.37	9.12	.816	3.143
2-Picoline	4.01	ug/L	04/95	2.81	5.33	5.34	5.46	3.91	6.02	3.10	4.57	1.275	3.143
3&4-Methylphenol	8.05	ug/L	04/95	15.88	16.75	18.97	20.08	23.74	19.53	18.21	19.02	2.560	3.143
3,3'-Dichlorobenzidine	7.81	ug/L	04/95	8.23	8.17	9.26	9.66	11.41	10.88	3.88	8.78	2.484	3.143
3,3'-Dimethylbenzidine	1.59	ug/L	04/95		4.15	5.05	4.48	4.88	5.41	4.52	4.75	.453	3.500
3-Chloropropionitrile	1.50	ug/L	04/95	4.13	3.58	3.85	4.57	4.18	3.55	3.15	3.86	.476	3.143
3-Methylcholanthrene	9.69	ug/L	04/95	23.61	20.76	18.72	18.95	19.90	19.49	13.34	19.25	3.084	3.143
3-Methylphenol	8.05	ug/L	04/95	15.88	16.75	18.97	20.08	23.74	19.53	18.21	19.02	2.560	3.143
3-Nitroaniline	4.31	ug/L	04/95	9.18	10.36	10.82	11.30	12.79	11.05	8.69	10.60	1.370	3.143
4,4'-Methylene bis(o-c	1.51	ug/L	04/95	5.99	7.19	6.86	6.48	7.14	7.38	6.69	6.82	.479	3.143
4,6-Dinitro-2-methylphenol	3.69	ug/L	04/95	7.13	7.03	7.90	8.23	10.33	8.76	9.20	8.37	1.173	3.143
4,6-Dinitro-o-cresol	0.00	ug/L	04/95								0.00	0.000	3.143
4-Aminobiphenyl	1.18	ug/L	04/95	5.73	6.51	6.87	6.41	6.76	6.70	6.43	6.49	.376	3.143
4-Bromophenyl phenyl ether	3.66	ug/L	04/95	9.51	9.18	10.16	10.93	12.59	11.41	10.84	10.66	1.166	3.143
4-Chloro-3-methylphenol	3.71	ug/L	04/95	7.87	8.11	9.36	9.62	11.41	9.93	9.44	9.39	1.182	3.143
4-Chloroaniline	6.95	ug/L	04/95	8.34	8.97	9.57	9.97	11.13	10.22	4.35	8.94	2.211	3.143

MDL Study performed according to specifications in:

40 CFR Part 136 Appendix B

Method Detection Limit Study

Matrix : Water

Analyte	MDL	Units	Date of MDL	Rep 1	Rep 2	Rep 3	Rep 4	Rep 5	Rep 6	Rep 7	Avg	Std Dev	Student t Multiplier
4-Chlorophenyl phenyl ether	2.95	ug/L	04/95	10.31	10.38	11.00	11.45	13.04	11.86	11.23	11.32	.938	3.143
4-Methylphenol	8.05	ug/L	04/95	15.88	16.75	18.97	20.08	23.74	19.53	18.21	19.02	2.560	3.143
4-Nitroaniline	6.23	ug/L	04/95	9.52	10.13	10.97	11.63	13.42	11.33	7.06	10.58	1.983	3.143
4-Nitrophenol	5.10	ug/L	04/95	8.85	8.35	10.99	10.27	13.06	11.77	10.46	10.54	1.623	3.143
4-Nitroquinoline-1-oxide	12.36	ug/L	04/95	17.58	15.52	11.48	7.04	14.81	12.79	7.85	12.44	3.933	3.143
5-Nitro-o-toluidine	0.00	ug/L	04/95								0.00	0.000	3.143
6-Methylchrysene	1.44	ug/L	09/95	2.52	3.70	2.98	3.24	3.50	3.30	2.52	3.11	.459	3.143
7,12-Dimethylbenz(a)anthracene	2.47	ug/L	04/95	4.46	4.70	5.56	3.64	3.90	5.71	4.27	4.61	.786	3.143
Acenaphthene	3.45	ug/L	04/95	10.44	10.28	11.62	12.04	13.54	12.00	11.48	11.63	1.097	3.143
Acenaphthylene	3.21	ug/L	04/95	10.11	10.10	11.17	11.38	13.15	11.32	11.04	11.18	1.022	3.143
Acetophenone	1.23	ug/L	04/95	7.93	8.45	7.66	7.64	7.94	8.10	7.22	7.85	.390	3.143
Aniline	9.65	ug/L	04/95	6.73	8.33	8.71	9.57	10.93	9.30	1.54	7.87	3.071	3.143
Anthracene	3.56	ug/L	04/95	9.80	9.31	10.49	11.33	12.77	11.28	10.85	10.83	1.133	3.143
Aramite, Total	0.00	ug/L	04/95								0.00	0.000	3.143
Benzidine	0.00	ug/L	04/95								0.00	0.000	3.143
Benzo(a)anthracene	3.43	ug/L	04/95	9.23	9.13	9.76	10.47	12.33	10.39	10.72	10.29	1.091	3.143
Benzo(a)pyrene	3.74	ug/L	04/95	9.33	9.32	10.61	10.84	12.76	11.17	10.14	10.60	1.191	3.143
Benzo(b)fluoranthene	4.02	ug/L	04/95	9.05	10.32	11.20	10.55	13.17	11.54	11.58	11.06	1.279	3.143
Benzo(ghi)perylene	3.53	ug/L	04/95	9.36	9.13	10.65	11.12	12.47	10.87	10.74	10.62	1.122	3.143
Benzo(k)fluoranthene	4.48	ug/L	04/95	11.54	10.58	12.15	14.07	14.75	12.55	12.65	12.61	1.426	3.143
Benzyl alcohol	10.71	ug/L	04/95	8.84	9.15	9.51	1.57	12.50	10.25	9.80	8.80	3.408	3.143
Bis(2-chloroethoxy)methane	2.99	ug/L	04/95	8.81	8.98	9.80	10.40	11.64	10.28	9.87	9.97	.952	3.143
Bis(2-chloroethyl)ether	3.40	ug/L	04/95	8.19	9.02	9.34	9.90	11.70	9.79	10.01	9.71	1.081	3.143
Bis(2-chloroisopropyl)ether	3.02	ug/L	04/95	8.62	8.41	9.67	9.85	11.32	9.72	9.21	9.54	.961	3.143
Bis(2-ethylhexyl)phthalate	4.80	ug/L	04/95	13.02	8.98	10.56	11.10	13.25	11.32	12.61	11.55	1.528	3.143
Butyl benzyl phthalate	4.03	ug/L	04/95	8.57	8.66	9.69	9.97	12.39	10.15	10.42	9.98	1.281	3.143
Carbazole	4.78	ug/L	04/95	11.25	11.07	12.31	12.72	15.65	13.13	13.02	12.74	1.522	3.143
Chrysene	3.69	ug/L	04/95	9.74	9.56	11.09	10.89	13.02	11.50	11.52	11.05	1.174	3.143

MDL Study performed according to specifications in:

40 CFR Part 136 Appendix B

Method Detection Limit Study

Matrix : Water

Analyte	MDL	Units	Date of MDL	Rep 1	Rep 2	Rep 3	Rep 4	Rep 5	Rep 6	Rep 7	Avg	Std Dev	Student t Multiplier
Cresols, total	11.57	ug/L	04/95	24.10	25.19	28.62	30.05	35.31	29.50	27.35	28.59	3.683	3.143
Di-n-butyl phthalate	4.30	ug/L	04/95	9.83	9.07	10.70	11.19	13.15	11.38	12.12	11.06	1.367	3.143
Di-n-octyl phthalate	4.43	ug/L	04/95	9.23	9.24	10.57	11.31	13.22	11.73	11.13	10.92	1.411	3.143
Diallate 1	1.54	ug/L	04/95	7.45	7.58	7.81	7.46	8.82	7.90	7.47	7.78	.491	3.143
Diallate 2	1.08	ug/L	04/95	7.28	8.28	7.62	7.74	7.30	7.84	7.59	7.66	.342	3.143
Diallate, Total	1.82	ug/L	04/95	14.54	15.38	14.30	14.75	15.88	15.08	14.37	14.90	.580	3.143
Dibenz(a,h)acridine	.73	ug/L	09/95	1.26	1.91	1.73	1.65	1.68	1.84	1.41	1.64	.231	3.143
Dibenz(a,h)anthracene	3.53	ug/L	04/95	9.36	9.13	10.65	11.12	12.47	10.87	10.74	10.62	1.122	3.143
Dibenzo(a,h)anthracene	3.53	ug/L	04/95	9.36	9.13	10.65	11.12	12.47	10.87	10.74	10.62	1.122	3.143
Dibenzofuran	2.96	ug/L	04/95	9.85	9.93	10.82	11.08	12.65	11.21	10.59	10.88	.943	3.143
Diethyl phthalate	3.28	ug/L	04/95	9.57	8.84	10.18	10.21	12.04	9.93	11.12	10.27	1.042	3.143
Dimethoate	1.55	ug/L	04/95	5.06	4.05	4.64	5.01	4.84	3.83	4.19	4.52	.492	3.143
Dimethyl phthalate	2.99	ug/L	04/95	9.24	7.83	9.64	9.48	11.08	9.16	9.42	9.41	.952	3.143
Dinoseb	4.28	ug/L	04/95	4.56	5.85	2.21	5.32	5.98	5.78	5.90	5.09	1.362	3.143
Diphenylamine	.50	ug/L	04/95	6.95	7.39	6.98	7.05	7.25	7.23	7.12	7.14	.160	3.143
Disulfoton	4.35	ug/L	04/95	5.18	5.01	6.89	3.96	4.37	6.36	2.86	4.95	1.384	3.143
Ethyl methacrylate	.84	ug/L	04/95	5.00	5.11	5.03	5.42	4.96	4.67	4.63	4.97	.268	3.143
Ethyl methanesulfonate	1.05	ug/L	04/95	7.64	7.96	7.31	7.16	7.40	7.63	6.97	7.44	.333	3.143
Famphur	8.28	ug/L	04/95	45.63	43.34	40.55	37.29	40.08	40.85	40.64	41.20	2.633	3.143
Fluoranthene	3.72	ug/L	04/95	10.22	10.22	10.89	11.75	13.57	12.09	11.75	11.50	1.184	3.143
Fluorene	3.22	ug/L	04/95	9.60	9.84	10.56	10.89	12.73	11.16	10.96	10.82	1.025	3.143
Hexachlorobenzene	3.82	ug/L	04/95	10.01	9.99	10.68	11.70	13.42	11.96	11.48	11.32	1.217	3.143
Hexachlorobutadiene	2.91	ug/L	04/95	8.81	8.63	9.72	9.71	11.49	9.69	9.83	9.70	.927	3.143
Hexachlorocyclopentadiene	1.32	ug/L	04/95	4.29	3.50	3.92	3.53	3.50	4.43	3.41	3.80	.420	3.143
Hexachloroethane	3.83	ug/L	04/95	8.01	8.37	8.90	10.32	11.59	9.28	9.48	9.42	1.218	3.143
Hexachloropropene	.99	ug/L	04/95	6.73	6.85	6.13	6.53	6.34	6.19	6.01	6.40	.316	3.143
Indene	1.69	ug/L	09/95	4.87	6.05	5.81	5.16	6.42	5.89	5.98	5.74	.538	3.143
Indeno(1,2,3-cd)pyrene	3.77	ug/L	04/95	9.23	8.98	10.14	10.70	11.90	12.11	10.59	10.52	1.201	3.143

MDL Study performed according to specifications in:

40 CFR Part 136 Appendix B

Method Detection Limit Study

Matrix : Water

Analyte	MDL	Units	Date of MDL	Rep 1	Rep 2	Rep 3	Rep 4	Rep 5	Rep 6	Rep 7	Avg	Std Dev	Student t Multiplier
Isophorone	3.29	ug/L	04/95	8.47	8.87	9.67	10.19	11.65	9.98	9.21	9.72	1.046	3.143
Isosafrole 1	1.19	ug/L	04/95	7.65	8.17	7.76	7.63	8.12	7.03	7.72	7.73	.377	3.143
Isosafrole 2	1.08	ug/L	04/95	6.36	6.50	6.31	6.17	6.12	6.93	5.83	6.32	.344	3.143
Isosafrole, Total	2.21	ug/L	04/95	13.91	14.55	13.97	13.69	13.64	14.97	12.77	13.93	.702	3.143
Malononitrile	4.40	ug/L	04/95	2.64	5.30	5.49	5.73	4.43	6.45	3.16	4.74	1.401	3.143
Methapyrilene	15.18	ug/L	04/95	16.96	26.47	21.37	11.28	20.43	17.46	15.51	18.50	4.831	3.143
Methyl methanesulfonate	7.83	ug/L	04/95	7.40	7.83	.68	6.97	7.12	7.18	6.73	6.27	2.492	3.143
N-Nitro-o-toluidine	.60	ug/L	04/95	7.40	8.00	7.49	7.65	7.68	7.70	7.71	7.66	.190	3.143
N-Nitrosodi-n-butylamine	1.07	ug/L	04/95	6.57	6.65	6.03	5.93	6.14	6.74	6.04	6.30	.340	3.143
N-Nitrosodi-n-propylamine	3.23	ug/L	04/95	8.23	8.53	9.46	10.00	11.12	9.69	8.50	9.36	1.027	3.143
N-Nitrosodiethylamine	1.24	ug/L	04/95	6.66	6.84	5.85	6.42	6.39	6.61	5.82	6.37	.395	3.143
N-Nitrosodimethylamine	4.30	ug/L	04/95	7.95	8.19	9.10	10.21	12.03	9.30	9.54	9.47	1.368	3.143
N-Nitrosodiphenylamine	3.99	ug/L	04/95	9.31	8.64	10.11	10.79	12.29	10.75	8.99	10.13	1.270	3.143
N-Nitrosomethylethylamine	1.44	ug/L	04/95	6.27	6.86	5.95	6.24	6.57	7.00	5.76	6.38	.457	3.143
N-Nitrosomorpholine	1.05	ug/L	04/95	5.96	5.86	5.95	5.43	5.93	6.49	5.59	5.89	.335	3.143
N-Nitrosopiperidine	1.02	ug/L	04/95	5.63	5.98	5.43	5.35	5.74	6.15	5.30	5.65	.324	3.143
N-Nitrosopyrrolidine	1.30	ug/L	04/95	5.69	6.11	5.57	5.98	5.81	6.60	5.32	5.87	.415	3.143
Naphthalene	2.59	ug/L	04/95	8.68	8.80	9.53	9.58	11.21	9.55	9.51	9.55	.824	3.143
Nitrobenzene	2.82	ug/L	04/95	8.90	9.21	9.90	10.11	11.70	9.71	10.13	9.95	.897	3.143
Nitrobenzene-d5	3.47	ug/L	04/95	8.69	8.56	10.10	9.72	11.87	9.59	9.38	9.70	1.103	3.143
O,O,O-Triethyl phosphorothioat	.92	ug/L	04/95	7.06	7.65	7.16	7.12	6.80	7.36	6.85	7.14	.293	3.143
Pentachlorobenzene	.92	ug/L	04/95	7.91	8.52	8.18	7.95	7.83	8.00	7.59	8.00	.292	3.143
Pentachloroethane	.89	ug/L	04/95	5.84	5.45	5.21	5.30	5.02	5.03	5.38	5.32	.282	3.143
Pentachloronitrobenzene	1.09	ug/L	04/95	7.81	8.07	8.13	7.69	8.11	8.42	7.36	7.94	.348	3.143
Pentachlorophenol	4.29	ug/L	04/95	6.22	6.68	6.78	7.90	10.21	8.33	8.33	7.78	1.364	3.143
Phenacetin	.59	ug/L	04/95	6.88	7.28	7.15	6.87	7.20	7.11	6.80	7.04	.188	3.143
Phenanthrene	3.56	ug/L	04/95	9.92	9.47	10.59	10.85	13.01	11.20	11.10	10.88	1.132	3.143
Phenol	3.24	ug/L	04/95	8.86	9.42	10.07	10.62	12.12	10.39	9.97	10.21	1.031	3.143

