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Revitalizing Auto Communities Environmental Response (RACER) Trust

Quality Assurance Project Plan

Lansing Plants 2, 3 and 6 Industrial Land

Lansing, Michigan

August 26, 2011

ARCADIS

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Quality Assurance Project Plan

Lansing Plants 2, 3 and 6
Industrial Land
Lansing, Michigan

Prepared for:
Revitalizing Auto Communities
Environmental Response (RACER) Trust

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Our Ref.:
B0064479, 64480 and 64481

Date:
August 26, 2011

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Acronyms and Abbreviations

CLP	Contract Laboratory Program
COC	chain of custody
CSA	Container Storage Area
CSV	comma separated value
cy	cubic yards
DNAPL	Dense Non-Aqueous Phase Liquid
DQI	data quality indicator
DQO	Data Quality Objective
EDD	Electronic Data Deliverable
ELPO	electro-deposition
FSP	Field Sampling Plan
ft	feet
GIS	Geographic Information System
HASP	Health and Safety Plan
HAZWOPER	Hazardous Waste Operations and Emergency Response
IDW	investigation-derived wastes
LNAPL	Light non-aqueous phase liquid
MDEQ	Michigan Department of Environmental Quality
MDNR	Michigan Department of Natural Resources

MDNRE	Michigan Department of Natural Resources and Environment
MS	Matrix Spike
MSD	Matrix Spike Duplicate
NAPL	Non-aqueous phase liquid
NIST	National Institute of Science and Technology
NREPA	Natural Resources and Environmental Protection Act
OSHA	Occupational Safety and Health Administration
OSWER	Office of Solid Waste and Emergency Response
PCB	polychlorinated biphenyl
PPE	personal protective equipment
QAC	QA Coordinator
QAPP	Quality Assurance Project Plan
QA/QC	Quality Assurance/Quality Control
RACER	Revitalizing Auto Communities Environmental Response Trust
RCRA	Resource, Conservation, and Recovery Act
RFI	RCRA Facility Investigation
RPD	relative percent difference
RRD	Remediation and Redevelopment Division
SDG	sample delivery group
SOP	Standard Operating Procedure

SOW	Scope of Work
SWMU	Solid Waste Management Unit
USEPA	United States Environmental Protection Agency
USTs	Underground Storage Tanks
VOC	volatile organic compound
WWTUs	wastewater treatment units

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1. Introduction

1.1 Overview

This document presents the Quality Assurance Project Plan (QAPP) for monitoring environmental activities and sampling activities that Revitalizing Auto Communities Environmental Response Trust (RACER) (formerly General Motors Corporation [GMC]) will perform at the Lansing Plants 2, 3 & 6, Industrial Land (Site) properties. Former Lansing Plants 2, 3 and 6 are part of the RACER owned property located off West Saginaw Street in Lansing, Michigan. Refer to the Resource, Conservation, and Recovery Act (RCRA) Facility Investigation (RFI) Work Plan for a site plan of each plant. This QAPP has been developed on behalf of RACER by ARCADIS and is a component of the RFI Work Plan (Work Plan) that also includes a Field Sampling Plan (FSP) and a Health and Safety Plan (HASP). This QAPP presents the organization, objectives, and specific quality assurance / quality control (QA/QC) procedures associated with this Project. Protocols for sample collection, sample handling and storage, chain-of-custody procedures, and laboratory and field analyses are described or specifically referenced to related investigation documents. Standard operating procedures (SOPs) associated with environmental monitoring activities are included in the associated FSP with the same name.

In June 2009, GMC declared bankruptcy and sold certain operating assets to a new company now known as General Motors LLC (GM LLC). RACER manages the remaining assets and obligations of GM LLC, in its capacity as debtor-in-possession. The Lansing Plants are currently owned and managed by RACER.

This QAPP addresses the QA/QC elements presented in the "United States Environmental Protection Agency (USEPA) RCRA QAPP Instructions" dated April 1998 and other relevant guidance documents, including "The Use of Field Methods to Support RFI Streamlining", USEPA Region 5 Memorandum, June 20, 1999, and the Michigan Department of Environmental Quality (MDEQ) Remediation Redevelopment Division (RRD) Operational Memorandum No. 2, Sampling and Analysis, dated October 22, 2004. The QA/QC procedures described in this QAPP are consistent with USEPA and Michigan Department of Environmental Quality (MDEQ) guidance.

1.2 QAPP Purpose and Objectives

This QAPP presents data collection and QA requirements for environmental data to be collected during the environmental investigation and monitoring activities including

groundwater and soil sampling as well as monitoring well installation. Environmental data collection activities associated with the environmental monitoring, as presented in the RFI Work Plan, include the following:

- Installation of borings;
- Soil sampling;
- Installation of groundwater monitoring wells;
- Groundwater sampling;
- Groundwater level gauging
- Surveying; and
- Non-aqueous phase liquid (NAPL) monitoring in both soil and groundwater.

1.3 QAPP Preparation

This QAPP was prepared consistent with the following reference and guidance documents:

- American National Standard. *Quality Systems for Environmental Data and Technology Programs – Requirements with Guidance for Use.* ANSI/ASQC E4-2004. (American National Standard, 2004);
- USEPA guidance document entitled *USEPA Requirements for QA Project Plans*, USEPA-QA/R-5 (USEPA, 2001a), which replaces QAMS-005/80, *Interim Guidance and Specifications for Preparing QA Project Plans* (USEPA, 1980);
- USEPA *Guidance for Quality Assurance Project Plans*, USEPA QA/G-5 (USEPA, 2002b); and
- Michigan Department of Environmental Quality (MDEQ) Remediation Redevelopment Division (RRD) Operational Memorandum No. 2, Sampling and Analysis, dated October 22, 2004.

1.4 QAPP Modifications

Under separate cover, RACER has submitted an RFI Work Plan to the MDEQ for work at the Site. Any future work plans submitted to MDEQ will be executed in accordance with this QAPP or any subsequent revisions. Future revisions to this document may be required, if monitoring plans are refined or adjusted during the project due to the complexity and nature of the activities conducted at the site. The QAPP will be revised if there are changes as determined by the RACER Project Manager (or by persons with delegated authority) that significantly impact the technical and quality objectives of the project. When a revision to the QAPP is warranted, RACER (or the RACER's contractor) shall modify the QAPP to document the change and submit the revision for MDEQ approval. Changes will only be implemented by RACER or RACER's contractors after acceptance by the MDEQ. To facilitate control of the document and to ensure that the most recent version is used by all project participants, a document control format will be used on each page. The document control format is found in the upper right corner of each page and consists of the project name, document title, revision number, and revision date.

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2. Project Organization

2.1 Project Organization

Sampling activities performed at the Site will require communications among personnel from the organizations identified below, collectively referred to as the "project team." A description of the responsibilities of each member of the project team regarding data quality assurance is presented below.

RACER Contractor's will perform related sampling activities and will evaluate data and prepare the deliverables as specified in the Work Plan or as otherwise required by RACER to safely and effectively implement the investigation. Project direction will be provided by ARCADIS, with oversight of certain sampling activities by the MDEQ. A list of key project management personnel is provided below.

Company/Organization	Title	Name	Phone Number
MDEQ	Environmental Engineer	Pete Quackenbush	(517) 373-7397
MDEQ	Geologist	Mr. Joe Rogers	(517) 373-9897
RACER	Clean-up Manager	Grant Trigger	(313) 486-2908
RACER	Deputy Clean-up Manager	David Favero	(313) 486-2908
ARCADIS	Project Officer	Amy Hoeksema	(810) 225-1911
ARCADIS	Project Manager	Scott Clearwater	(810) 225-1921
ARCADIS	Task Manager	Randy Christensen	(810) 225-1940
ARCADIS	Field Personnel	Varies	Varies
ARCADIS	Quality Control Coordinator	Joe Houser	(315) 671-9226
Analytical Laboratory			
Merit Laboratories	Project Manager	Andy Ball/Paula Shaw	(517) 332-0167
Merit Laboratories	QA Manager	Barbara Richardson	(517) 332-0167

2.2 Team Member Responsibilities

The responsibilities of the various team members related to data quality assurance are summarized below by organization.

2.2.1 MDEQ Project Team

The MDEQ Project Team has oversight responsibility for all activity at the RACER owned Lansing Plants 2, 3 & 6 property.

2.2.2 RACER

Clean-up Manager/Deputy Clean-up Manager

Responsibilities and duties include:

- Provide overall direction of Site actions,
- Direct RACER's contractors; and
- Review the contractor work products, including data, memoranda, letters, reports, and all other documents transmitted to the MDEQ.

2.2.3 ARCADIS Project Organization

Project Officer

Responsibilities and duties include:

- Oversee work products.
- Provide approval for major project deliverables.

Project Manager

Responsibilities and duties include:

- Manage and coordinate the implementation of project work and monitoring activities with an emphasis on adhering to the requirements of the QAPP

- Review laboratory data reports.
- Review prepared documents.
- Report data quality concerns to the ARCADIS project manager.
- Verify that corrective actions are taken for deficiencies cited during any audits of Site activities.

Task Managers

The RFI components will be managed by various Task Managers. Duties of each Task Manager include, as appropriate:

- Manage relevant day-to-day activities.
- Develop, establish, and maintain files on relevant Site activities.
- Review data reductions from the relevant Site activities.
- Perform final data review of field data reductions and reports on relevant Site activities.
- Verify that corrective actions are taken for deficiencies cited during audits of relevant Site activities.
- Perform overall QA/QC of the relevant portions of the Site activities.
- Review relevant field records and logs.
- Instruct personnel working on relevant Site activities.
- Coordinate field and laboratory schedules pertaining to relevant Site activities.
- Request sample bottles from laboratory.
- Review field instrumentation, maintenance, and calibration to meet quality objectives.

- Prepare reports pertaining to relevant Site activities.

- Maintain field and laboratory files of notebooks/logs, data reductions, and calculations. Transmit original files to the Project Manager.

Field Personnel

Responsibilities and duties include:

- Perform field procedures associated with the investigation as set forth in the RFI work plan(s).

- Perform field analyses and collect samples for laboratory analysis, including QA samples.

- Calibrate, operate, and maintain field equipment.

- Reduce field data.

- Maintain sample custody.

- Prepare field records and logs.

Quality Assurance Coordinator

- Responsibilities and duties include:

- Review laboratory data packages.

- Oversee and interface with the analytical laboratory.