MDL Study performed according to specifications in:

40 CFR Part 136 Appendix B

Method Detection Limit Study

Matrix : Water

Analyte	MDL	Units	Date of MDL	Rep 1	Rep 2	Rep 3	Rep 4	Rep 5	Rep 6	Rep 7	Avg	Std Dev	Student t Multiplier
Phenol-d5	3.26	ug/L	04/95	8.25	8.83	9.04	9.99	11.46	9.78	9.23	9.51	1.037	3.143
Phorate	1.61	ug/L	04/95	6.52	7.32	7.30	6.02	6.66	7.17	6.33	6.76	.512	3.143
Pronamide	.71	ug/L	04/95	7.51	7.85	7.85	7.20	7.49	7.66	7.58	7.59	.227	3.143
Pyrene	4.15	ug/L	04/95	9.77	9.59	11.05	11.51	13.57	11.33	11.45	11.18	1.320	3.143
Pyridine	5.02	ug/L	04/95	1.59	4.93	2.06	4.23	5.72	2.70	2.23	3.35	1.598	3.143
Quinoline	2.18	ug/L	09/95	5.80	7.08	6.11	5.79	7.01	7.21	5.64	6.38	.693	3.143
Safrole, Total	.96	ug/L	04/95	6.99	7.49	6.78	6.89	7.01	7.35	6.62	7.02	.307	3.143
Terphenyl-d14	4.04	ug/L	04/95	9.97	9.75	11.30	11.68	13.59	11.92	11.52	11.39	1.287	3.143
Tetraethyl dithiopyrop	1.22	ug/L	04/95	6.89	7.49	7.27	6.54	6.99	7.16	7.71	7.15	.389	3.143
Tetraethyldithiopyrophosphate	0.00	ug/L	04/95								0.00	0.000	3.143
Thiophenol (Benzenethiol)	3.03	ug/L	09/95	3.78	2.40	2.31	4.39	3.87	3.15	4.85	3.54	.963	3.143
Zinophos	1.15	ug/L	04/95	7.54	8.53	8.13	7.66	8.05	7.60	7.67	7.88	.365	3.143
a,a-Dimethyl-phenethyl	16.24	ug/L	04/95	3.60	14.47	19.30	16.29	14.00	17.95	16.23	14.55	5.167	3.143
o-Toluidine	1.42	ug/L	04/95	6.80	8.15	7.51	7.37	7.04	7.71	7.13	7.39	.453	3.143
p-(Dimethylamino)azobenzene	.72	ug/L	04/95	5.81	6.51	6.18	6.25	6.06	6.35	6.04	6.17	.228	3.143
p-Chlorobenzilate	1.69	ug/L	04/95	6.45	7.08	6.57	5.48	6.17	6.09	6.90	6.39	.538	3.143
p-Phenylene diamine	22.73	ug/L	04/95	11.42	23.58	22.01	9.98	27.29	9.82	20.47	17.80	7.233	3.143
Indene	1.69	ug/L	09/95	4.87	6.05	5.81	5.16	6.42	5.89	5.98	5.74	.538	3.143
Quinoline	2.18	ug/L	09/95	5.80	7.08	6.11	5.79	7.01	7.21	5.64	6.38	.693	3.143
6-Methylchrysene	1.44	ug/L	09/95	2.52	3.70	2.98	3.24	3.50	3.30	2.52	3.11	.459	3.143
Dibenz(a,h)acridine	.73	ug/L	09/95	1.26	1.91	1.73	1.65	1.68	1.84	1.41	1.64	.231	3.143
Benzenethiol	3.03	ug/L	09/95	3.78	2.40	2.31	4.39	3.87	3.15	4.85	3.54	.963	3.143

MDL Study performed according to specifications in:

40 CFR Part 136 Appendix B

Pesticide/PCBs
Method Detection Limit Study
Matrix : Water

Analyte	MDL	Units	Date of MDL	MDL Conc	Rep 1	Rep 2	Rep 3	Rep 4	Rep 5	Rep 6	Rep 7	Avg	Std Dev	Student t Multiplier
4,4'-DDD	.0143	ug/L	04/95	.100	.1151	.1022	.1146	.1102	.1130	.1138	.1140	.1118	.0046	3.143
4,4'-DDE	.0161	ug/L	04/95	.100	.0902	.0993	.1004	.1015	.1041	.1017	.1064	.1005	.0051	3.143
4,4'-DDT	.0310	ug/L	04/95	.100	.1028	.1201	.1357	.1196	.1229	.1234	.1155	.1200	.0099	3.143
Aldrin	.0122	ug/L	04/95	.050	.0421	.0429	.0470	.0500	.0505	.0498	.0520	.0478	.0039	3.143
Alpha-BHC	.0054	ug/L	04/95	.050	.0494	.0508	.0531	.0522	.0542	.0534	.0534	.0524	.0017	3.143
Alpha-Chlordane	.0095	ug/L	04/95	.050	.0430	.0497	.0501	.0502	.0509	.0501	.0525	.0495	.0030	3.143
Aroclor 1016	.0374	ug/L	04/95	.250	.2129	.1914	.1990	.2014	.1786	.2121	.2021	.1996	.0119	3.143
Aroclor 1221	.0725	ug/L	04/95	.250	.2060	.1757	.2030	.2077	.2222	.1932	.1533	.1945	.0231	3.143
Aroclor 1232	.0668	ug/L	04/95	.250	.2690	.2439	.2741	.2245	.2159	.2467	.2502	.2463	.0212	3.143
Aroclor 1242	.0811	ug/L	04/95	.250	.2708	.2471	.2603	.1927	.2274	.2527	.2501	.2430	.0258	3.143
Aroclor 1248	.1183	ug/L	04/95	.250	.2809	.2559	.1655	.2446	.2031	.2372	.2424	.2328	.0377	3.143
Aroclor 1254	.1054	ug/L	04/95	.500	.4885	.5399	.4568	.5445	.5081	.4740	.4788	.4986	.0335	3.143
Aroclor 1260	.0984	ug/L	04/95	.500	.5289	.4688	.4898	.4963	.4366	.5213	.4977	.4913	.0313	3.143
Beta-BHC	.0284	ug/L	04/95	.050	.0397	.0575	.0556	.0634	.0656	.0632	.0639	.0584	.0090	3.143
Delta-BHC	.0145	ug/L	04/95	.050	.0402	.0510	.0487	.0515	.0528	.0516	.0540	.0500	.0046	3.143
Dieldrin	.0111	ug/L	04/95	.100	.1011	.0971	.1048	.1026	.1066	.1049	.1073	.1035	.0035	3.143
Endosulfan I	.0075	ug/L	04/95	.050	.0489	.0480	.0532	.0521	.0540	.0527	.0537	.0518	.0024	3.143
Endosulfan II	.0140	ug/L	04/95	.100	.0931	.1010	.1013	.1031	.1053	.1025	.1071	.1019	.0045	3.143
Endosulfan Sulfate	.0133	ug/L	04/95	.100	.1005	.1021	.1082	.1050	.1075	.1050	.0962	.1035	.0042	3.143
Endrin	.0350	ug/L	04/95	.100	.1104	.1083	.1144	.0836	.1140	.1125	.1148	.1083	.0111	3.143
Endrin Aldehyde	.0197	ug/L	04/95	.100	.1203	.1157	.1311	.1280	.1192	.1273	.1315	.1247	.0063	3.143
Endrin Ketone	.0125	ug/L	04/95	.100	.1010	.1029	.1089	.1057	.1072	.1057	.0973	.1041	.0040	3.143
Gamma-BHC	.0073	ug/L	04/95	.050	.0483	.0489	.0531	.0512	.0540	.0532	.0535	.0517	.0023	3.143
Gamma-Chlordane	.0088	ug/L	04/95	.050	.0445	.0504	.0504	.0507	.0516	.0505	.0537	.0503	.0028	3.143
Heptachlor	.0069	ug/L	04/95	.050	.0510	.0519	.0553	.0537	.0562	.0555	.0566	.0543	.0022	3.143
Heptachlor Epoxide	.0133	ug/L	04/95	.050	.0362	.0477	.0458	.0464	.0479	.0464	.0485	.0456	.0042	3.143
Hexachlorobenzene	.0125	ug/L	04/95	.050	.0403	.0338	.0292	.0328	.0400	.0372	.0361	.0356	.0040	3.143
Isodrin	.0156	ug/L	04/95	.050	.0502	.0530	.0398	.0444	.0475	.0413	.0417	.0454	.0050	3.143

MDL Study performed according to specifications in:
40 CFR Part 136 Appendix B

Pesticide/PCBs
Method Detection Limit Study
Matrix : Water

Analyte	MDL	Units	Date of MDL	MDL Conc	Rep 1	Rep 2	Rep 3	Rep 4	Rep 5	Rep 6	Rep 7	Avg	Std Dev	Student t Multiplier
Kepone	.1615	ug/L	04/95	.800	.8453	.8863	.7566	.7862	.8497	.8143	.7483	.8124	.0514	3.143
Methoxychlor	.0649	ug/L	04/95	.500	.5340	.5329	.5385	.5126	.4839	.5290	.5442	.5250	.0206	3.143
Methyl Parathion	.0096	ug/L	04/95	.050	.0518	.0544	.0476	.0475	.0518	.0509	.0458	.0500	.0031	3.143
Parathion	.0234	ug/L	04/95	.100	.1035	.1072	.0893	.0929	.1029	.0987	.0884	.0976	.0074	3.143
Technical Chlordane	.0271	ug/L	04/95	.250	.2380	.2271	.2262	.2243	.2252	.2093	.2197	.2243	.0086	3.143
Toxaphene	.5180	ug/L	04/95	1.250	.5715	.7471	.9972	.8438	.8102	1.0741	.7943	.8340	.1648	3.143

MDL Study performed according to specifications in:
40 CFR Part 136 Appendix B

Quanterra Environmental Services' North Canton
METHOD DETECTION LIMIT STUDY

DATE COMPLETED:	February - 1996	PROG/PROJECT:	NA
METHOD NUMBER:	200.7, 6010	PROJECT NUMBER:	1996 - MDLs
METHOD DESCRIPTION:	ICP	ANALYST:	Metals
PREP METHOD:	WATER	QUALITY ASSURANCE:	MJL

ANALYTE	SPIKE CONC ug/L	REPLICATE MEASUREMENT 1	2	3	4	5	6	7	AVG ug/L	Recovery of Spike %	PREC. ug/L	MDL ug/L	Report. Limit ug/L	STATUS
Aluminum	200	136.00	135.00	133.00	139.00	131.00	103.00	136.00	130.43	65.21%	12.35	38.83	200	pass
Antimony	60	72.00	74.00	68.00	62.00	72.00	59.00	70.00	68.14	113.57%	5.61	17.63	60	pass
Arsenic	100	98.00	96.00	100.00	104.00	105.00	107.00	110.00	102.86	102.86%	5.05	15.86	300	pass
Barium	10	12.00	13.00	13.00	12.00	13.00	13.00	13.00	12.71	127.14%	0.49	1.53	200	pass
Beryllium	4	4.00	4.00	3.00	3.00	4.00	4.00	4.00	3.71	92.86%	0.49	1.53	5	pass
Boron	250	194.00	217.00	201.00	196.00	195.00	191.00	214.00	201.14	80.46%	10.29	32.33	200	pass
Cadmium	10	10.00	11.00	9.00	12.00	11.00	11.00	11.00	10.71	107.14%	0.95	2.99	5	pass
Calcium	500	312.00	445.00	334.00	309.00	328.00	331.00	342.00	343.00	68.60%	46.50	146.1	5000	pass
Chromium	10	11.00	12.00	12.00	10.00	8.00	11.00	9.00	10.43	104.29%	1.51	4.75	10	pass
Cobalt	50	57.00	57.00	60.00	57.00	55.00	54.00	54.00	56.29	112.57%	2.14	6.72	50	pass
Copper	10	11.00	12.00	11.00	9.00	13.00	10.00	11.00	11.00	110.00%	1.29	4.06	25	pass
Iron	100	117.00	122.00	150.00	114.00	137.00	112.00	121.00	124.71	124.71%	13.83	43.46	100	pass
Lead	50	52.00	62.00	38.00	51.00	41.00	57.00	66.00	52.43	104.86%	10.31	32.40	100	pass
Magnesium	200	225.00	244.00	207.00	200.00	227.00	209.00	201.00	216.14	108.07%	16.31	51.27	5000	pass
Manganese	10	10.00	9.00	8.00	9.00	9.00	10.00	10.00	9.29	92.86%	0.76	2.38	15	pass
Molybdenum	100	105.00	102.00	104.00	112.00	104.00	103.00	100.00	104.29	104.29%	3.77	11.86	20	pass
Nickel	40	42.00	40.00	45.00	56.00	45.00	40.00	41.00	44.14	110.36%	5.64	17.73	40	pass
Potassium	500	511.00	545.00	524.00	517.00	594.00	513.00	506.00	530.00	106.00%	31.0	97.3	5000	pass
Selenium	250	162.00	205.00	201.00	206.00	202.00	197.00	230.00	200.43	80.17%	20.07	63.09	250	pass
Silver	20	13.00	13.00	14.00	13.00	13.00	12.00	14.00	13.14	65.71%	0.69	2.17	10	pass
Sodium	1000	1230.0	1327.0	1298.0	1201.0	1376.0	1201.0	1240.0	1267.57	126.76%	67.39	211.81	5000	pass
Strontium	10	10.1	10.2	9.5	9.6	10.2	9.6	9.6	9.83	98.29%	0.32	1.01	50	pass
Thallium	200	140.00	112.00	131.00	166.00	154.00	112.00	173.00	141.14	70.57%	24.50	77.00	2000	pass

fail => MDL Value is above RL, Accuracy is < 50% or > 150%, or MDL <10% or > 10X spike level

Quanterra Environmental Services' North Canton
METHOD DETECTION LIMIT STUDY

DATE COMPLETED:	February - 1996	PROG/PROJECT:	NA
METHOD NUMBER:	200.7, 6010	PROJECT NUMBER:	1996 - MDLs
METHOD DESCRIPTION:	ICP	ANALYST:	Metals
PREP METHOD:	WATER	QUALITY ASSURANCE:	MJL

ANALYTE	SPIKE CONC ug/L	REPLICATE MEASUREMENT 1	2	3	4	5	6	7	AVG ug/L	Recovery of Spike %	PREC. ug/L	MDL ug/L	Report. Limit ug/L	STATUS
Tin	75	78.00	74.00	81.00	71.00	80.00	77.00	74.00	76.43	101.90%	3.60	11.31	100	pass
Titanium	20	24.00	25.00	25.00	25.00	22.00	20.00	23.00	23.43	117.14%	1.90	5.98	50	pass
Tungsten	100	127.00	136.00	151.00	124.00	148.00	131.00	141.00	136.86	136.86%	10.32	32.43	500	pass
Vanadium	20	22.00	20.00	21.00	24.00	22.00	19.00	18.00	20.86	104.29%	2.04	6.40	50	pass
Zinc	50	69.00	75.00	67.00	64.00	68.00	62.00	62.00	66.71	133.43%	4.61	14.48	20	pass

fail => MDL Value is above RL, Accuracy is < 50% or > 150%, or MDL <10% or > 10X spike level

Purge: 25ml
Method: AF
Instrument: hp-1

COMPOUND	DATE	MDL	AMOUNT SPIKED	AVG CONC	PERCENT RECOVERY	CONC. > MDL?	CONC. < 10 x MDL?
1,1,1,2-Tetrachloroethane	04/10/95	0.14	0.4	0.42	105.0	YES	YES
1,1,1-Trichloroethane	04/10/95	0.12	0.4	0.41	102.5	YES	YES
1,1,2,2-Tetrachloroethane	04/10/95	0.16	0.4	0.41	102.5	YES	YES
1,1,2-Trichloroethane	04/10/95	0.20	0.4	0.39	97.5	YES	YES
1,1-Dichloroethane	04/10/95	0.12	0.4	0.42	105.0	YES	YES
1,1-Dichloroethene	04/10/95	0.19	0.4	0.45	112.5	YES	YES
1,1-Dichloropropene	04/10/95	0.05	0.4	0.42	105.0	YES	YES
1,2,3-Trichlorobenzene	04/10/95	0.28	0.4	0.46	115.0	YES	YES
1,2,3-Trichloropropane	04/10/95	0.27	0.4	0.35	87.5	YES	YES
1,2,4-Trichlorobenzene	04/10/95	0.24	0.4	0.47	117.5	YES	YES
1,2,4-Trimethylbenzene	04/10/95	0.14	0.4	0.49	122.5	YES	YES
1,2-Dibromo-3-chloropropane	04/10/95	0.24	0.4	0.43	107.5	YES	YES
1,2-Dibromoethane	04/10/95	0.10	0.4	0.38	95.0	YES	YES
1,2-Dichlorobenzene	04/10/95	0.13	0.4	0.45	112.5	YES	YES
1,2-Dichloroethane	04/10/95	0.13	0.4	0.42	105.0	YES	YES
1,2-Dichloroethene (total)	04/10/95	0.18	0.8	0.83	103.8	YES	YES
1,2-Dichloropropane	04/10/95	0.09	0.4	0.46	115.0	YES	YES
1,3,5-Trimethylbenzene	04/10/95	0.12	0.4	0.50	125.0	YES	YES
1,3-Dichlorobenzene	04/10/95	0.11	0.4	0.45	112.5	YES	YES
1,3-Dichloropropane	04/10/95	0.13	0.4	0.44	110.0	YES	YES
1,4-Dichloro-2-butene	04/10/95	0.20	0.4	0.46	115.0	YES	YES
1,4-Dichlorobenzene	04/10/95	0.10	0.4	0.52	130.0	YES	YES
2,2-Dichloropropane	04/10/95	0.23	0.4	0.35	87.5	YES	YES
2-Butanone	04/10/95	4.88	10	12.31	123.1	YES	YES
2-Chloroethyl vinyl ether	04/10/95	0.29	0.4	0.28	70.0	YES	YES
2-Chlorotoluene	04/10/95	0.12	0.4	0.50	125.0	YES	YES
2-Hexanone	04/10/95	4.59	10	11.21	112.1	YES	YES
4-Chlorotoluene	04/10/95	0.12	0.4	0.45	112.5	YES	YES
4-Isopropyltoluene	04/10/95	0.16	0.4	0.49	122.5	YES	YES
4-Methyl-2-pentanone	04/10/95	3.03	10	12.38	123.8	YES	YES
Acetone	04/11/95	4.43	10	11.09	110.9	YES	YES
Acrolein	04/10/95	3.30	20	8.85	44.3	YES	YES
Acrylonitrile	04/10/95	0.32	0.4	0.47	117.5	YES	YES
Benzene	04/10/95	0.08	0.4	0.52	130.0	YES	YES
Bromobenzene	04/10/95	0.13	0.4	0.46	115.0	YES	YES
Bromochloromethane	04/10/95	0.10	0.4	0.38	95.0	YES	YES
Bromodichloromethane	04/10/95	0.12	0.4	0.43	107.5	YES	YES
Bromoform	04/10/95	0.21	0.4	0.29	72.5	YES	YES
Bromomethane	04/10/95	0.24	0.4	0.41	102.5	YES	YES
Carbon disulfide	04/10/95	0.06	0.4	0.42	105.0	YES	YES
Carbon tetrachloride	04/10/95	0.14	0.4	0.38	95.0	YES	YES
Chlorobenzene	04/10/95	0.09	0.4	0.45	112.5	YES	YES
Chloroethane	04/10/95	0.30	0.4	0.37	92.5	YES	YES
Chloroform	04/10/95	0.14	0.4	0.46	115.0	YES	YES
Chloromethane	04/10/95	0.19	0.4	0.34	85.0	YES	YES
Dibromochloromethane	04/10/95	0.13	0.4	0.40	100.0	YES	YES
Dibromomethane	04/10/95	0.22	0.4	0.39	97.5	YES	YES
Dichlorodichloromethane	04/10/95	0.15	0.4	0.28	70.0	YES	YES
Ethylbenzene	04/10/95	0.11	0.4	0.45	112.5	YES	YES

Purge: 25ml
Method: AF
Instrument: hp-1

COMPOUND	DATE	MDL	AMOUNT SPIKED	AVG CONC	PERCENT RECOVERY	CONC. > MDL?	CONC. < 10 x MDL?
Hexachlorobutadiene	04/10/95	0.23	0.4	0.50	125.0	YES	YES
Iodomethane	04/10/95	0.20	0.4	0.35	87.5	YES	YES
Isopropylbenzene	04/10/95	0.12	0.4	0.48	120.0	YES	YES
Methylene chloride	04/10/95	0.37	0.4	0.53	132.5	YES	YES
Naphthalene	04/10/95	0.24	0.4	0.43	107.5	YES	YES
Styrene	04/10/95	0.08	0.4	0.42	105.0	YES	YES
Tetrachloroethene	04/10/95	0.07	0.4	0.45	112.5	YES	YES
Toluene	04/10/95	0.07	0.4	0.49	122.5	YES	YES
Trichloroethene	04/10/95	0.15	0.4	0.51	127.5	YES	YES
Trichlorofluoromethane	04/10/95	0.28	0.4	0.43	107.5	YES	YES
Vinyl acetate	04/10/95	2.93	10	10.44	104.4	YES	YES
Vinyl chloride	04/10/95	0.21	0.4	0.36	90.0	YES	YES
Xylenes (total)	04/10/95	0.24	1.2	1.35	112.5	YES	YES
cis-1,2-Dichloroethene	04/10/95	0.07	0.4	0.44	110.0	YES	YES
cis-1,3-Dichloropropene	04/10/95	0.11	0.4	0.41	102.5	YES	YES
m + p-Xylene	04/10/95	0.17	0.4	0.91	227.5	YES	YES
n-Butylbenzene	04/10/95	0.16	0.4	0.49	122.5	YES	YES
n-Propylbenzene	04/10/95	0.12	0.4	0.49	122.5	YES	YES
o-Xylene	04/10/95	0.08	0.4	0.44	110.0	YES	YES
sec-Butylbenzene	04/10/95	0.12	0.4	0.46	115.0	YES	YES
tert-Butylbenzene	04/10/95	0.11	0.4	0.49	122.5	YES	YES
trans-1,2-Dichloroethene	04/10/95	0.13	0.4	0.39	97.5	YES	YES
trans-1,3-Dichloropropene	04/10/95	0.09	0.4	0.38	95.0	YES	YES
1-Chlorohexane	04/10/95	0.10	0.4	0.46	115.0	YES	YES

QUANTERRA STANDARD OPERATING PROCEDURE

TITLE: CHLORIDE - AUTOMATED FERRICYANIDE

(SUPERSEDES: ENSECO SOP #LM-WALN-1091 (DRAFT))

Prepared by: _____

Reviewed by: _____
Technology Specialist

Approved by: _____
Quality Assurance Manager

Approved by: _____
Environmental Health and Safety Coordinator

Approved by: _____
Laboratory Director

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1. SCOPE AND APPLICATION

1.1. This method is applicable to the preparation of samples for the determination of Chloride in drinking, surface, and saline waters, domestic and industrial wastewaters. It is based on EPA Method 325.2 and SW846 Method 9251. The linear working range is 1 to 100 mg/L.

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 by the laboratory QA department.

2. SUMMARY OF METHOD

2.1. Thiocyanate ion (SCN) is liberated from mercuric thiocyanate by sequestering mercury via chloride ion to form unionized mercuric chloride. In the presence of ferric ion, the liberated SCN forms ferric thiocyanate which is colored solution whose concentration is proportional to the original chloride concentration.

3. DEFINITIONS

3.1. Refer to the glossary in the Quality Assurance Management Plan (QAMP).

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.

5. SAFETY

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

5.2. Eye protection that satisfies ANSI Z87.1 (as per the Chemical Hygiene Plan), 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 health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the Material Safety Data Sheets (MSDS) maintained in the laboratory. The following specific hazards are known:

5.3.1. Chemicals known to be **flammable** are: **Methanol.**

5.3.2. The following materials are known to be **corrosive: Nitric Acid.**

5.3.3. **Mercury** and **cyanide** are highly toxic compounds that must be handled with care. The analyst must be aware of the handling and clean-up techniques before using this material.

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. 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 Quanterra associate. The situation must be reported **immediately** to a laboratory supervisor.

6. EQUIPMENT AND SUPPLIES

6.1. Autoanalyzer: Bran-Leubbe Traacs 800

Equipment necessary includes:

1. Probe - 0.027
2. Flowcell - 10 mm
3. Wavelength cell - 480 nm
4. Manifold - Multitest Cartridge with Normal Tubing
5. See Operation Manual for further requirements

6.2. Filter paper

6.3. Erlenmeyer flasks: various

6.4. Analytical balance: capable of accurately weighing ± 0.0001 g

7. REAGENTS AND STANDARDS

7.1. Reagents

7.1.1. Brij-35: reagent grade

7.1.2. Purchased Color Reagent (Ricca or other supplier). Add 5 - 6 drops of Brij -35 per 150 mL prior to analysis. Alternatively, color reagent may be prepared as in 7.1.2.

7.1.3. Prepared Color Reagent

7.1.3.1. Methanol: reagent grade

7.1.3.2. Mercuric Thiocyanate: reagent grade

7.1.3.3. Mercuric Thiocyanate Solution, $Hg(SCN)_2$: Dissolve 4.17 g $Hg(SCN)_2$ in 500 mL of methanol. Dilute to 1 liter with methanol, mix, and filter.

7.1.3.4. Nitric acid: concentrated, reagent grade

7.1.3.5. Ferric Nitrate: reagent grade

7.1.3.6. Ferric Nitrate Solution, $Fe(NO_3)_3$, 20.2%: Dissolve 202 g of $Fe(NO_3)_3 \bullet 9H_2O$ in 500 mL of reagent water. Add 31.5 mL of concentrated nitric acid (HNO_3), mix, and dilute to 1 liter with reagent water.

7.1.3.7. Color Reagent: Add 150 mL of mercuric thiocyanate solution to 150 mL of ferric nitrate solution, mix, and dilute to 1 liter with reagent water. Add 5 - 6 mL Brij-35 to each 150 mL aliquot used for analysis.

7.1.4. 30% Brig-Solution: Add 2 mL Brig-35 to 1000 mL reagent water.

7.2. Standards

7.2.1. Primary (1°) Chloride Stock Standard, 1000 mg/L: Purchased from Hach or other supplier.

7.2.1.1. Chloride Calibration Standards: Pipet appropriate volumes of the 1000 mg/L primary chloride standard into 100 mL volumetric flasks and bring to volume with reagent water. Stable for 1month.

Concentration Cl	mL Cl	Final Volume
100 mg/L	10	100 mL
50 mg/L	5	100 mL
25 mg/L	2.5	100 mL
10 mg/L	1.0	100 mL
1 mg/L	0.1	100 mL

7.2.2. Secondary (2°) Chloride Stock Standard, 1000 mg/L: Add 0.8241 g pre-dried sodium chloride (NaCl) to a 500 mL reagent water in a 1000 mL volumetric flask and dilute to volume with reagent water. Stable for 6 months.

7.2.2.1. Chloride Standards: Pipet 5.0 mL of the 1000 mg/L secondary Chloride standard into a 200 mL volumetric flask. Dilute to volume with reagent water. Stable for 1 month. This standard can be used for the LCS, ICV/CCV and MS/MSD.

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 twenty-eight days from sampling to analysis.

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, 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.

9.2. 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. A blank consisting of reagent water must be 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 aqueous 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. A midrange LCS consisting the 25 mg/L standard (Section 7.2.2.1) must be analyzed with each analytical batch of samples.

9.3.3. Corrective Action for LCS

9.3.3.1. If any analyte is outside established control limits the system is out of control and corrective action must occur.

9.3.3.2. 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. 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.

9.4.2. A MS/MSD consisting of 2 mL of the 25 mg/L standard (Section 7.2.2.1) and 2 mL of sample will be analyzed with each analytical batch of samples.

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 DIL (diluted out).

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.

10. CALIBRATION AND STANDARDIZATION

10.1. Initial Calibration

10.1.1. The instrument is calibrated at the beginning of each run with five calibration standards and is verified at the beginning of the run by using a midrange ICV (25 mg/L). The correlation coefficient of the original curve must be ≥ 0.995 or recalibration is required.

10.2. Continuing Calibration

10.2.1. The run is checked every ten samples and at the end of the run using a midrange CCV (25 mg/L) to verify continued linearity. It cannot vary from the original curve by more than ± 10% or recalibration is required.

10.2.2. System cleanliness is checked every ten samples and at the end of the run using a CCB (reagent water). It cannot contain Chloride above the reporting limit or recalibration is required.

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. Solid Samples: Prepared according to NC-WC-0073, Solid Extraction Method.