- Coordinate field QA/Quality Control (QC) procedures with Task Managers (including audits of field activities), concentrating on field analytical measurements and practices to meet data quality objectives (DQOs).

- Review field reports.

- Perform and review audit reports.

- Prepare interim QA/QC compliance reports.
- Prepare a QA/QC report in accordance with MDEQ guidelines, including an evaluation of field and laboratory data and data usability reports.

2.2.4 Merit Laboratories

General responsibilities and duties of the analytical laboratories include:

- Supply sampling containers and shipping cartons.
- Maintain laboratory custody of sample.
- Perform sample analyses and associated laboratory QA/QC procedures.
- Strictly adhere to all protocols in the QAPP.
- Report any potential data quality concerns to the ARCADIS Project Manager.

Project Manager

Responsibilities and duties include:

- Serve as primary communication link between the Site Contractor and laboratory technical staff.
- Monitor workloads and maintain availability of resources.
- Oversee preparation of analytical reports.
- Supervise laboratory chain-of-custody.

Quality Assurance Manager

Responsibilities and duties include:

- Supervise personnel reviewing and inspecting all project-related laboratory activities.
- Conduct audits of all laboratory activities.

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3. Project Background

3.1 Plant 2 Site Location and Description

Plant 2 is located on approximately 63 acres of land in a mixed residential, commercial, and industrial area at 2801 West Saginaw Street, Lansing, Michigan. Plant 2 is located in Township 04N, Range 02W, and Section 18 and is bordered by Lansing Plant 3 to the north, Lansing Plant 6 to the east, and residential buildings to the south and west. A site layout of Plant 2 can be found in the RFI Work Plan.

3.2 Plant 2 Site Background

Buildings comprising Plant 2 were originally constructed between 1900 and 1910. Early Plant 2 operations involved multiple aspects of automobile manufacturing. Major production operations included gear manufacturing, steel and cast iron machining, heat treating, and assembly. In addition, a foundry (Building 242) was used and operated to melt steel into bar stock for forging operations. Foundry operations ceased between 1978 and 1980. Rear axles were produced at Plant 2 between 1945 and 1985. In August 1985 rear axle manufacturing stopped, at which point Plant 2 was converted to manufacture the Buick Reatta. Production of the Reatta occurred between 1987 and 1990. After the production of the Reatta, Plant 2 was inactive except for Building 207, Building 250, and the wastewater treatment system. Building 207 was used for welding operations, while Building 250 was used for car and truck maintenance operations. The wastewater treatment system treated process waste water for Plants 2 and 6, which included electro-deposition (ELPO) primer wastes.

Solid Waste Management Units (SWMUs) identified at Plants 2 and 3 in the Part A permit application included the Building 242 Former Drum Storage Area (DSA) (SWMU 7 – AOI 2-7), Former Outdoor Storage Area (SWMU 8 – AOI 2-8), Plant 3 East Side Hazardous Waste Container Storage Area (CSA) (SWMU 15 – AOI 3-1), Former Electroplating Waste Treatment System (SWMU 20 – AOI 3-6), and Former Electroplating Waste Treatment Sludge Storage Area (SWMU 21 – AOI 3-7). The application also listed the following wastes as being generated at Plants 2 and 3: ignitable waste (D001), corrosive waste (D002), reactive waste (D003), spent halogenated solvents used in degreasing (F001), spent cyanide plating bath solutions (F007), plating bath residues (F008), spent stripping and cleaning bath solutions (F009), 2,4-dichlorophenol (F015), dichloromethane (U080), trichlorofluoromethane (U121), and methyl chloroform (U226).

Plant 2 along with 3 submitted a revised Part A permit application in October 1988. The revised application indicates that an additional 15,840 gallons and 136 cubic yards (cy) of S01 existed at Plants 2 and 3. The revised application listed the following wastes: D001, lead (D008), F001, spent halogenated solvents (F002), spent non-halogenated solvents (F005), and wastewater treatment sludge (F006).

Plant 2 completed a Certification Regarding Potential Release from the SWMU form and submitted it to the USEPA in June 1985. Three types of SWMUs were identified at Plant 2: underground storage tanks (USTs), CSAs, and wastewater treatment units.

In December 1987, Plant 2 submitted a Michigan Natural Resources and Environmental Protection Act (MNREPA) 64 (Act 64; Hazardous Waste Management Act) closure plan. The closure plan addressed the Plant 2 Hazardous Waste CSA (SWMU 2 – AOI 2-2). The Michigan Department of Natural Resources (MDNR) issued Notices of Violation (NOVs) to Plant 2 for the closure plan in September 1988. Plant 2 responded with a revised closure plan, which was approved with stipulations in December 1988. Plant 2 submitted a closure plan certification report to the MDNR in December 1990. Soil borings were completed and sampling was performed in the vicinity of SWMU 2 (AOI 2-2) as part of closure activities. Laboratory analytical results did not indicate the presence of metal or organic chemical contamination in exceedance of Michigan Environmental Response Act 307 (Act 307) Risk Assessment Type B soil and groundwater cleanup criteria. The MDNR released Plant 2 from financial responsibility for SWMU 2 (AOI 2-2) in May 1992. The MDNR also acknowledged the closure of Plant 2 in accordance with Act 307 Type B criteria in May 1992.

3.3 Plant 3 Site Location and Description

Plant 3 is located on approximately 104 acres of land in a mixed residential, commercial, and industrial area at 2800 West Saginaw Street, Lansing, Michigan. Plant 3 is located in Township 04N, Range 02W, Section 21 and is bordered by St. Joseph Cemetery to the north, railroad tracks and residential buildings to the east, Lansing Plant 2 to the south, and residential buildings to the west. A site layout of Plant 3 can be found in the RFI Work Plan.

3.4 Plant 3 Site Background

Buildings comprising Plant 3 were constructed in the 1930s. Similar to Lansing Plant 2, early operations at Plant 3 involved various aspects of automobile manufacturing. Production operations at Plant 3 consisted of stamping and electroplating bumpers,

general machining of crankshafts and connecting rods, and machining, welding, and stamping of automobile parts. In May 1987, electroplating operations ceased.

As previously discussed SWMUs identified at Plants 2 and 3 in the Part A permit application included the Building 242 Former DSA (SWMU 7 – AOI 2-7), the Former Outdoor Storage Area (SWMU 8 – AOI 2-8), the Plant 3 East Side Hazardous Waste CSA (SWMU 15 – AOI 3-1), the Former Electroplating Waste Treatment System (SWMU 20 – AOI 3-6), and the Former Electroplating Waste Treatment Sludge Storage Area (SWMU 21 – AOI 3-7). The application also listed the following wastes: ignitable waste (D001), corrosive waste (D002), reactive waste (D003), spent halogenated solvents used in degreasing (F001), spent cyanide plating bath solutions (F007), plating bath residues (F008), spent stripping and cleaning bath solutions (F009), 2,4-dichlorophenol (F015), dichloromethane (U080), trichlorofluoromethane (U121), and methyl chloroform (U226).

Plant 3 along with Plant 2 submitted a revised Part A permit application in October 1988. The revised application indicates that an additional 15,840 gallons and 136 cy of S01 existed at Plants 2 and 3. The revised application listed the following wastes: D001, D008, F001, F002, F005, and F006.

Plant 3 completed a CRPR from the SWMU form and submitted it to the USEPA in June 1985. Three types of SWMUs were identified as existing at Plant 3: USTs, CSAs, and wastewater treatment units (WWTUs).

In December 1987, Plant 3 along with Plant 2 submitted an Act 64 closure plan (PRC, 1994). The closure plan addressed the Plant 3 East Side Hazardous Waste CSA (SWMU 15 – AOI 3-1), Former Electroplating Waste Treatment Sludge Storage Area (SWMU 21 – AOI 3-7), and Building 301A CSA (SWMU 22 – AOI 3-8). The MDNR issued a Notice of Deficiency (NOD) to Plant 3 for the closure plan in September 1988. Plants 2 and 3 responded with a revised closure plan, which was approved with stipulations in December 1988. Plant 3 along with Plant 2 submitted a closure plan certification report (PRC, 1994) to the MDNR in December 1990. Soil borings were completed and sampling was performed in the vicinity of SWMUs 15, 21, and 22 (AOIs 3-1, 3-7 and 3-8) as part of closure activities. Laboratory analytical results did not indicate the presence of metal or organic chemical contamination in exceedance of the criteria at the time (i.e., Michigan Public Act, Act 307 Type B soil and groundwater cleanup criteria). The MDNR released Plant 3 from financial responsibility for SWMUs 15, 21, and 22 (AOIs 3-1, 3-7 and 3-8) in a letter dated May 1992. The MDNR also acknowledged the closure of the Plant 2 SWMU 2 in accordance with Act 307 Type B criteria in a letter dated May 1992 (PRC, 1994).

3.5 Plant 6 Site Location and Description

Plant 6 is located on approximately 72 acres of land in a mixed residential, commercial, and industrial area at 401 North Verlinden Street, Lansing, Michigan. Plant 6 is located in Township 04N, Range 02W, Section 17 and is bordered by residential building, a day care center, and West Saginaw Street to the north, residential buildings to the east, Sexton High School and Michigan Avenue to the south, and Lansing Plant 2 to the west. A site layout of Plant 6 can be found in the RFI Work Plan.

3.6 Plant 6 Site Background

The Lansing Plant 6 *PR/VSI* (PRC, 1993) was reviewed for information pertaining to historical waste management practices at Plant 6. In the past, hazardous and non-hazardous wastes generated at Plant 6 have been stored or accumulated in one of twelve identified SWMUs (SWMUs 1 through 12 – AOIs 6-1 through 6-12). SWMUs 1, 2, 4, 7, and 8 (AOIs 6-1, 6-2, 6-4, 6-7 and 6-8) were inactivated prior to 1993. From 1980 to 1990, hazardous waste streams were accumulated at the Original Hazardous Waste Storage Area (SWMU 1 – AOI 6-1). From 1990 to 1992, these waste streams were accumulated at the Former Hazardous Waste Storage Unit (SWMU 2 – AOI 6-2). From 1992 through present, the following nonhazardous wastes were known to be generated at Plant 6: epoxy purge, grinding waste, wash water, phosphoric acid, paint vapors, paint and bonderite sludge, oven condensate, organic vapors, trim purge, coal ash, hydraulic oil, wash water filters, asbestos, and ELPO sludge. Wastes generated at Plant 6 were stored or accumulated in one of 12 identified SWMUs (SWMUs 1 through 12 – AOIs 6-1 through 6-12).