11.3.2. Filter samples that contain particulates.

11.4. Sample Analysis

11.4.1. Recommended Instrument Conditions (Base and Gain)

11.4.1.1.Start-up Solutions (and Wash Solutions)

11.4.1.1.1.All 5-lines in 30% Brig Solution

11.4.1.2.Running Solutions

11.4.1.2.1.Gray/Gray (#1) in the chloride color reagent (plus brig)

11.4.1.2.2.Lines 2-5 in 30% Brig Solution

11.4.1.3.Base and Gain

11.4.1.3.1.A daily Base and Gain should be performed using the highest calibration standard (100 mg/L).

Normal Values: Base = 70

Gain = 20

These values are for reference only and change slightly with new reagents and standards.

11.4.1.4.Normal Tray Protocol from Traacs 800 edit Program of Chloride

11.4.1.4.1.P@1, 5C>1, H@1, 2L@4, 3I@3, X>6, H@1, 2L@4, G@1, E.
Where X = Number of Samples -(minus) the five calibration cups.

11.5. Sample Analysis Procedure

11.5.1. Operate the instrument per manufacturer's specifications.

11.5.2. Analyze the LCS/CCV and a reagent water blank at the beginning of the run.

11.5.3. Analyze CCV's and CCB's every 10 samples and at the end of the run.

11.5.4. Any samples that are higher than the highest standard (100 mg/L) must be diluted a with reagent water and reanalyzed.

11.5.5. Any sample analyzed after a high sample should be reanalyzed if carryover is suspected.

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 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. Calculations

12.1.1. ***Chloride, mg/L = Instrument Value (x Dilution)***

12.1.2. ***LCS Recovery:*** $\frac{\text{Instrument Value}}{\text{25 (true)}} \times 100 = \%\ \text{Recovery}$

12.1.3. ***CCV Recover:*** $\frac{\text{Instrument Value}}{\text{25 (true)}} \times 100 = \%\ \text{Recovery}$

12.1.4. ***MS/MSD Recovery:*** $\frac{A - B}{\text{12.5 (true)}} \times 100 = \%\ \text{Recovery}$

Where:

A = Instrument value for MS/MSD

B = Instrument value for sample x 0.5

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.

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 analyzed samples may be rinsed down the drain with large quantities of reagent water.

15.2. Chloride aqueous waste resulting from analysis must be emptied into the acidic mercury waste container. It may not be emptied into the sink.

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

15.4. Acid waste must be collected in clearly labeled acid waste containers.

15.5. Solid materials (gloves, soiled paper products, etc.) are placed in the solid debris container. Do not put liquids in the solid waste container.

15.6. Refer to the Laboratory Sample and Waste Disposal plan.

15.7. Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices of Quanterra.

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. MCAWW EPA 600, Chloride (Colorimetric, Automated), Method 325.2

16.1.2. SW846, Test Methods for Evaluating Solid Waste, 3rd Edition, Chloride, Method 9251.

16.2. SOP References

16.2.1. Solid Extraction Procedure, NC-WC-0073

17. MISCELLANEOUS (TABLES, APPENDICES, ETC...)

17.1. Reporting limits

17.1.1. The lower reporting limit (RL) for undiluted samples is 1 mg/L.

17.1.2. If samples require dilution or smaller volumes than specified in this method, the RL will be elevated.

17.2. Troubleshooting Guide

17.2.1. Consult the autoanalyzer operations manual for guidance on instrument problems and routine maintenance.

QUANTERRA STANDARD OPERATING PROCEDURE

TITLE: NITRITE (NO_2), NITRATE/NITRITE (NO_3 NO_2) AND NITRATE (NO_3) AUTOMATED

(SUPERSEDES: NC-WC-0001 (REVISION 0))

Prepared by: _____

Reviewed by: _____
Technology Specialist

Approved by: _____
Quality Assurance Manager

Approved by: _____
Environmental Health and Safety Coordinator

Approved by: _____
Laboratory Director

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1. SCOPE AND APPLICATION

1.1. This method is applicable to the determination of Nitrite singly or Nitrite and Nitrate combined in surface and saline waters and domestic and industrial wastes. It is also applicable to solid samples if they have been prepared according to SOP NC-WC-0073. Nitrite and Nitrate combined minus Nitrite only results in a Nitrate value. This method is based on EPA Method 353.2. The working linear range is highly instrument dependent, but for reference purposes is 0.04 - 1 mg/L for Nitrite, 0.04 - 2 mg/L for Nitrate, and 0.08 - 2 mg/L for combined Nitrite/Nitrate. For solid samples, the linear range is 0.08 - 20 mg/kg for Nitrite, 0.08 - 40 mg/kg for Nitrate, and 0.16 - 40 mg/kg for combined Nitrite/Nitrate.

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 by the laboratory QA department.

2. SUMMARY OF METHOD

2.1. An aliquot of sample is analyzed on two autoanalyzer manifolds simultaneously. One manifold determines Nitrite only. The other manifold reduces Nitrate to Nitrite and produces a total value. A manual subtraction determines the concentration of Nitrate.

2.2. A filtered sample is passed through a column containing cadmium to reduce nitrate to nitrite. The nitrite (that originally present plus reduced nitrate) is determined by diazotizing with sulfanilamide and coupling with N-(1-naphthyl)-ethylendiamine dihydrochloride to form a highly colored azo dye which is measured colorimetrically. Separate, rather than combined nitrate-nitrite, values are readily obtained by carrying out the procedure first with, and then without, the Cu-Cd reduction step.

3. DEFINITIONS

3.1. Refer to the glossary in the Quality Assurance Management Plan (QAMP).

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. Suspended matter may interfere and restrict sample flow. The sample may be filtered, settled, or centrifuged prior to analysis.

4.3. Iron, copper, and other metals may interfere causing low results. The addition of (Ethylenedinitro)-tetraacetic acid (EDTA) will eliminate this interference.

4.4. Oil and grease in the sample coat the surface of the cadmium and prevent complete reduction of nitrate to nitrite. This interferences is usually removed by filtration prior to analysis. If filtration is not adequate, the interference can be removed by pre-extracting the sample with an organic solvent.

4.5. In acidic samples (pH < 4.5), Nitrate is not reduced in the cadmium column. The sample must have a pH between 6 - 8 prior to analysis.

5. SAFETY

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

5.2. Eye protection that satisfies ANSI Z87.1 (as per the Chemical Hygiene Plan), 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 health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the Material Safety Data Sheets (MSDS) maintained in the laboratory. The following specific hazards are known:

5.3.1. The following materials are known to be **corrosive: Hydrochloric Acid, Nitric Acid, and Phosphoric Acid**

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. 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 Quanterra associate. The situation must be reported **immediately** to a laboratory supervisor.

6. EQUIPMENT AND SUPPLIES

6.1. Traacs 800

6.2. Probe 0.016"

6.3. Flowcells 10 mm

6.4. Wavelength cells - 520 nm

6.5. Manifold - Multitest board with multitest tubing

6.6. Manifold - NO_2NO_3 Cartridge

6.7. Erlenmeyer flasks: various

6.8. Compressed Nitrogen Gas

6.9. Volumetric flasks: various

6.10. Volumetric pipettes: various

6.11. Syringe: 10 cc

6.12. Nitrate-free 45 μm filter paper

6.13. Amber bottles

6.14. pH paper

6.15. Drying oven

6.16. Dessicator

6.17. Top loading balance: capable of accurately weighing ± 0.01 g

6.18. Analytical balance: capable of accurately weighing ± 0.0001 g

6.19. 40 mL vials

6.20. Disposable pipettes

7. REAGENTS AND STANDARDS

7.1. Reagents (for use with TRAACS 800)

7.1.1. Brij Solution, 30%: Add 3 mL of Brij-35 to 1 liter of reagent water and mix.

7.1.2. Triton Solution, 50/50: Add 1 mL of 50% triton (½ triton X-100 and ½ isopropyl alcohol) to 1 liter of reagent water and mix.

7.1.3. Sulfanilamide Solution: Add 200 mL of concentrated phosphoric acid (H_3PO_4) to 700 mL of reagent water in a 1 liter volumetric flask. Add 10 g of sulfanilamide and add 0.8 g NED (N-1-naphthlethylenediamine). Mix and dilute to volume. Pour into an amber bottle and add 2 mL of Brij - 35. Stable for one month.

7.1.4. Stock Imidazole Buffer: Add 6.81 g of imidazole to a 1 liter volumetric flask and add about 800 mL of reagent water. Adjust the pH to 7.5 (± 0.05) using 1:1 hydrochloric acid (HCl). Dilute to 1 liter with reagent water and store in amber container.

7.1.5. Copper Sulfate Solution, 0.01 M: Add 2.5 g of copper sulfate ($CuSO_4$) to a 1 liter volumetric flask and bring to volume with reagent water.

7.1.6. Copper Sulfate Solution, 0.001 M: Add 10 mL of 0.01 M $CuSO_4$ to a 100 mL volumetric flask and bring to volume with reagent water.

7.1.7. Working Imidazole Buffer: Add 50.0 mL of stock imidazole buffer and 0.5 mL of 0.001 M $CuSO_4$ to a 100 mL volumetric flask. Bring to volume with reagent water and add 5 drops of 50% triton. Make daily.

7.1.8. SAN Solution: Add 5.0 g sulfanilamide to a 1 liter volumetric flask containing 800 mL of reagent water and 50 mL of concentrated HCl. Mix, bring to volume with reagent water, and add 15 drops of 50% triton. Store in an amber container at 4°C ± 2°C.

7.1.9. NED Solution: Add 0.5 g (N-l-naphthylethylenediamine) dihydrochloride to a 1 liter volumetric flask and bring to volume with reagent water. Add 15 drops of 50% triton and store in amber container at 4°C ± 2°C.

7.1.10. Hydrochloric Acid, HCl, 2 N: Add 165 mL of concentrated HCl to a 1 liter volumetric flask and bring to volume with reagent water. Add 15 drops of 50% triton.

7.1.11. Nitric Acid, 2 N: Add 12.5 mL of concentrated nitric acid (HNO_3) to 50 mL of reagent water in a 100 mL volumetric flask and bring to volume with reagent water.

7.1.12. Activating Solution: Add 50 mL of 0.01 M $CuSO_4$ to a 100 mL volumetric flask and bring to volume with reagent water. Add 4 drops of 50% triton.

7.1.13. Concentrated Sulfuric Acid (H_2SO_4): reagent grade

7.1.14. Concentrated Hydrochloric Acid (HCl): reagent grade

7.1.15. Concentrated Nitric Acid (HNO_3): reagent grade

7.1.16. Concentrated Phosphoric Acid (H_3PO_4): reagent grade

7.1.17. Isopropyl Alcohol: reagent grade

7.1.18. Brij-35

7.1.19. Triton-100

7.1.20. Sulfanilamide: reagent grade

7.1.21. NED (N-1-napthylethylenediamine) dihydrochloride: reagent grade

7.1.22. Imidazole: reagent grade

7.1.23. Copper Sulfate ($CuSO_4 \bullet 5H_2O$): reagent grade

7.1.24. Trichlorotrifluoroethane (freon)

7.1.25. n-Hexane (80%) and methyl-tert-butyl ether (20%)

7.2. Start Up Solutions (and Wash Solutions):

7.2.1. Nitrite

7.2.1.1. 4 lines (#2-5) in reagent water

7.2.1.2. 1 line (#1) in 30% Brij solution

7.2.2. Nitrate/Nitrite

7.2.2.1. All lines (3 reagent lines) in 50/50 triton solution.

7.3. Standards

7.3.1. Primary Nitrate Stock Standard NO_3, 100 mg/L: Add 0.1518 g of KNO_3 from one solid standard source to a 250 mL volumetric flask and dilute to volume with reagent water. Stable for three months. Store in a glass, amber bottle at 4°C ± 2°C.

7.3.2. Secondary Nitrate Stock Standard, NO_3, 100 mg/L: Add 0.1518 g of KNO_3 from a solid standard source, not used to make primary source, to a 250 mL volumetric flask and dilute to volume with reagent water. Stable for one month. Store in a glass, amber bottle at 4°C ± 2°C.

7.3.3. Primary Nitrite Stock Standard, NO_2, 100 mg/L: Add 0.1804 g of KNO_2 from one solid standard source to a 250 mL volumetric flask and dilute to volume with reagent water. Stable for one month. Store in a glass, amber bottle at 4°C ± 2°C.

7.3.4. Secondary Nitrite Stock Standard, NO_2, 100 mg/L: Add 0.1804 g of KNO_2 from a solid standard source, not used to make primary source, to a 250 mL volumetric flask

and dilute to volume with reagent water. Stable for one month. Store in a glass, amber bottle at 4°C ± 2°C.

7.3.5. Calibration Standards - (See **TABLE I**)

7.3.5.1. Prepare a series of at least five standards from the primary nitrate stock and primary nitrite stock that cover the linear range of the instrument.

Add appropriate volume of indicated standard to 250 mL volumetric flask and bring to volume with reagent water. Add the appropriate volume of indicated standard to a 1 liter volumetric flask for the CCV, LCS, and MS/MSD.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Samples are not chemically preserved.

8.2. Samples are stored in glass containers at 4°C ± 2°C.

8.3. Samples can be preserved with 2 mL of concentrated H_2SO_4 and refrigerated at 4°C (for NO_2 NO_3 only).

8.4. The holding time is forty-eight hours from sampling to analysis for unpreserved samples and twenty-eight days from sampling to analysis for preserved 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, 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.

9.2. 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 taken in consultation with the client and must be addressed in the project narrative.**

9.3. Laboratory Control Sample (LCS)

9.3.1. One aqueous 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. A midrange LCS (0.5 mg/L NO_2/0.5 mg/L NO_3 = 1.0 NO_2 NO_3) must be analyzed with each analytical batch of samples.

9.3.3. Corrective Action for LCS

9.3.3.1. If any analyte is outside established control limits the system is out of control and corrective action must occur.

9.3.3.2. 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. 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.

9.4.2. An MS/MSD consisting of 2 mL of sample and 2 mL of MS/MSD standard 0.5/0.5 = 1.0) will be analyzed with each analytical batch of samples.

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 DIL (diluted out).

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.

10. CALIBRATION AND STANDARDIZATION

NOTE: Consult manufacturers instructions for operation procedures.

10.1. Summary

10.1.1. A daily Base and Gain is performed to determine high and low ranges.

10.1.2. The autoanalyzer is then calibrated at the beginning of each run using five calibration standards.

10.2. Perform a daily Base and Gain using the high standard. See Section 11.4.2.1 for normal values.

10.3. Initial Calibration

10.3.1. The instrument is calibrated at the beginning of each run and is verified at the beginning of the run by using a midrange Laboratory Control Sample/Continuing Calibration Verification (LCS/CCV). The correlation coefficient of the original curve must be ≥ 0.995 or recalibration is required.

10.4. Continuing Calibration

10.4.1. The run is checked every ten samples and at the end of the run using a midrange LCS/CCV to verify continued linearity. It cannot vary from the original curve by more than ± 15% or the previous ten samples from the last valid LCS/CCV are reanalyzed.

10.4.2. System cleanliness is checked every ten samples and at the end of the run using a Continuing Calibration Blank (CCB). It cannot contain the analyte of interest above the reporting limit (RL) or the previous ten samples from the last valid CCB are reanalyzed.