Hazardous wastes generated at Plant 6 included purge thinner, purge paint, solvent wipe, and waste petroleum naphtha. Purge thinner was generated when paint lines were purged with solvents. The thinner was accumulated in the Current Waste Thinner Tank (SWMU 5 – AOI 6-5). Purge paint was generated when paint supply lines were purged with a new paint. Purge paint was accumulated in drums and transferred to SWMU 3 (AOI 6-3). Solvent wipe, which consists of rags with solvents and oil, was generated during manufacturing operations when oil was removed from automobile parts. Solvent wipe was accumulated in drums and accumulated in SWMUs 1 and 2 (AOIs 6-1 and 6-2). Paint-related waste was generated during painting operations. Rags and spent paint cans were accumulated in drums and transferred to SWMU 3 (AOI 6-3). Each of these hazardous wastes were transported to a licensed disposal facility by Inland Waters Pollution Control (Inland Waters).

Waste petroleum naphtha was generated from degreasing activities. Safety-Kleen Corporation picked up and disposed of petroleum naphtha. Petroleum naphtha was not accumulated or managed at Plant 6.

Beginning in 1992, the following non-hazardous wastes were known to be generated at Plant 6: epoxy purge, grinding waste, wash water, phosphoric acid, paint vapors, paint and bonderite sludge, oven condensate, organic vapors, trim purge, coal ash, hydraulic oil, wash water filters, asbestos, and ELPO sludge.

Continuous filtering of ELPO solution for reuse generated waste ELPO filters that were accumulated in drums and then transferred to SWMU 3 (AOI 6-3). ELPO sludge was generated from cleaning of tanks containing ELPO solution. The sludge was accumulated with waste ELPO filters in drums and transferred to SWMU 3 (AOI 6-3). Waste filters and sludge were transported by Inland Waters for disposal at Michigan Disposal, Inc.

Epoxy purge was generated at the body shop. Epoxy was purged into drums at the Nonhazardous Waste Accumulation Areas (SWMU 15 – AOI 6-15) and transferred to the Nonhazardous Waste Consolidation Area (SWMU 10 – AOI 6-10). Grinding waste was generated from grinding automobiles after assembly. The waste was accumulated in drums in SWMU 15 (AOI 6-15) and transferred to SWMU 10 (AOI 6-10). Each of these wastes were transported by Granger Container Company for disposal at Granger Landfill.

Wash water was generated from washing automobiles after assembly. Phosphoric acid was generated from automobile pickling operations. From the wastewater cistern, both the wash water and phosphoric acid were transferred through pipes to the wastewater treatment unit at Plant 2.

Bonderite sludge was generated from cleaning bonderite solution tanks. The sludge was accumulated in a Nonhazardous Waste Roll off Box (SWMU 9 – AOI 6-9). Trim purge was generated at the trim shop during automobile assembly. Trim was purged into drums in SWMU 15 (AOI 6-15) and transferred to SWMU 10 (AOI 6-10). Wash water filters were generated from filtering wash water from cleaning automobiles. Asbestos was generated during non-routine asbestos abatement activities. Asbestos was accumulated in SWMU 9 (AOI 6-9). These wastes were transported by Granger Container for disposal at Granger Landfill.

Paint vapors were generated from painting operations. The mixture of air and paint vapors was collected from the paint booth and transferred through ducts to the APCS Incinerator (SWMU 12 – AOI 6-12) for destruction.

Oven condensate was generated from liquids that condensed in ovens used to dry painted automobile bodies. The condensate was collected in drums in SWMU 15 (AOI 6-15) and transferred to SWMU 10 (AOI 6-10). Oven condensate was collected by Inland Waters for treatment.

Coal ash was generated during boiler operations. The coal ash was accumulated in SWMU 9 (AOI 6-9) and transported by Plant 6 vehicles for disposal at Granger Landfill.

Used hydraulic oil was generated from equipment maintenance. Used oil was accumulated in drums in the Oil Accumulation Areas (SWMU 14 – AOI 6-14) and transferred to SWMU 10 (AOI 6-10). The oil was transported to a licensed disposal/recycling facility by General Oil.

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4. Project Description

This section presents the performance objectives of the investigation and describes the associated activities to be conducted at the site.

4.1 Objectives

The purpose of the investigation is to achieve the performance objectives associated with the Site described in the RFI Work Plan. The performance objective of the investigation, as stated in the RFI Work Plan, is "…to fill the data gaps in order to define the nature and extent of contamination on and in the vicinity of the Site. The sampling locations proposed in the RFI Work Plan are designed to define the impact of contamination from previous Site releases, so that appropriate response activities can be implemented."

4.2 Approach

As presented in the RFI Work Plan, groundwater and soil chemical monitoring will be conducted to determine the effectiveness of the investigation in meeting the remedial objective of the project, which is ultimately preventing unacceptable exposure (both on-Site and off-Site) of contaminants released from the Site to humans and the environment. As specified in the RFI Work Plan, groundwater and soil samples will be analyzed for those analytical parameters listed in Table 4 of the RFI Work Plan.

4.3 Project Schedule

This QAPP and the RFI Work Plan are submitted for approval to the MDEQ. Following approval of these documents, the investigation activities will commence. The investigation activities will include:

- Soil Borings,
- Soil Sampling and Analysis,
- Monitoring Well Installation,
- Water Level Measurements,

- Light non-aqueous phase liquid (LNAPL) and Dense non-aqueous phase liquid (DNAPL) potential presence will be investigated and measurements, as needed,
- Surveying, and
- Groundwater sampling and analysis.

Field work for the initial phase of the investigation will occur between July and October 2011. Refer to the Project Schedule in the RFI Work Plan. A subsequent phase of investigation will be performed in the 2012.

5. Quality Objectives and Criteria for Measurement Data

The DQO process, as described in Guidance for Quality Assurance Project Plans (USEPA, 2002b), is intended to provide a "logical framework" for planning monitoring programs. This QAPP was prepared following the DQO process, which includes seven sequential steps in the USEPA's QAPP DQO process.

The seven-step DQO process defined by the USEPA is as follows:

Step 1: Problem Statement

Step 2: Decision Identification

Step 3: Identifying Decision Inputs

Step 4: Defining the Study Boundaries

Step 5: Developing a Decision Rule

Step 6: Limits on Decision Errors

Step 7: Design Optimization

DQOs for each type of data including groundwater monitoring well and LNAPL gauging, groundwater chemical monitoring, and soil sampling are required. Table 1 presents the DQO's for monitoring activities during the investigation program and incorporates the seven-step process. DQOs for the investigation activities will be refined upon development of the RFI Work Plan, and, if required, the QAPP will be modified.

A DQO summary for the investigation monitoring activities presented in the RFI Work Plan is presented in the following section. The summary consists of stated DQOs relative to data uses, data types, data quantity, sampling and analytical methods, and data measurement performance criteria.

5.1 Data Categories

Three data categories have been defined to address various analytical data uses and the associated QA/QC effort and methods required to achieve the desired levels of quality. These categories are:

Screening Data: Screening data affords a quick assessment of Site characteristics or conditions. The associated DQO is applicable to data collection activities that involve rapid, non-rigorous methods of analysis and QA. This objective is generally applied to physical and/or chemical properties of samples, the degree of contamination relative to concentration differences, and preliminary health and safety assessment.

Screening Data with Definitive Confirmation: Screening data allows rapid identification and quantification, although the quantification can be relatively imprecise. The associated DQO is applicable to data collection activities that require qualitative and/or quantitative verification of a select portion of sample findings (10% or more). This objective can also be used to verify less rigorous laboratory-based methods.

Definitive Data: Definitive data are generated using analytical methods such as approved USEPA reference methods. Data are analyte-specific, with confirmation of analyte identity and concentration. Methods produce raw data (e.g., chromatograms, spectra, digital values) in the form of paper printouts or computer-generated electronic files. DQOs for definitive data from chemical sampling activities for the RI will follow standard USEPA requirements.

Field parameters (e.g., turbidity, conductivity, temperature, pH) that will be obtained during water column sampling for use in qualitatively interpreting other Site data will be determined using screening techniques. All remaining parameters will be determined using definitive techniques.

For this project, reporting as defined in section 7.5.2 will be used for the analysis. This includes all groundwater or soil samples collected for laboratory chemical analysis.

The analytical work will be performed by RACER's contracted Laboratory. The analytical results will be reported by the lab in the electronic data deliverable (EDD) format and in a PDF format (from data sheets) within 10 working days from date of receipt. The full data packages from the laboratory will be due within 30 working days from date of receipt.

5.2 Environmental Sample Analysis

Monitoring and sampling activities will be conducted to support the DQOs associated with the investigation performance objectives. Monitoring and sampling activities, operation and maintenance, and health and safety are presented in the RFI Work Plan and the HASP.

Data Use – The data to be collected as described in the RFI Work Plan will be used to ensure the performance objectives of the investigation are met.

Data Quantity – The sample quantities and parametric requirements for groundwater chemical monitoring are summarized in Table 2. Additional information regarding specific sample collection locations and required analyses can be found in the RFI Work Plan and in Section 8 of this document.

Sampling and Analytical Methods – Sampling methods for groundwater chemical monitoring will be as specified in Section 9. The analytical methods are as specified in Table 3. Full documentation will be included in the data package for this project.

Data Comparability – Data representativeness is addressed by the sample quantities and locations identified in the RFI Work Plan. Data comparability is intended to be achieved through the use of standard USEPA-approved methods.

6. Special Training Requirements/Certification

ARCADIS field sampling team members are required to have received the 40-hour Hazardous Waste Operations and Emergency Response (HAZWOPER) safety training and annual 8-hour refresher courses required by 29 CFR Parts 1910 and 1926. On-Site subcontractor personnel involved in invasive activities (e.g., drilling, excavation) are required to have received the same training. The subcontractor is responsible for compliance of their personnel with the applicable regulations.

Laboratory personnel training records are maintained at the laboratory. No special training or certification requirements are required for the laboratory for this project.

Persons in field supervisory positions will have also completed the additional Occupational Safety and Health Administration (OSHA) 8-Hour Supervisory Training.

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7. Documentation and Records

7.1 General

Required and appropriate environmental monitoring and sampling activities will be completed at the Site as part of the Investigation activities at the Site. Documentation, reporting, and record keeping will be performed consistent with RFI Work Plan requirements. Specific documentation and reporting requirements are described below.

7.2 Sample Designation System

Samples will be identified with a unique designation system for unambiguous sample tracking. The sample designation system to be employed throughout the project will be consistent, yet flexible, to accommodate unforeseen changes where required. An alpha-numeric system will be used by field personnel to assign each sample with a unique sample identification number. The sample identification number will begin with a two-letter prefix indicating the Plant number followed be a two letter prefix indicating the type and digits indicating the sequential sample number collected starting at 1, followed by the depth interval the sample was collected and then the date the sample was collected. For monitoring wells nests, in addition to the two-letter prefix, each sample identification number will have an "S" or "D" following the number to indicate whether the well is shallow or deep, respectively. Following the sample identification number will be the full date in parenthesis (e.g. MW-100S (10/26/2010).

The sample types potentially collected include the following and will be designated using the indicated codes in quotations:

- Monitoring Wells – "MW"
- Soil Boring – "SB"
- Trip Blank – "TB"
- Rinse Blank – "RB"
- Duplicate – "DUP"
- Matrix Spike/Matrix Spike Duplicate – "MS/MSD"

Where necessary, the code system will be supplemented to accommodate additional sample identification information. For example, the code for soil samples collected from soil boring or monitoring well locations will include a qualifier to identify the section increment (e.g., 0 to 0.5 ft).

Additional sample volumes collected for matrix spike (MS) and matrix spike duplicate (MSD) analysis will be noted on the chain-of-custody forms, and the associated additional sample containers will be labeled accordingly. Field duplicates will be labeled as ordinary field samples with a unique identification number (e.g., the first field duplicate associated with soil collection would be named DUPSS01). Duplicate samples will not be identified, and the laboratory will analyze them as "blind" quality control samples.

7.3 Field Documentation

Field personnel will provide comprehensive documentation covering various aspects of field sampling, field analysis, and sample chain-of-custody. This documentation consists of a record that allows reconstruction of field events to aid in the data review and interpretation process. Documents, records, field log books, and other information relating to the performance of the field work will be retained in the contractor project file.

The various forms of documentation to be maintained throughout the project include:

- Daily Production Documentation -The personnel performing the field activities will keep field logs that detail all observations and measurements made during the Investigation. Data will be recorded directly into Site-dedicated, bound notebooks, with each entry dated and signed. So that it can be confirmed at any future date that notebook pages are not missing, each page will be sequentially numbered. Erroneous entries will be corrected by crossing out the original entry, initialing it, and then documenting the proper information. In addition, certain media sampling locations will be surveyed to accurately record their locations. The survey crew will use their own field logs and will supply the sampling location coordinates to the Task Manager. A more detailed discussion of field logs is provided in Section 10.2.1.

- Sampling Documentation - Detailed notes will be made as to the exact sampling location, physical observations, and weather conditions (as appropriate).

- Sample Chain-of Custody (COC) - COC forms are used as a means of documenting and tracking sample possession from time of collection to the time of disposal by the laboratory. A COC form will accompany each field sample collected, and one copy of the form will be filed in the field office. All field personnel will be trained on the proper use of the COC procedure. COC forms will be filled out at each sampling site, at a group of sampling sites, or at the end of each day of sampling by the Site Contractor field personnel responsible for sample custody. In the event that samples are relinquished by the designated sampling person to other sampling or field personnel, the COC form will be signed and dated by the appropriate personnel to document the sample transfer. The original COC form will accompany the samples to the laboratory, and copies will be forwarded to the project files. A sample COC form is included in Appendix B of this QAPP. Additional details on COC forms are provided in Section 10.2.3.

- Persons will have custody of samples when the samples are in their physical possession, in their view after being in their possession, or in their physical possession and secured so they cannot be tampered with. In addition, when samples are secured in a restricted area accessible only to authorized personnel, they will be deemed to be in the custody of such authorized personnel.

- Field Equipment, Calibration, and Maintenance Logs - To document the calibration and maintenance of field instrumentation, calibration and maintenance logs will be maintained for each piece of field equipment that is not factory calibrated.

7.4 Laboratory Documentation Files

7.4.1 Laboratory Project Files

The laboratory will establish a file for project data. The file will include correspondence with RACER, ARCADIS and MDEQ, faxed information, phone logs, and COC forms. The laboratory will retain project files and data packages for a period not less than 5 years.

7.4.2 Laboratory Logbooks

Workbooks, bench sheets, instrument logbooks, and instrument printouts will be used to trace the history of samples through the analytical process and to document important aspects of the work, including the associated quality controls. As such,

logbooks, bench sheets, instrument logs, and instrument printouts will be part of the permanent record of the laboratory.

Each page or entry will be dated and initialed by the analyst at the time of entry. Errors in entry will be crossed out in indelible ink with a single stroke, corrected without the use of white-out or by obliterating or writing directly over the erroneous entry, and initialed and dated by the individual making the correction. Pages of logbooks that are not used will be completed by lining out unused portions.

Information regarding the sample, analytical procedures performed, and the results of the testing will be recorded on laboratory forms or personal notebook pages by the analyst. These notes will be dated and will also identify the analyst, the instrument used, and the instrument conditions.

Laboratory notebooks will be periodically reviewed by the laboratory group leaders for accuracy, completeness, and compliance with this QAPP. All entries and calculations will be verified by the laboratory group leader. If all entries on the pages are correct, the laboratory group leader will initial and date the pages. Corrective action will be taken for incorrect entries before the laboratory group leader signs the laboratory notebooks.

7.4.3 Computer Tape and Hard Copy Storage by the Laboratory

All electronic files and deliverables will be retained by the laboratory for not less than 5 years; hard copy data packages (or electronic copies) will also be retained for not less than 5 years.

7.5 Data Reporting Requirements

Data will be reported both in the field and by the analytical laboratory, as described below.

7.5.1 Field Data Reporting

Information collected in the field through visual observation, manual measurement, and/or field instrumentation will be recorded in field notebooks or data sheets and/or on forms. Such data will be reviewed by the appropriate Task Manager for adherence to the required scope of work (SOW) and for consistency. Data quality concerns identified as a result of this review will be discussed with the field personnel, corrected

if possible, and (as necessary) incorporated into the data evaluation process. If questions remain that may impact data utility or interpretations, such concerns will be raised to the attention of ARCADIS.

If applicable, field data forms and calculations will be processed and included in appendices to the appropriate reports (when generated). The original field logs, documents, and data reductions will be kept in the project file at the Site Contractor's office.

7.5.2 Laboratory Data Reporting

For all media, the laboratory is responsible for preparing, at a minimum, a Level 2 data package for all laboratory analysis. Contract Laboratory Program (CLP)-equivalent (Level 3) data packages will be prepared for 10% of all laboratory analysis, per plant.

Level 2 data reports/packages for all parameters will include, at a minimum, the following items:

Narrative – Summary of activities that took place during the course of sample analysis, including the following information:

- laboratory name and address;
- date of sample receipt;
- cross reference of laboratory identification number to contractor sample identification;
- analytical methods used;
- deviations from specified analytical protocols; and
- corrective actions taken including description of any reanalysis.

Included with the narrative will be any sample handling documents, including field and internal COC forms, air bills, and shipping tags.

Analytical Results – These will be reported according to analysis type and include the following information, as applicable:

- sample ID;
- laboratory ID;
- date of collection;
- date of receipt;
- date of preparation;
- date of analysis;
- analyst initials;
- equipment ID; and
- detection limits.
- data quality indicator summary (QA/QC summary).

Sample results on the report forms will be corrected for dilutions. Soil and sediment data will be reported on a dry weight basis. Unless otherwise specified, all results will be reported uncorrected for blank contamination.

The data quality indicator (DQI) summary will include the following DQIs where applicable: laboratory control samples, MS/MSDs, laboratory duplicates, method blanks and surrogates (organics).

The data for CLP-equivalent (Level 3) reporting will be expanded to include supporting documentation necessary to provide a CLP-equivalent package. This additional documentation will include, but not be limited to, raw data required to recalculate any result, including instrument printouts and quantitation reports. The report also will include standards used in calibration and calculation of analytical results; sample extraction, digestion, and other preparation logs; standard preparation logs; instrument run logs; and moisture content calculations.

The analytical results will be reported by the laboratory in the EDD format outlined in Table 3 and in a PDF format (datasheets) within 10 working days from date of receipt of the samples. The full data packages from the laboratory will be due within 30 working days from date of receipt of the samples.

7.6 RACER Project File

Project documentation including computer files will be placed in RACER's or ARCADIS' project files according to the Site Contractor's filing requirements for document management and retained as discussed in Section 16.4.6.

8. Sampling Process Design

This QAPP applies to the following sampling and monitoring activities:

- groundwater sampling
- groundwater level monitoring (water levels),
- subsurface soil sampling, and
- elevation and coordinate surveys

Sampling and monitoring to confirm the effectiveness of the investigation in meeting the primary investigation performance objective, which is ultimately preventing unacceptable exposure (both on-Site and off-Site) of contaminants released from the Site to humans and the environment will be conducted according to the requirements described in the RFI Work Plan. Elevation and coordinate surveys are discussed in the RFI Work Plan, and the FSP, and health and safety is discussed in the HASP. The investigation sample design will be presented in the RFI Work Plan, which will be prepared to guide field activities. Investigation sampling procedures will follow applicable requirements of this QAPP.