10.4.3. A nitrate standard (1 ppm) is run after the calibration to ensure cadmium column efficiency. Standard recovery must be within 10% of the true value.

10.4.4. A nitrite standard (0.5 ppm) is run to insure both channels are unilaterally linear.

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. The samples should be filtered prior to analysis to remove any particulate matter. For solids preparation, see SOP NC-WC-0073.

11.3.2. Filter the sample prior to analysis using a Nitrate-free filter paper or filtering device. If nitrate free filters are not available, a blank correction may be done by analyzing a filtered blank simultaneously and subtracting it from all filtered samples.

11.3.3. If the sample contains any sort of petroleum hydrocarbon, such as oil, grease, or fuel, it must be extracted with an organic solvent prior to analysis.

11.3.3.1. Transfer 15 mL of homogenous sample and 15 mL of freon or hexane mixture to a 40 mL disposable glass vial. Cover tightly with a teflon lid and shake vigorously for 30-60 seconds. Allow the solution to separate. Decant or pipette the top layer into the 4 mL analytical cups used for analysis. Document that this procedure was performed on the analytical run and note which samples it applies to.

11.4. Sample Analysis

11.4.1. The sample is analyzed on the autoanalyzer for Nitrite/Nitrate using the Cadmium Reduction Method.

11.4.2. Recommended Instrument Conditions

11.4.2.1. Base and Gain *(These values are for reference only. Values will change with new reagents, standards, and manifold cleaning.)*

11.4.2.1.1. Nitrite: (1 mg/L NO_2) Nitrate: (1 mg/L NO_3)

Base = 80 Base = 70

Base = 20 Base = 10

11.4.3. Sample Analysis Procedure

11.4.3.1. Nitrite Running Solutions

11.4.3.1.1. #1 line (Gry/Gry) in 30% Brij solution

11.4.3.1.2. #2-4 lines (Blk/Blk, Orn/Yel, Orn/Orn) in reagent water

11.4.3.1.3. #5 line in sulfanilamide color reagent

11.4.3.2.Nitrate Running Solutions

11.4.3.2.1.Yel/Yel line into working buffer

11.4.3.2.2.Wht/Wht line into SAN solution

11.4.3.2.3.Wht/Wht line into NED solution

NOTE: Run reagents through for at least five minutes before connecting the cadmium coil. (See **Appendix I** for care of the cadmium coil). Nitrogen is the carrier gas not air.

11.4.3.3.Normal Tray Protocol for Nitrite and Nitrate/Nitrite

11.4.3.3.1. P, 5C72, H@2, 2L@∅, G@2, S>7, H@2, 2L@0, G@2,
X = total number of samples cups minus six (calibration cups)

11.4.3.4.Shut Down Solutions

11.4.3.4.1.Nitrite: Same as start up. Run for a least five minutes on high.

11.4.3.4.2.Nitrate/Nitrite

Be sure to disconnect cadmium coil before removing lines from reagents.

Place all reagent line into 50/50 triton solution and run on high for at least five minutes.

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.

$$NO_2, mg/L = Instrument\ Value\ of\ Channel\ 1 \times D$$

$$NO_2NO_3, mg/L = Instrument\ Value\ of\ Channel\ 2 \times D$$

$$NO_3, mg/L = NO_2NO_3, mg/L - NO_2, mg/L \times D$$

Where:

$$D = Dilution\ factor = \frac{Final\ Volume\ Analyzed}{Volume\ Sample}$$

12.2. *LCS Recovery:*

$$\frac{Instrument\ Value}{True} \times 100 = \%\ Recovery$$

Where:

$True$ = *0.5 true for nitrite* (NO_2)

0.5 true for nitrate (NO_3)

1.0 true for nitrite/nitrate (NO_2NO_3)

12.3. *CCV Recovery:*

$$\frac{\textit{Instrument Value}}{\textit{True}} \times 100 = \%\ \textit{Recovery}$$

Where:

True = 0.5 true for nitrite (NO_2)

1.0 true for nitrate/nitrite (NO_3 NO_2)

0.5 true for nitrate (NO_3)

12.4. *MS/MSD Recovery:*

$$\frac{A - B}{C} \times 100 = \%\ \textit{Recovery}$$

Where:

A = NO_2, NO_2NO_3, or NO_3 MS/MSD

B = NO_2, NO_2NO_3, or NO_3 sample value, mg/L x 0.5

C = 0.25 true for NO_2

0.25 true for NO_3

0.50 true for NO_2 NO_3

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.

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. Acid waste must be collected in clearly labeled acid waste containers.

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. Refer to the Laboratory Sample and Waste Disposal plan.

15.4. Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices of Quanterra. 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, Methods for Chemical Analysis of Water and Wastes, Nitrate/Nitrite (Automated Cadmium reduction), Method 353.2

16.2. Associated SOPs

16.2.1. Solid Extraction for Wet Chemistry Parameters, NC-WC-0073.

17. MISCELLANEOUS (TABLES, APPENDICES, ETC...)

17.1. Reporting limits

17.1.1. The lower reporting limits (RLs) for undiluted samples are 0.04 mg/L for Nitrite (NO_2) and 0.1 mg/L for Nitrate (NO_3) and 0.1 mg/L for Nitrite/Nitrate (NO_2NO_3).

17.1.2. If samples require dilution or smaller volumes than specified in this method, the RL will be elevated.

APPENDIX I

APPENDIX I

1. CADMIUM COIL ACTIVATION PROCEDURE

   1.1 Carefully remove column from the manifold.

   1.2 Using a 10 cc syringe, inject 2 mL 2N HCI through the column.

   1.3 Inject 5 mL Copper activating solution (0.01 M) through the column.

   1.4 Inject 10 mL 2 N HCI through the column.

   1.5 Inject 10 mL fresh buffer (working Imidazole) through the column.

   1.6 Carefully place the column on the manifold.

   1.7 The column should be activated before each use.

2. CADMIUM COIL CLEANING PROCEDURE

   2.1 Using a syringe, inject 1 mL 2N HNO_3 through the column.

   2.2 Inject 5 mL concentrated HCI through the column.

   2.3 Inject 5 mL reagent water through the column

   2.4 Repeat steps 2.2 and 2.3 three more times.

   2.5 Inject 20 mL reagent through the column.

   2.6 Follow the Activation Procedure at this point.

   2.7 Clean coil as needed (once a month is recommended).

Caution:

- During activation, be sure not to inject any air into column.
- During activation, be sure not to bend or twist it, this could cause kinking inside and ruin the column.
- Be sure all "Butt" joints are correct to insure a good bubble pattern going in and coming out of the column.

TABLE - STANDARDS

TABLE 1 - WORKING STANDARDS

Concentration NO_2/NO_3	1°/2°	Use	mL NO_2	Conc. NO_2	mL NO_3	Conc. NO_3
1 mg/L NO_3	1°	stock	---	---	2.5	100 mg/L
0.5 mg/L NO_2	1°	stock	1.25	100 mg/L	---	---
1 mg/L NO_2/1 mg/L NO_3	1°	calibrant	2.5	100 mg/L	2.5	100 mg/L
0.5 mg/L NO_2/0.5 mg/L NO_3	1°	calibrant	1.25	100 mg/L	1.25	100 mg/L
0.25 mg/L NO_2 /0.25 mg/L NO_3	1°	calibrant	0.625	100 mg/L	0.625	100 mg/L
0.1 mg/L NO_2/0.1 mg/L NO_3	1°	calibrant	0.25	100 mg/L	0.25	100 mg/L
0.04 mg/L NO_2/0.04 mg/L NO_3	1°	calibrant	0.1	100 mg/L	0.1	100 mg/L
0.5 mg/L NO_2/0.5 mg/L NO_3	2°	CCV, LCS, MS/MSD	5	100 mg/L	5	100 mg/L

QUANTERRA® STANDARD OPERATING PROCEDURE

TITLE: AMMONIA (ISE)

(SUPERSEDES: REVISION 1, DATED 02/19/96)

Prepared by: _____

Reviewed by: _____
Technology Specialist

Approved by: _____ 1/7/97
Quality Assurance Manager

Approved by: _____ (for S. Jackson)
Environmental Health and Safety Coordinator

Approved by: _____
Laboratory Director

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1. SCOPE AND APPLICATION

1.1. This method is applicable to the determination of Ammonia in waters and wastewaters. It is based on EPA Method 350.3 and Standard Methods 4500 NH_3-F. The approximate working range is 0.2 to 5 mg/L.

1.2. This document accurately reflects current laboratory standard operating procedure (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. Ammonia (as nitrogen) is determined potentiometrically using an ion-selective Ammonia electrode and specific ion meter.

3. DEFINITIONS

3.1. Refer to the glossary in the Quality Assurance Management Plan (QAMP).

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. Volatile amines cause a positive bias. Mercury complexes cause a negative bias.

5. SAFETY

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

5.2. Eye protection that satisfies ANSI Z87.1 (as per the Chemical Hygiene Plan), 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 health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the Material Safety Data Sheets (MSDS) maintained in the laboratory.

5.3.1. The following materials are known to be **corrosive**: **Sodium Hydroxide**

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. 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 at 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 Quanterra associate. The situation must be reported immediately to a laboratory supervisor.

6. EQUIPMENT AND SUPPLIES

6.1. Ion Selective ammonia electrode

6.2. Specific Ion meter

6.3. Stir plate and stir bars

6.4. Beakers: various

6.5. Graduated cylinders: various

6.6. Pipettes: various

6.7. Volumetric flasks: various

6.8. Autopipettor with disposable tips

6.9. Top-loading balance: capable of accurately weighing ± 0.01 g

6.10. Analytical balance: capable of accurately weighing ± 0.0001 g

6.11. pH paper

7. REAGENTS AND STANDARDS

7.1. Reagents

7.1.1. Ammonia pH adjusting solution: purchased

7.1.2. Sodium Hydroxide (NaOH): reagent grade

7.1.3. 10 N NaOH Adjusting Solution: Add 40 g sodium hydroxide to 80 mL reagent water. Cool and dilute to 100mL.

7.2. Standards

7.2.1. Stock Standards

7.2.1.1. Ammonium Chloride (NH_4Cl): reagent grade

7.2.1.2. Ammonia Standard, (Primary) 1000 mg/L, purchased

7.2.1.3. Ammonia Standard, (Secondary) 1000 mg/L, purchased or prepare a 100 mg/L ammonia standard by dissolving 0.3819 g ammonium chloride in 800 mL reagent water. Dilute to volume in a 1 L volumetric flask. Prepare every six months.

7.2.2. Calibration Standards: Pipet the suggested volumes of 100 mg/L primary ammonia standard into 100 mL volumetric flasks and dilute to volume with reagent water.

Concentration (mg/L)	mL	Source (mg/L)	Final Volume (mL)
100	10	1000	100
0.2	0.2	100	100
1	1	100	100
2.5	2.5	100	100
5	5	100	100

7.2.3. Verification Standards: Pipet the suggested volumes of 100 mg/L secondary ammonia standard into 100 mL volumetric flasks and dilute to volume with reagent water.

QC	Concentration (mg/L)	mL	Source (mg/L)	Final Volume (mL)
CCV	1	1	100	100
LCS	1	1	100	100
MS/MSD	1	1	100	100

8. SAMPLE COLLECTION, PRESENTATION AND STORAGE

8.1. Samples are preserved to a pH < 2 with sulfuric acid.

8.2. Samples are stored in plastic or glass containers at 4°C ± 2°C.

8.3. The holding time is twenty-eight days from sampling to the completion of analysis.

9. QUALITY CONTROL

9.1. Batch Definition

9.1.1. A batch is a group of no greater than 20 samples excluding QC samples (Method Blank, LCS, MS/MSD) which are processed similarly, with respect to the procedure. All sample setups must be initiated within a 24 hour period beginning 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. A method blank consisting of 50 mL of reagent water must be 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 aqueous 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. An LCS consisting of 50 mL of a 1.0 mg/L ammonia standard must be analyzed with each analytical batch of samples.

9.3.3. Corrective Action for LCS

9.3.3.1. If any analyte is outside established control limits the system is out of control and corrective action must occur.

9.3.3.2. 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. 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.

9.4.2. An MS/MSD consisting of 25 mL of 1.0 mg/L ammonia standard and 25 mL of sample should be analyzed with each analytical batch of samples.

10. CALIBRATION AND STANDARDIZATION

10.1. Initial Setup

10.1.1. See electrode instruction manual for electrode preparation, required solutions and any special requirements. See ion analyzer manual for checking electrode slope values.

10.1.2. The following procedure is applicable for use with the Orion 940 Ion Meter. Remove ammonia electrode from storing solution. Carefully put a new membrane on the electrode and add electrode filing solution. Assemble. Directions and equipment are found in the ammonia repair kit.

NOTE: It is recommended to prepare the electrode the day before analyzing samples to allow it to equilibrate.

10.1.3. Place probe in electrode stand and connect the fittings to their respective receptacles on the back of the instrument (use Ref. 1).

10.1.4. Press "Yes". "Operator Menu?" will appear - press "yes" to get into electrode specifics. Follow the Orion 940 flow chart and change the electrode to ammonia (NH3). Enter in 3 significant digits and set to "Relative mv" (to perform electrode check).

10.2. Electrode Check

10.2.1. Pour 50 L reagent water in a 150 mL beaker and begin stirring. Add 1 mL adjusting solution and 1.0 mL 1000 PPM ammonia standard. Slowly lower electrode into solution. (Note: Do not have electrode in contact with the sides or bottom of the beaker or the stir bar.)

10.2.2. Wait for the mv reading to stabilize and record the value. Add 10.0 mL 1000 PPM standard to the same solution and wait for the mv to stabilize. Record the value.

10.2.3. Subtract the two values (1.0 mL mv - 10.0 mL mv). The final number should be between -54 and -60. This insures that the electrode is in good condition. If the number is outside the range, change the membrane, refill electrode, check connections and repeat electrode check. If the number is within range, proceed to next step.

10.2.4. Press "Yes" and change the limits to 10.0 for the high limit and 0.01 for the low limit. Follow flow chart in instrument to the "Operator Menu?". Press "No" to get into the calibration mode.

10.3. Initial Calibration

10.3.1. See ion analyzer manual for instrument calibration.

10.3.2. The following procedure is applicable for use with the Orion 940 Ion Meter. Press "Yes" for calibration and "Yes" for direct measurement. Enter "4" standards and "Yes" to do a blank correction. Do a blank correction using 50mL reagent water and 1 mL of adjusting solution. Wait for the instrument to read ready. To continue, press "Yes". Remove electrode and rinse.

10.3.3. Pour 50 mL of the 5.0 PPM standard into a 150 mL beaker and add 1 mL adjusting solution. Begin stirring and lower electrodes into solution instrument will read "Electrodes Placed in Std. 1?" Press "Yes". Wait until the instrument reads "Calibrate at 1.0?" Press "No", "5.00", "Yes". Remove electrode and rinse.

10.3.4. Instrument will read "Electrodes in Std. 2?". Pour 50 mL 2.5 PPM standard into a beaker and add 1 mL adjusting solution. Begin stirring, lower electrode and press "Yes". Wait until the instrument reads "Calibrate at 1.0?", Press "No", "2.5", "Yes". Remove electrode and rinse.