8.1 Groundwater Monitoring Well Network

A monitoring well network will be created using existing wells and installing new wells to be used for groundwater elevation, NAPL thickness (if applicable), and chemical monitoring. The monitoring well network is presented in the RFI Work Plan and includes the following wells:

Plant	WELL ID	Associated AOI
2	OW-4 MW-1 MW-2 MW-3	2-4 and 2-16
2	Install 4 new wells	Installed at the perimeter of the plant and will be used primarily for hydrogeologic purposes
3	MW-19 MW-21 MW-22 MW-23 MW-24 MW-02-01 MW-02-02 MW-02-03 MW-02-04 MW-04-01 MW-04-03 MW-04-04 MW-88-1 MW-91-1 MW-91-2 MW-91-3 MW-91-4 MW-91-5 MW-91-6 MW-93-1 MW-93-2 MW-93-3	3-9 3-9 3-9 3-9 3-9 3-10 3-10 3-10 3-10 3-10 3-10 3-10 3-10 3-10 3-10 3-10 3-10 3-10 3-10 3-10 3-10 3-10
6	MW-02-01 MW-02-02 MW-02-03 MW-03-01 MW-03-02	6-18 6-18 6-18 6-18 6-18

Plant	WELL ID	Associated AOI
	MW-03-04	6-18
	MW-03-05	6-18
	MW-03-06	6-18
	MW-03-07	6-18
	MW-04-01	6-18
	MW-04-02	6-18
	MW-04-03	6-18
	MW-04-05	6-18
	MW-04-06	6-18
	SME-MW-2	6-18
	SME-MW-4	6-18
	MW-1	6-17
	MW-2	6-17
	MW-3	6-17
	MW-4	6-17
	MWBP-10-UST1-4	6-17
	MWBP-10A-UST1-4	6-17
	MWBP-11-UST1-4	6-17
	MWBP-12-UST1-4	6-17
	MWBP-12A-UST1-4	6-17
	MWBP-13-UST1-4	6-17
	MWBP-13A-UST1-4	6-17
	MWBP-10-UST5-6	6-13 and 6-16
	MWBP-11A-UST5-6	6-13 and 6-16
	MWBP-12UST5-6	6-13 and 6-16
6 cont.	Install one new overburden monitoring well to be used for groundwater quality and hydrogeological purposes	6-47

8.2 Baseline Groundwater Chemical Monitoring

As specified in the RFI Work Plan groundwater samples will be collected from the monitoring well network to determine groundwater quality. As specified in the RFI Work Plan, if conditions warrant a modification to sampling procedures during the establishment of the baseline groundwater quality, RACER may submit a request to

the MDEQ for review and approval to modify the analytical parameters and/or sampling frequency.

All water sample laboratory analysis will follow laboratory SOPs presented in Appendix C. Additional discussion of chemical monitoring is presented in the RFI Work Plan.

8.3 Groundwater Sampling Schedule

Gauging and sampling of the existing and newly installed groundwater monitoring wells will be performed after the completion of the phase I soil boring activities at the Site. See the Project Schedule in the RFI Work Plan for the groundwater sampling schedule.

8.4 Groundwater Level Monitoring

Manual water level measurements will be collected during groundwater gauging and sampling events from the monitoring wells on and near the Site. This data will be used to monitor groundwater levels which will be used to construct groundwater flow maps.

8.5 Elevation and Coordinate Surveys

The existing monitoring wells on the Sites have been recently surveyed by a licensed surveyor. All surveys will be conducted under the direction of a licensed surveyor.

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9. Sample Method Requirements

9.1 Groundwater Sampling

Groundwater samples will be collected for baseline chemical analysis from select existing and newly installed monitoring wells to establish baseline groundwater quality conditions to be used during corrective response activities, if necessary, and to evaluate potential off-Site contaminant migration. Investigation sampling procedures will be presented in the RFI Work Plan. All samples will be collected in accordance with Michigan Department of Environmental Quality (MDEQ)'s Remediation and Redevelopment Division (RRD) Operational Memorandum No. 2, Sampling and Analysis (Op Memo 2) (MDEQ, 2004a). Groundwater samples collected from on and off-site monitoring wells will be collected using a peristaltic pump and disposable tubing to prevent cross contamination. Samples will be collected using the low-flow sampling technique. Field parameters including pH, specific conductivity, temperature, dissolved oxygen, oxidation-reduction potential, and turbidity will be recorded during purging to determine stabilization prior to sampling.

9.2 Soil Sampling

Soil samples will be collected in accordance with the MDEQ's RRD Op Memo 2 (MDEQ, 2004a). Soil samples for laboratory analysis will be collected from the 0-2 foot bgs interval because potential impacts were generally believed to be at the surface and soils are generally fine grained, therefore limiting the potential for downward migration of contaminants. Additional samples may be collected if impacted soil is encountered based on high PID readings and visual observations. If there is no evidence of impacted soil throughout the sample, an additional sample may be collected from the interval above the water table as discussed in the RFI Work Plan. The samples will be field preserved with methanol for volatile organic compound (VOC) analysis.

10. Sample Handling and Custody Requirement

10.1 Sample Containers and Preservation

Appropriate sample containers, volumes, preservation methods, and laboratory holding times for investigation samples are shown in Table 3.

The analytical laboratory will supply appropriate sample containers and preservatives, as necessary. The bottles will be provided by the same laboratory that will be performing the analysis according to MDEQ RRD Operational Memorandum No. 2, Sampling and Analysis – Attachment 4; Sample Preservation, Sample handling and Holding time Specifications, dated October 2004 (MDEQ Op. Memo 2, attachment 4). The field personnel will be responsible for properly labeling containers and preserving samples (as appropriate). Laboratories will add preservative prior to delivery to the sampling staff when possible. Sample labeling procedures are discussed in Section 10.2.2.

10.2 Field Custody Procedures

The objective of field sample custody is to protect samples from tampering from the time of sample collection through time of transport to the analytical laboratory. Persons will have custody of samples when the samples are in their physical possession, in their view after being in their possession, or in their physical possession, and secured so they cannot be tampered with. In addition, when samples are secured in a restricted area accessible only to authorized personnel, they will be deemed to be in the custody of such authorized personnel.

Field custody documentation consists of both field logbooks and field COC forms.

10.2.1 Field Logbooks

Field logbooks will provide the means of recording the data collecting activities that are performed. As such, entries will be described in as much detail as possible so that persons going to the Site could reconstruct a particular situation without reliance on memory.

Field logbooks will be bound field survey books or notebooks. Logbooks will be assigned to field personnel, but will be stored in a secure location when not in use. Each logbook will be identified by the project specific document number. The title page of each logbook will contain the following:

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

Entries into the logbook will contain a variety of information. At the beginning of each entry, the date, start time, weather conditions, names of all sampling team members present, name of subcontractors on-site (if any), level of personal protection being used, and signature of the person making the entry will be provided. The names of visitors to the site and field sampling or investigation team personnel, as well as the purpose of their visit, will also be recorded in the field logbook.

Measurements made and samples collected will be recorded. Entries will be made in ink, with no erasures. If an incorrect entry is made, the information will be crossed out with a single strike mark and initialed. Whenever a sample is collected or a measurement is made, a detailed description of the location of the station will be recorded. The number of the photographs taken, if any, will also be noted. All equipment used to make measurements will be identified, along with the date of calibration.

Samples will be collected following procedures presented in the SOPs located in appendix A of the FSP. The equipment used to collect samples will be noted, along with the time of sampling, sample description, depth at which the sample was collected, volume, and number of containers. Sample identification numbers will be assigned prior to sample collection. Field duplicate samples, which will receive an entirely separate sample identification number, will be noted under sample description.

10.2.2 Sample Labeling

Preprinted sample labels will be affixed to sample bottles prior to delivery at the sampling site. The following information is required on each sample label:

- Plant number prefix
- sample number;
- project name;
- date collected;
- time collected;
- location;
- sampler;
- analysis to be performed; and
- preservative.

10.2.3 Field Chain of Custody Forms

Completed COC forms will be required for all samples to be analyzed. COC forms will be initiated by the sampling crew in the field. The COC forms will contain the unique sample identification number, sample date and time, sample type, preservation (if any), and analyses required. The original COC form will accompany the samples to the laboratory. Copies of the COC will be made prior to shipment (or multiple copy forms will be used) for field documentation. The COC forms will remain with the samples at all times. The samples and signed COC forms will remain in the possession of the sampling crew until the samples are delivered to the express carrier (e.g., Federal Express), hand delivered to a mobile or permanent laboratory, or placed in secure storage.

Sample labels will be completed for each sample using waterproof ink. The labels will include the information listed in Section 10.2.2, above. The completed sample labels will be affixed to each sample bottle and covered with clear tape.

Whenever samples are split with a government agency or other party, a separate COC will be prepared for those samples by that agency or party and marked to identify the party with whom the samples are being split. The person relinquishing the samples to

the facility or agency should request the representative's signature on the separate COC acknowledging sample receipt. If the representative is unavailable or refuses, this is noted in the "Received By" or "Taken By" space.

10.3 Management of Investigation-Derived Materials and Wastes

Investigation-derived wastes (IDW) include soils, groundwater, materials, and personal protective equipment (PPE). These wastes are generated during drilling, sampling, excavation, and other investigation activities. The intent of managing IDW is to insure that impacted materials and media are not allowed to contaminate non-impacted materials and media. Where necessary to insure the safe, efficient, and environmentally protective performance of work, management of investigation-derived materials and wastes will be performed consistent with the Guide to Management of Investigation-Derived Wastes, 9345.3-03FS (USEPA, 1992).

10.4 Packing, Handling, and Shipping Requirements

Sample packaging and shipment procedures are designed so that the samples will arrive at the laboratory, with the COC, intact.

Samples will be packaged for shipment as outlined below:

- Securely affix the sample label to the container with clear packing tape.
- Check the cap on the sample container to confirm that it is properly sealed.
- Complete the COC form with the required sampling information and confirm that the recorded information matches the sample labels. NOTE: If the designated sampler relinquishes the samples to other sampling or field personnel for packing or other purposes, the sampler will complete the COC prior to this transfer. The appropriate personnel will sign and date the COC form to document the sample custody transfer.
- Using duct tape, secure the outside drain plug at the bottom of the cooler.

When shipping sample containers via an overnight carrier the following procedures will be followed;

- Wrap sample containers in bubble wrap or other cushioning material.

- Place 1 to 2 inches of cushioning material at the bottom of the cooler.
- Place the sealed sample containers into the cooler.
- Place ice in plastic bags and seal. Place loosely in the cooler.
- Fill the remaining space in the cooler with cushioning material.
- Place COC forms in a plastic bag and seal. Tape the forms to the inside of the cooler lid.
- Close the lid of the cooler, lock, and secure with duct tape.
- Wrap strapping tape around both ends of the cooler at least twice.
- Mark the cooler on the outside with the shipping address and return address, affix "Fragile" labels, and draw (or affix) arrows indicating "this side up." Cover the labels with clear plastic tape.
- Place a signed custody seal over the sample cooler lid.

Where applicable samples will be packaged by the field personnel and transported as low-concentration environmental samples. Samples will be hand delivered or delivered by an express carrier within 72 hours of the time of collection, unless otherwise required by the laboratory. Shipments will be accompanied by the COC form identifying the contents. The original form will accompany the shipment; copies will be retained by the sampler for the sampling office records. If the samples are sent by common carrier, a bill of lading will be used. Receipts or bills of lading will be retained as part of the permanent project documentation. Commercial carriers are not required to sign off on the COC form as long as the forms are sealed inside the sample cooler, and the custody seals remain intact.

Sample custody seals and packing materials for filled sample containers will be provided by the analytical laboratory. The filled, labeled, and sealed containers will be placed in a cooler on ice and carefully packed to eliminate the possibility of container breakage.