10.3.5. Instrument will read "Electrodes Placed in Std. 3?". Pour 50 mL 1.0 PPM standard and 1 mL adjusting solution into a beaker. Begin mixing and lower electrode. Press "Yes". Wait until the instrument reads "Calibrate at 1.0". Press "Yes". Remove and rinse electrode.

10.3.6. Instrument will read "Electrodes in Std. 4?". Pour 50 mL of the 0.2 PPM standard and 1 mL adjusting solution into a beaker. Begin stirring and lower electrode. Press "Yes". Wait for instrument to read "Calibrate at 1.0?". Press "No", "0.2", "Yes". At this point the instrument will display "Slope = mv/dec". The mv value must be between -54 and -60 to insure proper calibration. If it does not, press "No" to continue. The instrument will go back to the calibration mode. Follow steps for initial calibration to recalibrate. Making new standards is recommended. If the value is within the range, press "Yes" to continue. Proceed with sample analysis procedure.

10.4. Continuing Calibration

10.4.1. The run is checked at the beginning, every 10 samples and at the end of the run using a midrange continuing calibration verification standard (CCV) to verify continued linearity. It cannot vary from the theoretical value by more than ± 10% or recalibration is required.

10.4.2. System cleanliness is checked at the beginning, every 10 samples and at the end of the run using a continuing calibration blank standard (CCB). It cannot contain the analyte of interest above the reporting limit or recalibration is required.

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 ion analyzer manual for sample concentration results.

11.3.2. The following procedure is applicable for use with the Orion 940 Ion Meter. Instrument will read "Measure Ammonia?" Press "Yes". Pour 50 mL of sample and pipette 1 mL adjusting solution into a beaker. Begin mixing and lower electrode. Wait for the instrument to read "Ready" and record value on the logsheet.

NOTE: 1 mL of adjusting solution may not be adequate to achieve a minimum pH of 11 in very acidic samples. If this is the case, add additional adjusting solution in 1 mL increments until a pH of 11 or greater is achieved. Use pH paper to test the pH and document the amount of adjusting solution used.

11.3.3. If the direct value exceeds the linear range of the instrument, a dilution is necessary. Prepare all dilutions to total volume of 50 mL, add 1 mL of adjusting solution and analyze.

Note: If a sample is very high in ammonia, the probe filling solution may become contaminated. Check electrode using a CCV; if it is outside of the limits, recalibrate the instrument after changing membrane and filling solution.

11.3.4. Analyze the rest of the samples and appropriate QC.

11.3.5. Shutting down the instrument: Press "No" and the instrument will read "Operator Menu?" Press "Yes" and follow flowchart until "Standby Mode?" is reached. Press "Yes.

11.3.6. Electrode storage: Disassemble the electrode and rinse with reagent water. Discard the membrane. Place the electrode (inner body only) in 10 mL of electrode filling solution in a small bottle. Cover with parafilm to slow evaporation.

11.4. Report Documentation

11.4.1. Record all analytical information on the analytical logsheet, including the analytical data from standards, blanks, LCSs, MS/MSDs, and any corrective actions or modifications to the method.

11.4.2. All standards are logged into the departmental standard logbook. All standards are assigned an unique number for identification. Logbooks are reviewed by the supervisor or designee.

11.4.3. 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.

12. DATA ANALYSIS AND CALCULATIONS

12.1.

$$\textbf{Ammonia, mg/L} = A \times D$$

Where:

A = Ammonia (as nitrogen), mg/L

$$D = \text{Dilution Factor} = \frac{\text{Final Volume, mL}}{\text{Initial Volume, mL}}$$

12.2. CCV/LCS % Recovery = $\frac{\text{mg / L (from 16.1)}}{\text{1.0 (True)}}$ x 100

12.3. MS/MSD % Recovery = $\frac{\text{MS / MSD} - [(0.5)\ \text{Sample (mg / L)}]}{\text{0.5 (True)}}$ x 100

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.

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. Acid waste must be collected in the clearly labeled acid waste containers.

15.2. Solid materials (soil, gloves, soiled paper products) are placed in the solid debris container. Do not put liquids in the solid waste container.

15.3. Refer to laboratory-specific waste disposal plan.

15.4. Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices of Quanterra. 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, Methods for Chemical Analysis of Water and Wastes, Nitrogen, Ammonia (Potentiometric, Ion Selective Electrode), Method 350.3

16.1.2. Standard Methods for the Examination of Water and Wastewater, 19th Edition, 1995, Ammonia Selective Electrode, Method 4500 NH_3-F

17. MISCELLANEOUS (TABLES, APPENDICES, ETC...)

17.1. Reporting limits

17.1.1. The lower reporting limit (RL) for undiluted samples is 0.2 mg/L.

17.1.2. If samples require dilution or smaller volumes than specified in this method, the RL will be elevated.

QUANTERRA® STANDARD OPERATING PROCEDURE

TITLE: SULFATE (TURBIDIMETRIC)

(SUPERSEDES: REVISION 2, DATED 07/17/96)

Prepared by: _____

Reviewed by: _____
Technology Specialist

Approved by: _____
Quality Assurance Manager

Approved by: _____
Environmental Health and Safety Coordinator

Approved by: _____
Laboratory Director

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1. SCOPE AND APPLICATION

1.1. This method is applicable to the determination of Sulfate in waters, wastewaters, and to the determination of water-soluble Sulfate in solids. It is based on EPA Method 375.4, Standard Method 4500-SO_4^{2-} and SW846 Method 9038. The approximate working range is 5 - 40 mg/L for waters in 100 - 800 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 by the laboratory QA department.

2. SUMMARY OF METHOD

2.1. Sulfate ion is precipitated in a hydrochloric acid medium with Barium Chloride to form Barium Sulfate crystals of uniform size. Light absorbance of the barium ion suspension is measured by a nephelometer or spectrophotometer. Sulfate ion concentration is determined by comparison of the reading with a standard curve.

3. DEFINITIONS

3.1. Refer to the glossary in the Quality Assurance Management Plan (QAMP).

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. Large quantities of organic matter may prohibit the precipitation of Barium Sulfate. Suspended matter and color interfere. Suspended matter can be removed by filtration. Color and turbidity interferences can eliminated by doing a background correction which is done by running samples both with and without barium chloride. Silica in excess of 500 mg/L will interfere.

5. SAFETY

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

5.2. Eye protection that satisfies ANSI Z87.1 (as per the Chemical Hygiene Plan), 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 health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the Material Safety Data Sheets (MSDS) maintained in the laboratory. The following specific hazards are known:

5.3.1. Chemicals known to be **flammable** are: **Isopropanol, Ethanol.**

5.3.2. The following materials are known to be **corrosive: Hydrochloric acid.**

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. 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 Quanterra associate. The situation must be reported **immediately** to a laboratory supervisor.

6. EQUIPMENT AND SUPPLIES

6.1. Stir bars and magnetic stirrer

6.2. Spectrophotometer

6.3. Stopwatch or timeclock

6.4. Measuring spoon: capacity 0.2 g to 0.3 g

6.5. Cells: spectrophotometer (1 cm)

6.6. Erlenmeyer flasks: various

6.7. Volumetric flasks: various

6.8. Graduated cylinders: various

6.9. Autopipettor and disposable tips

6.10. Analytical balance: capable of accurately weighing ± 0.0001 g

7. REAGENTS AND STANDARDS

7.1. Reagents

7.1.1. Sodium Chloride (NaCl): reagent grade

7.1.2. Hydrochloric Acid (HCl): concentrated, reagent grade

7.1.3. Isopropanol or ethanol: reagent grade

7.1.4. Glycerol: reagent grade

7.1.5. Conditioning Reagent: Dissolve 75 g NaCl in 300 mL reagent water, and 30 mL concentrated HCl. Add 100 mL isopropanol (2-propanol) or 95% ethanol and mix. Add 50 mL glycerol and mix. Do not dilute.

7.1.6. Barium Chloride ($BaCl_2$): 20 to 30 mesh

7.1.7. Sodium Sulfate (Na_2SO_4): anhydrous, reagent grade

7.2. Standards

7.2.1. Primary Sulfate Standard, 1000 mg/L: purchased

7.2.1.1. Calibration Standards: Add the following suggested volumes to volumtric flasks using primary standard.

Final Concentration (mg/L)	Pipet (mL)	Standard Concentration (mg/L)	Final Volume (mL)
5	0.5	1000	100
10	1	1000	100
15	1.5	1000	100
20	2	1000	100
25	2.5	1000	100
30	3	1000	100
35	3.5	1000	100
40	4.0	1000	100

7.2.2. Secondary Sulfate Standard, 1000 mg/L: Purchased or add 0.1479 g pre-dried sodium sulfate to a 100 mL volumetric flask and dilute to volume with reagent water. Prepare every 6 months.

7.2.2.1. Verification Standards: Add the following suggested volumes to volumetric flasks using secondary standard.

QC	Final Concentration (mg/L)	Pipet (mL)	Standard Concentration (mg/L)	Final Volume (mL)
CCV	25	2.5	1000	100
LCS	25	2.5	1000	100
MS/MSD	50	5.0	1000	100

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 twenty-eight days from sampling to the completion of analysis.

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, 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.

9.2. 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. A reagent water blank consisting of 100 mL of reagent water is 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 aqueous 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. A midrange LCS consisting of 100 mL of the 25 mg/L LCS standard is analyzed with each analytical batch of samples.

9.3.3. Corrective Action for LCS

9.3.3.1. If any analyte is outside established control limits the system is out of control and corrective action must occur.

9.3.3.2. 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. 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.

9.4.2. An MS/MSD consisting of 100 mL of the sample and 2.5 mL of the 1000 mg/L standard should be analyzed with each analytical batch of samples.

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 DIL (diluted out).

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.

10. CALIBRATION AND STANDARDIZATION

10.1. Turn on the spectrophotometer and allow at least 15 minutes for warm up. Adjust the wavelength to 420 nm. Set the instrument to the absorbance mode.

10.2. Initial Calibration

10.2.1. Zeroing the Instrument

10.2.1.1. Using 100 mL of reagent water follow procedures 11.4.1 - 11.4.6. Zero the instrument. Allow four minutes reacting time and record the final absorbance on the analytical logsheet.

10.2.1.2. Follow Section 11.4 for each calibration standard. Plot a graph using absorbance and concentration. Lines should be drawn from point to point. No correlation coefficient can be calculated so a visual inspection must be done on the curve. Any outlying standards must be reanalyzed.

10.3. Continuing Calibration

10.3.1. A CCV consisting of 100 mL of a 25 mg/L secondary standard is analyzed at the beginning, every ten samples and at the end of the analytical run to ensure calibration remains linear. The CCV cannot vary from the original calibration curve by more than ± 10% or recalibration is required.

10.3.2. System cleanliness is checked at the beginning, 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 and reanalysis of all samples analyzed since the last CCB that met criteria is required.

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 Procedure

11.3.1. Prepare 100 mL of water sample for analysis.

11.3.2. Prepare soil and sludge samples using SOP NC-WC-0073, Solid Extraction for Wet Chemistry Parameters.

11.4. Sample Analysis Procedure

11.4.1. Place 100 mL of sample (including calibration standards, blanks, LCSs, and MS/MSDs) or a suitable aliquot diluted to 100 mL with reagent water in a suitable container.

Note: For turbid or colored samples, a background correction is necessary. Follow the steps in sections 11.4.2 and 11.4.3. Record an absorbance reading. This value must be less than or equal to the highest calibration standard, or a dilution is required. Then continue with the analyses (section 11.4.4). Be sure both values (before and after $BaCl_2$) are recorded.

11.4.2. Add 5 mL of the conditioning agent.

11.4.3. Stir at a constant speed with a magnetic stirrer.

11.4.4. While the solution is stirring, add a measuring spoonful of barium choride and begin timing the analysis immediately.

11.4.5. Continue stirring for exactly one minute.

11.4.6. After stirring is completed, pour the solution into a clean absorbance cell. Place the cell in the sample compartment.

11.4.7. Measure the turbidity or absorbance at thirty second intervals for four minutes. Record the maximum reading obtained during the four minute period on the analytical logsheet. If the sample absorbance or turbidity exceeds that of the most

concentrated standard in the calibration curve, dilution is required and reanalysis is necessary.

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. Calculations

12.1.1. Sulfate concentration is determined by manually plotting the standard concentrations vs standard absorbances on graph paper. The Y-axis is the absorbance while the X-axis is the concentration in mg/L. After plotting the absorbance and concentration of each standard, draw a curve which is connected point-to-point. This curve may not be a straight line.

To determine the concentration of the sample, find the absorbance value on the graph, follow it to the drawn curve and down to the concentration scale. Where necessary, subtract background correction absorbances and then plot the value against the curve to obtain final results.

Note: Sulfate is not a linear curve and linear regression can not be determined.

12.1.2. **Sulfate, mg/L or mg/kg = AD**

Where:

A = *Sulfate determined from the calibration curve, mg/L*

$$D = \frac{\textit{Final Volume}}{\textit{Initial Volume}}$$

Note: For solids, $D = 10 \left[\frac{100\ \text{mL}}{10\ \text{g}}\right]$

12.1.3. **CCV / LCS % Recovery** $= \frac{\textbf{mg / L}}{\textbf{25 (true)}} \textbf{ x 100}$

12.1.4. **MS / MSD % Recovery** $= \frac{\textbf{A - B}}{\textbf{25 (true)}} \textbf{ x 100}$

Where:

A = *MS/MSD, mg/L*

B = *Sample mg/L ÷ 2*

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.

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 aqueous sample preparations can be rinsed down the drain with copious amounts of water.

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

15.3. Acid waste must be collected in clearly labeled acid waste containers.

15.4. Solid materials (gloves, soiled paper products, etc.) are placed in the solid debris container. Do not put liquids in the solid waste container.

15.5. Refer to the Laboratory Sample and Waste Disposal plan.

15.6. Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices of Quanterra. 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, Methods for Chemical Analysis of Water and Wastes, Method 375.4

16.1.2. Standard Methods, Sulfate Turbidimetric, Method 4500-SO_4^{2-}, 19th Edition, 1995

16.1.3. SW846, Method 9038, Sulfate (Turbidimetric)

16.2. Associated SOPs

16.2.1. Solid Extraction of Wet Chemistry Parameters, NC-WC-0073

17. MISCELLANEOUS (TABLES, APPENDICES, ETC...)

17.1. Reporting limits

17.1.1. The lower reporting limit (RL) for undiluted samples is 5 mg/L.

17.1.2. If samples require dilution or smaller volumes than specified in this method, the RL will be elevated.

17.2. Troubleshooting guide

17.2.1. Consult the instrument manufacturer's operating manual for guidance.

Quanterra
Environmental Services

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OPERATION-SPECIFIC STANDARD OPERATING PROCEDURE

TITLE: EPA METHOD TO-14 THE DETERMINATION OF VOLATILE ORGANICS (VOCS) IN AMBIENT AIR BY GC/MS - SCAN MODE

(SUPERSEDES: LM-ATL-7001)

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Laboratory Manager, Val Mallari

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evaluation process, access to these documents shall not be given to those parties unless those parties also specifically agree to these conditions.