10.5 Laboratory Custody Procedures

10.5.1 General

Upon sample receipt, laboratory personnel will be responsible for sample custody. The original field COC form will accompany all samples requiring laboratory analysis. The laboratory will use COC guidelines described in the MDEQ and/or USEPA guidance documents. Samples will be kept secured in the laboratory until all stages of analysis are complete. All laboratory personnel having samples in their custody will be responsible for documenting and maintaining sample integrity.

10.5.2 Sample Receipt and Storage

Immediately upon sample receipt, the laboratory sample custodian will verify the integrity of the cooler seal, open the cooler, and compare the contents against the field COC. If a sample container is missing, a sample container is received broken, the sample is in an inappropriate container, or the sample has not been preserved by appropriate means, the ARCADIS Project Manager will be notified. The laboratory sample custodian will be responsible for logging the samples in, assigning a unique laboratory identification number to each sample, labeling the sample bottle with the laboratory identification number, and moving the sample to an appropriate storage location to await analysis. The project name, field sample code, date sampled, date received, analysis required, storage location, date, and action for final disposition will be recorded in the laboratory tracking system. Relevant custody documentation will be placed in the project file.

10.5.3 Sample Analysis

Analysis of an acceptable sample will be initiated by worksheets that contain all pertinent information for analysis. The analyst will sign and date the laboratory COC form when removing the samples from storage.

Samples will be organized into sample delivery groups (SDGs) by the laboratory. A SDG may contain up to 20 field samples (field duplicates, trip blanks, and rinse blanks are considered field samples for the purposes of SDG assignment). All field samples assigned to a single SDG will be received by the laboratory within a maximum of 7 calendar days after sample collection and must be processed through the laboratory (preparation, analysis, and reporting) as a group.

10.5.4 Sample Storage Following Analysis

Samples will be maintained by the laboratory for at least 1 month after the final report is delivered to the Site Contractor. The laboratory will be responsible for the eventual and appropriate disposal of the samples. The analytical laboratory will inform the Site Contractor before any samples are disposed. Unused portions of the samples, sample extracts, and associated wastes will be disposed of by the laboratory in accordance with applicable rules and regulations, as specified in the SOP for waste disposal.

11. Analytical Method Requirements

11.1 Field Parameters and Methods

During investigation sampling activities, selected physical and chemical parameters will be measured. Field measurements include dissolved oxygen, pH, turbidity, and specific conductance. Field parameters and methods associated with investigation activities will be presented in the RFI Work Plan.

Because field instrumental analytical methodology is continually being updated, field personnel are required to consult the manufacture's instruction manual of each piece of field equipment for operation procedures.

11.2 Laboratory Methods, Project Target Compounds, and Laboratory Detection Limits

The parameters that samples are to be analyzed for and the laboratory analytical methods are shown in Table 3. The laboratory methods listed in Table 3 are taken from Attachment 1 of MDEQ Op Memo No. 2 (MDEQ, 2004).

Table 3 presents the analytes and their respective target detection limit (TDL). All TDLs presented are in accordance with MDEQ RRD Op Memo No. 2, Attachment 4 (MDEQ, 2004).

The methods listed in Table 3 include the range of analyses expected to be performed. Analytical results for all analyses will be reported in units identified in Table 3.

The primary sources to describe the analytical methods to be used during the investigation are provided in the SOPs which are referenced in Appendix C. These documents include "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods," SW-846, USEPA Office of Solid Waste, 3rd Edition and Promulgated Updates, 1986; and "Methods for Chemical Analysis of Water and Wastes", EPA-600/4-79-020, March 1983. USEPA SW-846 methods with QA/QC and reporting deliverables requirements will be used for all analytes.

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12. Quality Control Requirements

12.1 Quality Assurance Indicators

The overall QA objective for this QAPP is to develop and implement procedures for sampling, COC, laboratory analysis, instrument calibration, data reduction and reporting, internal QC, audits, preventive maintenance, and corrective action, such that valid data will be generated. These procedures are presented or referenced in the following sections. Specific QC checks are discussed in Section 12.2.

1. QA indicators are generally defined in terms of five parameters:

2. Representativeness;

3. Comparability;

4. Completeness;

5. Precision; and

6. Accuracy.

Each parameter is defined below. Specific objectives for the Site actions are set forth in other sections of this QAPP, as referenced below.

12.1.1 Representativeness

Representativeness is the degree to which sampling data accurately and precisely represent Site conditions, and is dependent on sampling and analytical variability and the variability of environmental media at the Site. The actions have been designed to assess the presence of the chemical constituents at the time of sampling. Related project documents (RFI Work Plan and HASP) present the rationale for sample quantities and location. This QAPP presents field sampling and laboratory analytical methodologies. The use of the prescribed field and laboratory analytical methods with associated holding times and preservation requirements are intended to provide representative data.

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12.1.2 Comparability

Comparability is the degree of confidence with which one data set can be compared to another. Comparability between phases of the actions (if additional phases are required) will be maintained through consistent use of the sampling and analytical methodologies set forth in this QAPP, established QA/QC procedures, and the utilization of appropriately trained personnel.

12.1.3 Completeness

Completeness is defined as a measure of the amount of valid data obtained from an event and/or investigation compared to the total amount that was obtained. This will be determined upon final assessment of the analytical results, as discussed in Section 12.6.

12.1.4 Precision

Precision is a measure of the reproducibility of sample results. The goal is to maintain a level of analytical precision consistent with the objectives of the action. To maximize precision, sampling and analytical procedures will be followed. All work for the Site actions will adhere to established protocols presented in the QAPP. Checks for analytical precision will include the analysis of MS/MSDs, laboratory duplicates, and field duplicates. Checks for field measurement precision will include duplicate field measurements. Further discussion of precision QC checks is provided in Section 12.4.

12.1.5 Accuracy

Accuracy is a measure of how close a measured result is to the true value. Both field and analytical accuracy will be monitored through initial and continuing calibration of instruments. In addition, reference standards, MSs, spike blanks, and surrogate standards will be used to assess the accuracy of the analytical data.

12.2 Field Quality Control Checks

12.2.1 Field Measurements

To verify the quality of data using field instrumentation, duplicate measurements will be obtained and reported for all field measurements. A duplicate measurement will involve obtaining measurements a second time at the same sampling location.

12.2.2 Sample Containers

Certified-clean sample containers (I-Chem 300 Series or equivalent) will be supplied by the laboratory. Certificates of analysis will be filed in the project file.

12.2.3 Field Duplicates

Field duplicates will be collected from the different sampling media to verify the reproducibility of the sampling methods. Field duplicates will be prepared by placing well-homogenized aliquots (except samples for VOC analysis) from the same sample location into individual sample containers, which will then be submitted blind to the laboratory. Field duplicate water and soil for VOC analysis will constitute co-located samples rather than homogenized aliquots. In general, field duplicates will be analyzed at a 10% frequency (every 10 samples) for the chemical constituents. Table 2 provides an estimated number of field duplicates to be prepared for each applicable parameter and matrix.

12.2.4 Rinse Blanks

Rinse blanks are used to monitor the cleanliness of the sampling equipment and the effectiveness of the cleaning procedures. Rinse blanks will be prepared and submitted for analysis once per week per matrix. Rinse blanks will be prepared by filling sample containers with analyte-free water (supplied by the laboratory) that has been routed through a cleaned sampling device. When dedicated sampling devices or sample containers are used to collect the samples, rinse blanks will not be necessary.

12.2.5 Field Blanks

Field blanks will be collected only during groundwater sampling of the permanent well network at the Site. Field blanks will be collected for the analysis of TCL VOCs. If low-level mercury sampling is being completed, then the field blank will also be analyzed for low flow mercury by USEPA method 1631E. Field blanks will be prepared by pouring laboratory supplied distilled water into the appropriate sample container and will be submitted to the analytical laboratory to provide the means to assess the quality of the data resulting from the field sampling program. The frequency of the field blank sample will generally be at least one sample per sampling event.

12.2.6 Trip Blanks

Trip blanks will be collected only for the analysis TCL VOCs. If low-level mercury sampling is being completed, then the trip blanks will also be analyzed for low flow mercury by USEPA method 1631E. Trip blanks will be prepared and supplied by the laboratory and will be submitted to the analytical laboratory to provide the means to assess the quality of the data resulting from the field sampling . The trip blanks are generally used for the purposes of tracking the samples while in the custody of a third party during shipment. In the case of this project the samples were either being delivered directly to the lab by the sampler or the lab was coming to the Site to pick-up the samples. Therefore, trip blanks were not being used. However, at the request of the MDEQ effective August 18, 2011 trip blanks were included with each sample container delivered to the lab. The frequency of the trip blank sample will generally be at least one sample per cooler.

12.3 Analytical Laboratory Quality Control Checks

12.3.1 General

Internal laboratory QC checks will be used to monitor data integrity. These checks will include method blanks, MS/MSDs, spike blanks, internal standards, surrogate samples, calibration standards, and reference standards. Project quality control limits for duplicates and MSs are identified in Table 4. Laboratory control charts will be used to determine long-term instrument trends.

12.3.2 Method Blanks

Sources of contamination in the analytical process, whether specific analyses or interferences, must be identified, isolated, and corrected. The method blank will be completed internally by the laboratory. The method blank is useful in identifying possible sources of contamination within the analytical process. For this reason, it is necessary that the method blank be initiated at the beginning of the analytical process and encompasses all aspects of the analytical work. As such, the method blank would assist in accounting for any potential contamination attributable to glassware, reagents, instrumentation, or other sources that could affect sample analysis. One method blank will be analyzed with each analytical series associated with no more than 20 samples.

12.3.3 MS/MSDs

MS/MSDs will be used to measure the accuracy of analyte recovery from the sample matrices and will be site-specific. MSD pairs will be analyzed at a 5% frequency (every 20 samples).

When MS recoveries are outside QC limits, associated control sample and surrogate spike recoveries will be evaluated, as applicable, to attempt to verify the reason for the deviation and to determine the effect on the reported sample results. Table 4 presents an estimated number of MS and MSD analyses for each applicable parameter.

12.3.4 Surrogate Spikes

Surrogates are compounds that are unlikely to occur under natural conditions but that have properties similar to the analytes of interest. This type of control is primarily used for organic samples analyzed by gas chromatography/mass spectrometry (GC/MS) and GC methods and is added to the samples prior to purging or extraction. The surrogate spike is utilized to provide broader insight into the proficiency and efficiency of an analytical method on a sample-specific basis. This control reflects analytical conditions that may not be attributable to sample matrix.

If surrogate spike recoveries exceed specified QC limits (Table 4), the analytical results must be evaluated thoroughly in conjunction with other control measures. In the absence of other control measures, the integrity of the data may not be verifiable, and reanalysis of the samples with additional control may be necessary. Surrogate spike compounds will be selected utilizing the guidance provided in the analytical methods.

12.3.5 Laboratory Duplicates

For inorganics, laboratory duplicates will be analyzed to assess laboratory precision. Laboratory duplicates are defined as a separate aliquot of an individual sample that is analyzed as a separate sample. Table 4 presents an estimated number of laboratory duplicates for each applicable parameter.

12.3.6 Calibration Standards

Calibration check standards analyzed within a particular analytical series provide insight regarding instrument stability. A calibration check standard will be analyzed at

the beginning and end of an analytical series, or periodically throughout a series containing a large number of samples.

In general, calibration check standards will be analyzed after every 12 hours or more frequently, as specified in the applicable analytical method. If results of the calibration check standard exceed specified tolerances, samples analyzed since the last acceptable calibration check standard will be reanalyzed.

Laboratory instrument calibration standards will be selected utilizing the guidance provided in the analytical methods as summarized in Section 14.

12.3.7 Reference Standards/Control Samples

Reference standards are standards of known concentration and are independent in origin from the calibration standards. The intent of reference standard analysis is to provide insight into the analytical proficiency within an analytical series. This includes preparation of calibration standards, validity of calibration, sample preparation, instrument set-up, and the premises inherent in quantitation. Reference standards will be analyzed at the frequencies specified within the analytical methods.

12.4 Data Precision Assessment Procedures

Field precision is difficult to measure because of temporal variations in field parameters. However, precision will be controlled through the use of experienced field personnel, properly calibrated meters, and duplicate field measurements. Field duplicates will be used to assess precision for the entire measurement system, including sampling, handling, shipping, storage, preparation, and analysis.

Laboratory data precision will be monitored through the use of MS/MSD and laboratory duplicate sample analyses.

The precision of data will be measured by calculation of the relative percent difference (RPD) by the following equation:

$$RPD = \frac{(A-B)}{(A+B)/2} \times 100$$

Where:

A = Analytical result from one of two duplicate measurements

B = Analytical result from the second measurement

Precision objectives for duplicate analyses are identified in Table 4.

12.5 Data Accuracy Assessment Procedures

The accuracy of field measurements will be controlled by experienced field personnel, properly calibrated field meters, and adherence to established protocols. The accuracy of field meters will be assessed by review of calibration and maintenance logs.

Laboratory accuracy will be assessed via the use of MSs, surrogate spikes, and reference standards. Where available and appropriate QA performance standards will be analyzed periodically to assess laboratory accuracy. Accuracy will be calculated in terms of percent recovery as follows:

$$\% \text{ Recovery} = \frac{A-X}{B} \times 100$$

Where:

A = Value measured in spiked sample or standard

X = Value measured in original sample

B = True value of amount added to sample or true value of standard

This formula is derived under the assumption of constant accuracy between the original and spiked measurements. Accuracy objectives for MS recoveries are identified in Table 4.

12.6 Data Completeness Assessment Procedures

Completeness of a field or laboratory data set will be calculated by comparing the number of valid sample results generated to the total number of results generated.

$$\text{Completeness} = \frac{\text{Number valid results}}{\text{Total number of results generated}} \times 100$$

As a general guideline, overall project completeness is expected to be at least 90%. The assessment of completeness will require professional judgment to determine data usability for intended purposes.

12.7 Proficiency Samples

Proficiency samples are samples from third parties with known composition and provided to many laboratories on a scheduled basis. Results from the samples are used to independently evaluate the competency of the laboratory to produce acceptable results and compare performance with peer laboratories. The laboratory may participate in proficiency sample studies on a biannual basis and have the provider of such samples report to RACER, ARCADIS, and the MDEQ the results upon completion of the study. Deficiencies will be addressed through a corrective action process on an expedited schedule and results similarly reported.

13. Instrument/Equipment Testing, Inspection, and Maintenance Requirements

Testing and maintenance schedules have been developed for both field and laboratory instruments. A summary of the testing and maintenance activities to be performed is presented below.

13.1 Field Instruments and Equipment

Prior to each field sampling event, each piece of field equipment will be inspected to confirm that it is operational. If the equipment is not operational, it will be serviced prior to its use. All meters that require charging or batteries will be fully charged or have fresh batteries. If instrument servicing is required, it is the responsibility of the appropriate Task Manager or field personnel to follow the maintenance schedule and arrange for timely service. Field instruments will be maintained according to the manufacturers' instructions. Calibration frequency and results along with any maintenance needs will be recorded in the daily field log books kept by field personnel. Logbooks for each piece of equipment will be maintained in project records. The Task Managers will review calibration and maintenance logs.

All measuring and test equipment to be used in support of the investigation activities that directly affect the quality of the analytical data shall be subject to preventative maintenance measures that minimize equipment downtime. Equipment will be examined to certify that it is in operating condition prior to each field sampling event. This includes checking the manufacturer's operating manual to confirm that all maintenance requirements are being observed. Field notes from previous sampling events will be reviewed to verify that any prior equipment problems are not overlooked and that any necessary repairs to equipment have been carried out.

Field equipment returned from a site will be inspected to confirm that it is in working order. The inspection will be recorded in the logbook or field notebooks, as appropriate. It will also be the obligation of the last user to record any equipment problems in the logbook. Non-operational field equipment will either be repaired or replaced. Appropriate spare parts will be made available for field meters. Consultant-/subcontractor-owned or leased equipment maintenance will be in accordance with the manufacturer's instructions.

13.2 Laboratory Instruments and Equipment

13.2.1 General

Laboratory instrument and equipment documentation procedures include details of any observed problems, corrective measure(s), routine maintenance, and instrument repair (including information regarding the repair and the individual who performed the repair).

Preventive maintenance of laboratory equipment generally will follow the guidelines recommended by the manufacturer. A malfunctioning laboratory instrument will be repaired immediately by in-house staff or through a service call from the manufacturer.

13.2.2 Instrument Maintenance

Maintenance schedules for laboratory equipment adhere to each manufacturer's recommendations. Records reflect the complete history of each instrument and specify the time frame for future maintenance. Major repairs or maintenance procedures are performed through service contracts with the manufacturer or qualified contractors. Paperwork associated with service calls and preventative maintenance calls will be kept on file by the laboratory.

Laboratory Systems Managers are responsible for the routine maintenance of instruments used in the particular laboratory. Any routine preventative maintenance carried out is logged into the appropriate logbooks. The frequency of routine maintenance is dictated by the nature of samples being analyzed, the requirements of the method used, and/or the judgment of the Laboratory Systems Manager.

All major instruments are backed up by comparable (if not equivalent) instrument systems in the event of unscheduled downtime. An inventory of spare parts is also available to minimize equipment/instrument downtime.

14. Instrument Calibration and Frequency

14.1 Field Instruments and Equipment

Instruments and equipment used to gather, generate, or measure environmental data will be calibrated at the intervals specified by the manufacturer or more frequently, and in such a manner that accuracy and reproducibility of results are consistent with the manufacturer's specifications. In the event that an internally calibrated field instrument fails to meet calibration/checkout procedures, it will be returned to the manufacturer for service. More detailed information will be provided in the specific manufacturer's instruction manuals prior to use. Equipment found to be out of tolerance during the period of use will be removed from the field, and measuring and testing activities performed using the equipment will be addressed via the corrective action system described in Section 17.4 of this QAPP.

Field instruments to be used for health and safety or environmental monitoring include:

- Air VOC monitoring for health and safety – Photo ionization detector (Mini-Rae 2000 or equivalent)
- Groundwater field parameters (pH, conductivity, temperature, dissolved oxygen) – YSI model 556 multi-parameter flow cell meter (or equivalent)
- Groundwater level monitoring – Solinst electronic water level meter (or equivalent)

Specific calibration procedures associated with operation and maintenance of these instruments are provided in the manuals for the equipment.

Field personnel are responsible for confirming that a master calibration/maintenance log is maintained following the procedures specified for each measuring device. Where applicable, each log will include, at a minimum, the following information:

- name of device and/or instrument calibrated;
- device/instrument serial/identification numbers;
- calibration method;
- tolerance;

- calibration standard used;
- frequency of calibration;
- date(s) of calibration(s); and
- name of person(s) performing calibration(s).

14.2 Laboratory Instrument and Equipment

When analyses are conducted according to USEPA SW-846 methods, the calibration procedures and frequencies specified in the applicable method will be followed. For analyses governed by SOPs, see the appropriate SOP for the required calibration procedures and frequencies in Appendix A of the FSP. Records of calibrations will be filed and maintained by the laboratory. These records will be subject to QA audit. For all instruments, the laboratory will maintain trained repair staff with in-house spare parts or will maintain service contracts with vendors.

All standards used in the calibration of equipment are traceable, directly or indirectly, to National Institute of Standards and Technology (NIST). All standards received shall be logged into standard receipt logs maintained by the individual analytical groups. Each group will maintain a standards log that tracks the preparation of standards used for calibration and QC purposes.

15. Inspection/Acceptance Requirements for Supplies and Consumables

All supplies to be used in the field and laboratory will be available when needed. They will be free of target chemicals and interferences. All sample containers will be certified clean prior to use. All reagents will be tested prior to use with Site samples. All standards will be verified against a second source standard. The laboratory will follow a "first in/first out" procedure for the storage and use of all consumables to minimize the risk of contamination and degradation.

16. Data Management

Appropriate data management activities will provide for the accuracy and ready accessibility of all of the necessary data to meet the analytical and reporting objectives of the project. Due to the large amount of data that will be generated, a structured, comprehensive, and efficient program for management of data is necessary.

The data management program for this project includes field documentation and sample QA/QC procedures, methods for tracking and managing the data, and a system for filing all Site-related information. Established electronic and hard copy data management procedures will be employed to efficiently process the information collected such that the data are readily accessible and accurate on electronic and hard copy format. These procedures are described in detail in the following section.

The data management plan has four elements: 1) sample designation system; 2) field activities; 3) sample tracking and management; and 4) data management system.