1. SCOPE AND APPLICATION

1.1. Analytes: VOC's with molecular weights in the general range of 40-200 g/mol suitable for GC/MS analysis. Target analytes are listed in Table 1.

1.2. Method detection limits (see current MDL study).

1.3. Reporting limits: in the general range of 2-20 ppbv (See Table 1).

1.4. Applicable matrices - air, vapor

1.5. Dynamic range (See Table 1)

1.6. Approximate analytical time

1 min. - cool down of cryotrap
1 min. - flush of inlet system with internal standard
1 min. - collection of 100 ml internal standard on trap
1 min. - flush of inlet system on trap
5 min. - collection of 500 ml of sample/standard on trap
1 min. - flush of trap with HP Helium and GC oven cool down
24 min. - GC run time

When running multiple samples, steps can be overlapped to reduce run time to approximately 25 min.

2. SUMMARY OF METHOD

2.1. An air sample is metered through a mass flow controller and concentrated onto a cryogenically cooled trap. After 100 ml of internal standard and 500 ml (nominal) of the sample has been trapped, a valve is switched and the trap is heated to purge the trap's contents onto the gas chromatography column. The target compounds are analyzed with a mass spectrometer operated in the scan mode.

3. DEFINITIONS

3.1. Standard pressure is defined as 1.0 atmosphere, 14.6 psia, 0" Hg, and 0 psig, assuming Quanterra Air Toxics Lab, City of Industry elevation and average barometric pressure.

3.2. Standard molar volume is defined as 24.5 l/mol at room temperature.

4. INTERFERENCES

4.1. Gas regulators are cleaned by the manufacturer using Freon 113, which is one of the target compounds. Before using ultra high purity (UHP) Nitrogen (N_2), Hydrocarbon (HC) free air, Internal Standard (I.S.), or a target compound standard mix, each regulator should be purged a minimum of three times with the appropriate gas.

4.2. Contamination may occur in sample or standard results if canisters are not properly cleaned prior to use. Canisters should not be used for the collection of samples until a batch blank analysis indicates that no target compounds are present above 0.2 ppbv, or a level previously agreed upon by Quanterra and Client. All other sampling equipment including pumps, flow controllers and filters must be thoroughly cleaned to ensure that the filling apparatus will not contaminate samples.

4.3. High levels of CO_2 and/or moisture may limit the amount of sample that can be concentrated due to plugging of the trap. High levels of CO_2 may also over-pressurize the instrument's vacuum system requiring delay of scan start time or the reduction of amount of sample trapped. High levels of CO_2 have been shown to shift the retention time of the first several target compounds earlier.

5. SAFETY

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

5.2. Eye protection that satisfied ANSI Z87.1 (as per the Chemical Hygiene Plan), laboratory coat, and appropriate gloves should 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 health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the Material Safety Data Sheets (MSDS) maintained in the laboratory.

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. 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. At no time should SUMMA canisters be pressurized over 40 psig.

5.7. All work must be stopped in the event of a known or potential compromise to the health and safety of a Quanterra associate. The situation must be reported immediately to a laboratory supervisor.

6. EQUIPMENT AND SUPPLIES

6.1. Gas chromatograph - capable of subambient temperature programming for the oven and with the jet separator option (Hewlett Packard 5890).

6.2. Mass-selective detector - equipped with computer and appropriate software (Hewlett Packard 5970B with HP-1000 RTE-A data system).

6.3. Cryogenic trap with temperature control assembly (Nutech 8533 and 3538). See Figure 1.

6.4. Electronic mass flow controller - for maintaining constant sample flow through Nutech concentrators (Unit Instruments)

6.5. Chromatographic grade stainless steel or nickel tubing and stainless steel plumbing fittings.

6.6. Chromatographic column - DB-624 0.53 ID, 30 meter length (J&W Scientific).

6.7. Stainless steel vacuum/pressure gauge capable of measuring from 30" of mercury (Hg) to 40 psig (Span Instruments) or equivalent.

6.8. High precision vacuum gauge - for making daily standards. (Wallace & Tiernan Pennwalt)

6.9. Pressure regulators for carrier gas and standards - 2 stage, stainless steel diaphragm (single stage acceptable for standards).

6.10. SUMMA passivated canisters 6 L or 15 L (Scientific Instrumentation Specialists, Anderson Instruments) or equivalent.

6.11. 7 micron filters (Nupro), or equivalent.

6.12. Vacuum flow regulators capable of flow settings to give required time sample flows (Valin or equivalent).

6.13. Diaphragm type vacuum pump to draw sample through mass flow controller.

7. REAGENTS AND STANDARDS

7.1. 4-Bromofluorobenzene, 25 ng/uL in methanol (for tuning of mass spectrometer)

7.2. High purity air and helium for making dilutions and for carrier gas.

7.3. Pressurized air source for valve actuation.

7.4. Gas calibration stock standards are at a nominal concentration of 1 ppmv (CS_2 is not as stable and so the concentration is 5 ppmv). Standards are prepared in a balance gas of nitrogen and are analytically certified by the supplier (Scott-Marrin, Scott Specialty, or equivalent). To facilitate certification by vendor, the standards were divided into several cylinders. (See current stock cylinder standard certifications)

7.5. Internal standard mix of Bromochloromethane, 1,4-Difluorobenzene, and Chlorobenzene-d5 at 250 ppbv each in a balance gas of nitrogen (Scott-Marrin or equivalent).

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Samples should be collected in precleaned and batch analyzed SUMMA passivated canisters. A 7 micron filter should be placed on the inlet of the can to protect the valve from particulates. Canisters should never be pressurized over 40 psig.

8.2. The absolute pressure of the canister should be recorded before and after sample collection. See Section 11.1 Sample preparation.

8.3. Samples must be kept at <25°C.

8.4. Tedlar bag samples should be protected from sunlight.

8.5. Canisters samples should be analyzed within 14 days of collection.

8.6. Tedlar Bag samples should be analyzed within 3 days of collection.

9. QUALITY CONTROL

9.1. For every 12 hour shift the mass spectrometer must meet the tuning criteria described in Section 11.2.

9.2. After tuning, a single point check standard must be analyzed. Ninety percent of the target compound response factors must be within ± 30 percent difference of the initial multipoint calibration curve average response factors. If the check standard fails to meet this criterion, the system and standard conditions should be evaluated and the standard reanalyzed. If the reanalysis fails to meet linearity criteria a new five point calibration curve must be run.

9.3. A laboratory control sample (LCS) must be analyzed daily or every 20 samples, whichever is more frequent. This sample will consist of target VOCs prepared in a separate canister from a second source. Five compounds will be used to assess control for the LCS: methylene chloride, 1,1-dichloroethene, trichloroethene, toluene and 1,1-2,2-tetrachloroethane. The percent recovery for the five control compounds must be within a window of 80-115% or a window established using historical lab data. QC sample limits may change once established using historical lab data.

9.4. For each lot of 20 samples analyzed, a duplicate control sample (DCS) must be analyzed. The DCS sample is identical to the LCS in composition and source. The same LCS percent recovery criterion must be met. In addition, the relative percent difference (RPD) for the LCS and DCS must be ≤ 10%. If either of the control samples fail the criteria the system should be checked and the LCS that failed reanalyzed. Samples will not be considered reportable until the DCS criteria are met.

9.5. A method blank must be analyzed every 12 hour shift before samples. The blank results must indicate that there are no target compounds present above the reporting limits (RL). The method blank is prepared by adding zero grade air to a SUMMA canister. Internal standards are added to the trap and the blank is processed exactly as a sample or standard.

9.6. If any of the above criteria are not met, corrective actions must be implemented before analyses can proceed.

9.7. Internal Standards and their associated key ions are noted in Table 2. The internal standard areas are monitored for each 12 hour shift by comparing the areas of the internal standards in each sample with the areas of the internal standards in the daily continuing calibration standard. **Sample areas are considered acceptable if they fall between 50% and 150% of the daily standard areas. Any sample outside this criteria should be reanalyzed. Samples failing upon repeat analysis should be documented on the analysis benchsheet and in the report narrative. The internal standard area of Bromochloromethane should always be greater than 50,000 area counts to reliably achieve standard reporting limits.**

10. CALIBRATION AND STANDARDIZATION

10.1. A low level static dilution of the stock standard gas mixtures is made in a 6 or 15 liter SUMMA canister. The high precision vacuum gauge is flushed with HC free air and attached to the top valve of the clean, evacuated canister. After recording the absolute pressure, 2.00 psi of each of the 4 standard mixtures and 1.00 psi of CS2 are added to the canister (each regulator and the transfer line should be flushed several times before transfer of standard to the canister). Close the canister valves and replace the high precision gauge with a vacuum/pressure gauge of known accuracy. Pressurize the can with HC free air to 30 psig. This will yield a standard with a nominal concentration of 45 ppbv for most compounds. Actual concentrations of each compound as certified should be used in all calculations.

10.2. A high level static dilution of the stock standard gas mixtures is made in a 6 or 15 liter SUMMA canister. The high precision vacuum gauge is flushed with HC free air and attached to the top valve of the clean, evacuated canister. After recording the absolute pressure, **8.00 psi of each of the 4 standard mixtures and 2.00 psi of CS2 are added to the canister (each regulator and the transfer line should be flushed several times before transfer of standard to the canister). Close the canister valves and replace the high precision gauge with a vacuum/pressure gauge of known accuracy. Pressurize the can with HC free air to 30 psig. This will yield a standard with a nominal concentration of 179 ppbv for most compounds. Actual concentrations of each compound as certified should be used in all calculations.**

10.3. **An initial, minimum 5 point, curve is run in the linear working range of the system for each compound. The nominal concentration of the standards are 2.2, 4.5, 11, 45, 144, 287, and 448 ppbv. More than 5 levels are run in order to maximize each compound's linear working range and to verify reporting limits. These concentrations are achieved by varying the amount of standard trapped on the instrument and/or the concentration of the standard being analyzed. A percent relative standard deviation (%RSD) is calculated for each target analyte in that analytes dynamic range as indicated in Table 1 using the calculation in section 14.4. 90% of the target**

compounds must be less than 30% RSD to accept the curve for analysis. Refer to section 11 for RSD calculation. All compounds should have a response factor greater than 0.05.

10.4. **During every 12 hours of operation, after tuning criteria is verified, a one point midrange standard (500 ml of 44 ppbv) is run to verify linearity with the initial calibration. A percent difference is calculated between the response factors (RFs) from the continuing calibration standard and the average RFs from the initial curve for each target analyte using the calculation in section 11. 90% of the target compound response factors must be within 30% difference of the initial multipoint curve average Response Factor, or a new initial calibration must be run. All compounds should have a response factor greater than 0.05.**

10.5. The daily, one point check standard response factors (RFs) are used to quantitate the results of the samples for the 12 hour shift.

11. PROCEDURE

11.1. Sample Preparation

11.1.1. The initial pressure of the sample canister is checked and recorded by attaching a vacuum/pressure gauge to the canister. The gauge should be rinsed before use with zero grade nitrogen by physically holding against the air outlet and flushing for a few seconds. If the pressure is less than approximately 6 psig, pressurize the canister to 10 psig with zero grade nitrogen and record the final pressure. Pressures should be recorded in the sample pressurizing log and on the individual canister field sheets.

11.1.2. **If the canister pressure is increased, a dilution factor (DF) is calculated and applied to results:**

$$DF = \frac{Y_a}{X_a}$$

Where:

X_a = *absolute canister pressure before dilution (initial pressure)*
Y_a = *absolute canister pressure after dilution (final pressure)*

11.2. Initial/Daily GC/MS Tuning

11.2.1. After a successful autotune as per manufacture recommendations each instrument is manually tuned using PFTBA so that m/z 69 is 100%, m/z 131 is approximately 34%, and m/z 213 is approximately 36%. The width and axis

parameters are set using the routines in the software. This initial tune should remain stable for extended periods of time, and retuning with PFTBA should not be necessary every day.

11.2.2. **At the beginning of each 12 hour shift, prior to any analytical runs, the GC/MS system must be verified that acceptable tune performance criteria are achieved. If any of the key ions fail the abundance criteria listed in Section 11.2.4, the system is considered out of tune and any subsequent sample/standard analysis should be considered unacceptable.**

11.2.3. For shift tune verification the cryotrap is not used and should be left at 150C. Alternatively the trap can be cold or cooling down but should be out of line with the column. The GC program (see Table 2) is initiated by using the BAMON commands. The GC programs are named "GCBFB1" and "GCBFB2" for systems A and B respectively. Tune files are typically "MTBFB1" and "MTBFB2." Once the data system has iniated the run and GC oven has stabilized, the remote start light will turn on and the system is ready for injection.

2 uL of a 25 ng/uL 4-Bromofluorobenzene (BFB) standard is injected into the injection port of the concentrator unit and the remote start button is activated.

11.2.4. Once the tuning run is complete (~ 6 minutes), run the program TUNVOA, data file." This is a program that will evaluate the tuning analysis and print out the required information automatically. If the BFB tuning criteria cannot be met on the first injection, retuning the instrument with PFTBA and or system maintenance may be required prior to re-injection of BFB.

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	<2% of mass 174
174	>50% of mass 95
175	5 to 9% of mass 174
176	>95% but <101% of mass 174
177	5 to 9% of mass 176

11.3. One time procedural variations are allowed only if deemed necessary and appropriate by 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 including approval by a Technical Specialist and QA Manager. If it is determined that the quality of the sample data is significantly affected and/or if contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file.

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

12. ANALYSIS

12.1. The continuing standard and the QA/QC samples are analyzed the same as samples. After the one-point continuing calibration standard is analyzed an evaluated (section 9.2), duplicate laboratory control samples (DCS) are analyzed and evaluated (See sections 9.3 and 9.4).

12.2. Before sample analysis a zero grade nitrogen method blank is analyzed and evaluated (see section 9.5), The method blank consists of a SUMMA canister that is filled with zero grade nitrogen.

12.3. At the beginning of a sample or standard run the sample valve is in the purge position and the trap valve is in the column position. The trap is cooled to <150C. The internal standard canister attached and approximately 100 ml is flushed through (this can be concurrent with the trap cool down). After flushing the trap valve is placed in the sample position and the trap temperature is checked to be at -150C or less.

Trapping is started by switching the sample valve to sample position and activating a timer. When 100 ml has been trapped (1 minutes at 100 ml/min) the sample valve is switched to purge and the internal standard canister is closed and removed.

12.4. The sample/standard canister is then attached and approximately 100 ml is flushed through. Trapping is again started by switching the sample valve to sample and starting a timer. After the appropriate amount of time (5 minutes for 500 ml at 100 ml/min) the sample valve is switched back to purge, the canister is closed and the data system is set up.

12.5. Typically, the "Name" field in the data system set up screen contains the Quanterra sample number and the name of the client. The "Misc." section contains the volume of the sample that was trapped, the client sample ID, the canister number (or a note of "Tedlar bag"), and the canister or Tedlar bag dilution factor (final/initial pressure, if applicable).

12.6. The GC system methods are "GCNEW1: and "GCNEW2" (see Table 3). When the GC reaches ready at the programmed start temperature, and after waiting at least 30 seconds after trapping, the trap valve is switched to column, and then the cryotrap is switched to heat and the run is started simultaneously.

12.7. A canister filled with zero grade air is attached to the sample line in between samples. The line is allowed to flush until it is time for the next sample.

12.8. Trapped sample volumes are adjusted for pressurization to give an undiluted volume of 500 ml.

13. DATA INTERPRETATION

13.1. Qualitative Analyses

13.1.1. Two criteria must be satisfied to verify positive identification. (1) elution of sample component at the same GC relative or absolute retention time as those of the standard component; and (2) correspondence of the sample component and the standard component mass spectra.

13.1.1.1. The sample component relative retention time (RRT) must compare within ± 0.06 RRT units of the RRT of the standard component. As an option, RT must compare within 0.5 minutes of the standard component absolute retention time (RT). For reference, the RT standard must be run within the same 12 hour shift as the sample.

13.1.1.2. (1) All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100%) must be present in the sample spectrum. (2) The relative intensities of ions specified in (1) must agree within plus or minus 20% between the standard reference and sample spectra. (Example: For an ion with an abundance of 50% in the reference spectra, the corresponding sample abundance must be between 30 and 70 percent. Standard reference mass spectra must be obtained on each individual system.

13.1.1.3. If a compound cannot be verified by all of the criteria in the above paragraphs but in the technical judgment of the analytical chemist the identification is correct, then the compound may be reported.

13.1.2. 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 analysis being conducted. normally, compounds will be given general names consisting of major functional groups and number of carbon atoms unless a retention time reference is available. Guidelines for making tentative identification are:

13.1.2.1. Relative intensities of major ions in the reference spectrum (ions > 10% of the most abundant ion) should be present in the sample spectrum.

13.1.2.2. 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 must be between 30 and 70%).

13.1.2.3. Molecular ions present in the reference spectrum should be present in the sample spectrum.

13.1.2.4. Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.

13.1.2.5. 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.

13.1.2.6. Only peaks having a total ion current greater than 10% of the nearest eluting Internal Standard total ion current will be evaluated for reporting.

13.1.2.7. Semiquantitative results will be calculated for tentatively identified compounds using total ion current areas and assuming a relative response factor of 1.0 of the nearest internal standard.

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 with the nearest library searches will the mass spectral interpretation specialist assign a tentative identification.

13.2. Quantitative Analysis:

13.2.1. When a compound has been identified, the quantification of that compound will be based on the integrated abundance from the EICP of the primary characteristic ion. Quantification will take place using the internal standard technique. A summary table of primary and secondary ions for target compounds and internal standards is listed in Table 4. The calculation for quantitation of sample is found in section 14.

14. DATA ANALYSIS AND CALCULATIONS

14.1. The HP data system is set up to automatically quantitate the sample results based on a 500 ml sample size. The default result units are in ppbv.

14.2. If a sample size other than 500 ml was used and/or a canister sample was pressurized, the result must be adjusted as shown below:

$$Final\ result\ ppbv = raw\ result\ ppbv\ X \frac{500\,mL}{sample\,volume\,injected}\ X \frac{final\ psia}{initial\ psia}$$

14.3. Calculation for Relative Response Factor (RRF):

$$RRF = \frac{Area\ cpd\ in\ Std.}{Area\ I.S.}\ X \frac{Conc.\ I.S.}{Conc.\ cpd\ in\ Std.}$$

The area of the primary quantitation ion is used in the calculation.
I.S.: Internal Standard

14.4. Calculation for Percent Relative Standard Deviation (%RSD):

$$\%RSD = \frac{Std.\ Dev.\ of\ RRFs}{Mean\ of\ RRFs}\ X\,100$$

14.5. Calculation for Percent Difference (%D):

$$\%D = \frac{Average\ RRF\ from\ initial\ curve\ RRF\ cpd.}{Average\ RRF\ from\ initial\ curve}\ X\,100$$

14.6. Calculation for Determining Concentration of Compounds:

$$Conc.\ Cpd(ppbv) = \frac{Area\ cpd\ in\ sample}{Area\ I.S.\ in\ sample}\ X \frac{Conc.\ I.S.}{RRF\ daily\ Std.}\ X\ Dil.\ Factor(See\ 14.2)$$

The area of the primary quantitation ion is used in the calculation.
I.S.: Internal Standard

14.7. Calculation for Percent Recovery (%Rec):

$$\%\,Rec = \frac{Amount\ cpd.\ recovered}{Amount\ cpd.\ spiked} X\,100\%$$

14.8. Calculation for Relative Percent Difference (RPD):

$$RPD = \frac{Value\ A - Value\ B}{Average\ of\ Values} X\,100$$

15. REPORTING

15.1. Standard reporting units are ppbv. If results are to be reported in ng/L or ug/m^3 use the following equation:

$$result\ ppbv\ X \frac{Molecular\ weight\ of\ compound}{24.5} = results\ ng/L\ or\ ug/m^3$$

Note: 24.5 is the molar volume of ideal gas at 25° Centigrade and 1 atm.

15.2. Reporting limits

15.2.1. See Table 1. All reporting limits and MDLs must be derived on GC/MS systems at the Quanterra Air Toxics laboratory and are periodically updated.

15.2.2. "J" values (results below the normal reporting limit but above the MDL) are issued on request only.

15.3. Significant figures

15.3.1. All results should be reported to two significant figures.

15.4. No conversion of the analytical results to standard conditions is made.

16. METHOD PERFORMANCE

17. POLLUTION PREVENTION

18. WASTE MANAGEMENT

19. REFERENCES

19.1. Method Source

19.1.1. "EPA Compendium Method TO-14. The Determination of Volatile Organic Compounds (VOCs) in Ambient Air using SUMMA Passivated Canisters Sampling and Gas Chromatographic Analysis."

19.2. Deviations from Method

19.2.1. Nitrogen is used for dilution/pressurization purposes.

19.2.2. TO-14 recommends the use of a 0.32 mm column coupled directly to the MSD. With the HP system, the MSD can only handle flow of 1 ml/min or less. The 0.32 mm column provides ~ 3 ml/min. Quanterra uses a 0.53 mm column through a jet separator.

19.2.3. TO-14 describes an inlet system that uses a vacuum to pull the sample through the trap. Quanterra optionally uses the pressure of the sample canister to drive the sample through the trap.

19.2.4. TO-14 describes the use of a Nafion dryer to remove excess moisture from air matrices. Quanterra does not use a Nafion dryer since polar compounds may be lost during this removal step.

19.2.5. TO-14 describes the use of SUMMA passivated steel canisters for sampling and analysis. No mention is made of Tedlar sampling bags. Quanterra analyzes samples in Tedlar bags for VOCs using the same procedures described herein. A modification to the method is noted on the final report.

20. MISCELLANEOUS (TABLES, APPENDICES, ECT...)

Table 1 VOC Target Compounds

Compound	R.T. (approx.)	Report Limits (ppbv)	Dynamic Range (ppbv)

Compound	R.T. (approx.)	Report Limits (ppbv)	Dynamic Range (ppbv)
Dichlorodifluoromethane (Freon 12)	2.05	2.0	2-450
Chloromethane	2.62	4.0	4-450
1,2-Dichloro-1,1,2,2-tetrafluoroethane (Freon 114)	2.66	2.0	2-450
Vinyl Chloride	2.89	2.0	2-450
Bromomethane	3.34	2.0	2-450
Chloroethane	3.52	4.0	4-450
Trichlorofluoromethane (11)	3.85	2.0	2-450
1,1-Dichloroethene	4.44	2.0	2-450
Carbon Disulfide	4.54	10.0	10-360
1,1,2-Trichloro-1,2,2-trifluoroethane (Freon 113)	4.52	2.0	2-450
Acetone	4.62	10.0	10-450
Methylene Chloride	5.07	2.0	2-450
trans-1,2-Dichloroethene	5.38	2.0	2-450
1,1-Dichloroethane	5.91	2.0	2-450
Vinyl Acetate	6.13	10.0	10-450
cis-1,2-Dichloroethene	6.70	2.0	2-450
2-Butanone	6.84	10.0	10-450
Chloroform	7.23	2.0	2-450
1,1,1-Trichloroethane	7.33	2.0	2-450
Carbon Tetrachloride	7.56	2.0	2-450
Benzene	7.88	2.0	2-450
1,2-Dichloroethane	7.97	2.0	2-450
Trichloroethene	8.95	2.0	2-450
1,2-Dichloropropane	9.31	2.0	2-450
Bromodichloromethane	9.88	2.0	2-450
cis-1,3-Dichloropropene	10.70	2.0	2-450
4-Methyl-2-pentanone	11.11	10.0	10-450
Toluene	11.21	2.0	2-450
trans-1,3-Dichloropropene	11.82	2.0	2-450
1,1,2-Trichloroethane	12.12	2.0	2-450
Tetrachloroethene	12.19	2.0	2-450
2-Hexanone	12.78	30.0	30-450
Dibromochloromethane	12.80	2.0	2-450
1,2-Dibromoethane	12.90	2.0	2-450
Chlorobenzene	13.98	2.0	2-450
Ethylbenzene	14.33	2.0	2-450
1,4-and 1,3-(p,m)Xylene	14.61	2.0	2-900

Compound	R.T. (approx.)	Report Limits (ppbv)	Dynamic Range (ppbv)
1,2-(ortho)Xylene	15.43	2.0	2-450
Styrene	15.49	2.0	2-450
Bromoform	15.78	2.0	2-450
1,1,2,2-Tetrachloroethane	17.18	2.0	2-450
Benzyl Chloride	17.30	10.0	10-450
4-Ethyltoluene	17.55	2.0	2-450
1,3,5-Trimethylbenzene	17.73	2.0	2-450
1,2,4-Trimethylbenzene	18.55	2.0	2-450
1,3-Dichlorobenzene	19.02	2.0	2-450
1,4-Dichlorobenzene	19.26	2.0	2-450
1,2-Dichlorobenzene	19.83	2.0	2-450
1,2,4-Trichlorobenzene	21.32	20.0	20-450
Hexachlorobutadiene	21.52	2.0	4-450

TABLE 2 BFB GC Method

Method file: GCBFB1(2)

METHOD FILE LIST

Method file:	GCBFB1 GCBFB2	GC Type: 5890 Column: Cap	Run type: SCAN,GC,E1 Splitless: Yes

Temperature:	Inj.P	Intfc	Source
	90.0	250.0	0.0

GC/DIP		LEVEL A	LEVEL B	POST RUN
Temp 1	30.0	100.0	0.0	0.0
Time 1	1.0	3.0	0.0	0.0
Rate	35.0	0.0	0.0	
Temp 2	100.0	0.0	0.0	
Time	15.0	0.0	0.0	

Oven equilibration Time. 0.10 min

Run time: 6.00
Scan Start time 2.50

Scan Parameters:			
	Mass Range:	34 to 260	
	Multiplier voltage:	varies	Number of A/D samples: 8
	GC Peak threshold:	20000 counts	
	Threshold:	100 counts	

TABLE 3 GC Analytical Method

Method file: GCNEW1(2)

METHOD FILE LIST

Method file:	**GCSYS1**	**GC Type: 5890**	**Run type: SCAN,GC,E1**
	GCSYS2	**Column: Cap**	**Splitless: Yes**

Temperature:	Inj.P	Intfc	Source
	90.0	250.0	0.0

GC/DIP		LEVEL A	LEVEL B	POST RUN
Temp 1	-50.0	10.0	100.0	0.0
Time 1	1.5	0.0	0.0	0.0
Rate	50.0	5.5	40.0	
Temp 2	10.0	100.0	160.0	
Time	0.0	0.0	3.4	

Oven equilibration Time. 0.10 min

Run time: 24.00
Scan Start time 1.60

Scan Parameters:			
	Mass Range:	34 to 260	
	Multiplier voltage:	varies	Number of A/D samples: 8
	GC Peak threshold:	20000 counts	
	Threshold:	10 counts	

TABLE 4 VOC Key Ions

Compound	Primary	Secondary
Bromochloromethane I.S. #1	49	130, 128
Dichlorodifluoromethane (Freon 12)	85	87, 50
Chloromethane	50	52
1,2-Dichloro-1,1,2,2-tetrafluoroethane (Freon 114)	85	135, 87
Vinyl Chloride	62	64
Bromomethane	94	96, 79
Chloroethane	64	66, 49
Trichlorofluoromethane (11)	101	103, 66
1,1-Dichloroethene	61	96, 63, 98
Carbon Disulfide	76	78, 44
1,1,2-Trichloro-1,2,2-trifluoroethane (Freon 113)	151	101, 103, 85
Acetone	43	58
Methylene Chloride	84	49, 86
trans-1,2-Dichloroethene	96	61, 98, 63
1,1-Dichloroethane	63	65, 83
Vinyl Acetate	43	44, 86, 42
cis-1,2-Dichloroethene	96	61, 98, 63
2-Butanone	72	57, 43
Chloroform	83	85, 47
1,1,1-Trichloroethane	97	99, 61
Carbon Tetrachloride	117	119, 121, 82
1,4-Difluorobenzene I.S. #2	114	63, 88
Benzene	78	50, 52, 77
1,2-Dichloroethane	62	64, 49, 98
Trichloroethene	130	95, 132, 97
1,2-Dichloropropane	63	62, 41, 39
Bromodichloromethane	83	85, 129
cis-1,3-Dichloropropene	75	77, 39
4-Methyl-2-pentanone	43	58, 57, 85
Toluene	91	65, 92
Chlorobenzene-d5 I.S. #3	117	52, 54, 82
trans-1,3-Dichloropropene	75	77, 39
1,1,2-Trichloroethane	97	83, 85, 61
Tetrachloroethene	164	129, 131, 166
2-Hexanone	58	43, 57
Dibromochloromethane	129	127, 208, 131
1,2-Dibromoethane	107	109, 188

TABLE 4 VOC Key Ions

Compound	Primary	Secondary		
Chlorobenzene	112	77,	114	
Ethylbenzene	91	106		
1,4-and 1,3-(p,m)Xylene	91	106,	105	
1,2-(ortho)Xylene	91	106,	105	
Styrene	104	78,	103,	51
Bromoform	173	171,	175,	93
1,1,2,2-Tetrachloroethane	83	85,	133,	131
Benzyl Chloride	91	126,	63	
4-Ethyltoluene	105	120,	77	
1,3,5-Trimethylbenzene	105	120,	77	
1,2,4-Trimethylbenzene	105	120,	77	
1,3-Dichlorobenzene	146	148,	111,	75
1,4-Dichlorobenzene	146	148,	111,	75
1,2-Dichlorobenzene	146	148,	111,	75
1,2,4-Trichlorobenzene	180	182,	109,	145
Hexachlorobutadiene	225	227,	223	
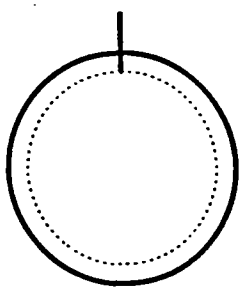
FIGURE 1. Nutech 8533 Flow Diagram