16.1 Sample Designation System

A concise and easily understandable sample designation system is an important part of the project sampling activities. It provides a unique sample number that will facilitate both sample tracking and easy re-sampling of select locations to evaluate data gaps, if necessary. The sample designation system to be employed during the sampling activities will be consistent, yet flexible enough to accommodate unforeseen sampling events or conditions. A combination of letters and numbers will be used to yield a unique sample number for each field sampled collected, as outlined in Section 7.2.

16.2 Field Activities

Field activities designed to gather the information necessary to make decisions during the investigation process require consistent documentation and accurate record keeping. During Site activities, standardized procedures will be used for documenting field activities, data security, and QA. These procedures are described in further detail in the following subsections.

16.2.1 Field Documentation

Field documentation will be managed as discussed in Section 7.3

16.2.2 Field Deliverables

In order to maintain control of data quality collected in the field, three separate deliverables were required from each field event:

- Field Sample Key (FSK) EDD
- Field Data EDD
- Survey EDD

These deliverables will be uploaded to the database maintained by ARCADIS and ensures consistency with the Laboratory EDD.

16.2.3 Data Security

Measures will be taken during the investigation activities to prevent samples and records from being lost, damaged, or altered. When not in use, all media containing project notes and sample data including field notebooks, computer storage disks and external hard drives, sample and monitoring forms, and cameras will be stored at the field office or locked in the field vehicle. Access to these files will be limited to the field personnel who utilize them.

16.3 Sample Management and Tracking

A record of all field documentation will be maintained to provide verification of the validity of data used in the site analysis. To effectively execute such documentation, specific sample tracking and data management procedures will be used throughout the sampling program.

Sample tracking will begin with the completion of COC forms, as summarized in Section 10.2.3. The completed COC forms associated with samples collected will be faxed to the ARCADIS Project Manager. Copies of all completed COC forms will be maintained in the field office. The laboratory will verify receipt of the samples electronically (via email to the task manager or ARCADIS Project Manager) on the following day.

When analytical data are received from the laboratory, the QA Coordinator (QAC) will review the incoming analytical data packages against the information on the COCs to

confirm that the correct analyses were performed for each sample and that results for all samples submitted for analysis were received. Any discrepancies noted will be promptly followed up by the QAC.

16.4 Data Management System

In addition to the sample tracking system, a data management system will be implemented. The central focus of the data management system will be the development of a personal computer-based project database. The project database, to be maintained by ARCADIS database team members, will combine pertinent geographical, field, and analytical data for each sample. Information that will be used to populate the database will be derived from four primary sources: public/historical records, surveying of sampling locations, field observations, and analytical results. RACER requires that all data for their sites be managed on the EQuIS 4 data management system. This database will allow ARCADIS and RACER database team members to query the database and generate data tables for the project in a timely manner, preventing potential bottlenecks in generating the necessary deliverables for reports. Typically, training for the EQuIS 4 Enterprise takes 20 minutes and is accessible using LiveMeeting for those team members who may be unfamiliar with the software.

16.4.1 Computer Software

The database will be written in the EQuIS 4 database management system and will run on the Windows Operating System. Geographic Information System (GIS) applications will be developed in ESRI ArcGIS, with additional customization performed with Visual Basic. Tables and other database reports will be generated through EQuIS 4 and/or Microsoft® Excel and Microsoft® Word. These software products will be upgraded as necessary to maintain industrial and corporate standards.

16.4.2 Survey Information

Each location sampled as part of the investigation will be surveyed to provide accurate documentation of sample locations for mapping purposes; to facilitate the re-sampling of select sampling locations during future monitoring programs, if needed; and for any additional activities. All survey data will be computed in NGVD 29 and converted to IGLD 85 for MDEQ reporting. All field books associated with the surveying activities will be stored as a record of the project activities. A Survey EDD will be completed in the field to ensure data quality as mentioned previously in section 16.2.2.

16.4.3 Field Observations

An important part of the information that will ultimately reside in the data management system for use during the project will originate in the observations that are recorded in the field.

During each sampling event, appropriate field documentation will be prepared by the field personnel who performed the sampling activities. The purpose of the documentation is to create a summary and a record of the sampling event. Items to be included are the locations sampled, the sampling methodologies used, field measurements including pH, conductivity, turbidity data, blind duplicate and MS/MSD sample identification numbers, equipment decontamination procedures, personnel involved in the activity, and any noteworthy events that occurred. See Section 16.2.2 for further field documentation.

16.4.4 Analytical Results

Analytical results will be provided by the laboratory in both digital (EDD) and a hard copy format or portable document format (pdf). The data packages will be examined to confirm that the correct analyses were performed for each sample submitted and that all of the analyses requested on the COC form were performed. If discrepancies are noted, the QAC will be notified and will promptly follow up with the laboratory to resolve any issues.

Each data package will be validated in accordance with the procedures presented in Section 20. Any data that do not meet the specified standards will be flagged pending resolution of the issue. The flag will not be removed from the data until the issue associated with the sample results is resolved. Although flags may remain for certain data, the use of those data may not necessarily be restricted.

Following completion of the data validation, the digital files will be used to populate the appropriate database tables. This format specifies one data record for each constituent for each sample analyzed. Specific fields include:

- sample identification number;
- date sampled;
- date analyzed;

- parameter name;
- analytical result;
- units;
- detection limit; and
- qualifier(s).

The individual EDDs, supplied by the laboratory in either an ASCII comma separated value (CSV) format or in a Microsoft® Excel worksheet, will be loaded into the appropriate database table via a custom-designed user interface Visual Basic program. Any analytical data that cannot be provided by the laboratory in electronic format will be entered manually. After entry into the database, the EDD data will be compared to the field information previously entered into the database to confirm that all requested analytical data have been received.

16.4.5 Data Analysis and Reporting

The database management system will have several functions to facilitate the review and analysis of the investigation data. Routines have been developed to permit the user to electronically scan a copy of the analytical data from a given site for a given media. Several output functions are also available that can be modified, as necessary, for use in the data management system.

A valuable function of the data management system will be the generation of tables of analytical results from the project databases. The capability of the data management system to directly produce tables reduces the redundant manual entry of analytical results during report preparation and precludes transcription errors that may occur otherwise. This data management system function creates a digital file of analytical results and qualifiers for a given media. The file can then exported into a table of rows and columns that can be transferred to word processing software (e.g., Microsoft® Word) for final formatting and addition of titles and notes. Tables of analytical data will be produced as part of data interpretation tasks and the reporting of data to the MDEQ.

The data management system also has the capability of producing a digital file of select parameters that exists in one or more of the databases. This type of custom

function is accomplished on an interactive basis and is best used for transferring select information into a number of analysis tools, such as statistical or graphing programs.

16.4.6 Document Control and Inventory (Archiving, Storage and Retrieval)

Project archiving, storage and retrieval of project documents, reports, records, and data (both hardcopy and electronic formats) will be managed according to RACER's requirements for document management. Documents, reports, records, and data will be retained for future reference and hardcopy formats of project documents will be maintained in ARCADIS' project files.

17. Assessment and Response Actions

17.1 General

Performance and systems audits will be completed in the field and laboratory during the investigation, as described below.

17.2 External Field Performance and System Audit Procedures

The following field performance and systems audits will be completed during this project.

The appropriate Task Manager will monitor field performance. Field performance audit summaries will contain an evaluation of field activities to verify that the activities are performed according to established protocols. The ARCADIS Project Manager will review field reports and communicate concerns to the Task Managers and/or field staff, as appropriate. The Project Manager will review the field blank rinse and trip blank data to identify potential deficiencies in field sampling and cleaning procedures. Systems audits comparing scheduled QA/QC activities from this QAPP with actual QA/QC activities completed will be performed. The appropriate Task Manager and Project Manager will periodically confirm that work is being performed consistent with this QAPP and the RFI Work Plan.

External audits may be conducted by the MDEQ at any time during the field operations. These audits may or may not be announced and are at the discretion of the MDEQ field Officer. The external field audits can include (but are not limited to) the following:

- sampling equipment decontamination procedures;
- sample bottle preparation procedures;
- sampling procedures and;
- procedures for verification of field duplicates; and field screening practices.

17.3 Laboratory Audits

External audits will be conducted as required, by appropriate QA personnel of the MDEQ and may be conducted at least once prior to sampling and analysis activities.

External audits may include any of the following:

i. Review of laboratory analytical procedures;

ii. Laboratory on-site visits; and

iii. Submission of performance evaluation samples for analysis.

Failure of any of the above audit procedures can lead to laboratory disqualification, and another suitable laboratory will have to be chosen. An on-site review can consist of:

i. Sample receipt procedures;

ii. Custody, sample security, and log-in procedures;

iii. Review of instrument calibration logs;

iv. Review of QA procedures;

v. Review of log books;

vi. Review of analytical SOPs; and

vii. Personnel interviews.

A review of a data package from samples recently analyzed by the laboratory can include (but not be limited to) the following:

i. Comparison of resulting data to the SOP or method

ii. Verification of initial and continuing calibrations within control limits

iii. Verification of surrogate recoveries and instrument timing results

iv. Review of extended quantitation reports for comparisons of library spectra to instrument spectra, where applicable; and

v. Assurance that samples are run within holding times.

17.4 Corrective Action Procedures

17.4.1 Field Procedures

Corrective action is intended to address problems that arise by identification, recommendation, approval, and implementation of measures that counter unacceptable procedures or deficient quality control performance. Examples of situations that would require corrective actions are provided below:

- protocols as defined by the QAPP and RFI Work Plan have not been followed;
- equipment is not in proper working order or is not properly calibrated;
- QC requirements have not been met; and
- issues resulting from performance or systems audits have not been resolved.

Project personnel will continuously monitor ongoing work performance in the normal course of daily responsibilities.

17.4.2 Laboratory Procedures

In the laboratory, when a condition is noted to have an adverse effect on data quality, corrective action will be taken so as not to repeat this condition. Condition identification, cause, and corrective action taken will be documented and reported to the appropriate Project Manager and QAC.

Corrective action may be initiated, at a minimum, under the following conditions:

- protocols as defined by this QAPP have not been followed;
- predetermined data acceptance standards are not obtained;
- equipment is not in proper working order or calibrated;
- sample and test results are not completely traceable;
- QC requirements have not been met; and
- issues resulting from performance or systems audits have not been resolved.

Laboratory personnel will continuously monitor ongoing work performance in the normal course of daily responsibilities. Corrective action is initiated at the point where the problem has been identified. At whatever level this occurs (analyst, supervisor, data review, or quality control) it is brought to the attention of the Laboratory QA Manager and, ultimately, the Laboratory Director. Final approval of any action deemed necessary is subject to the approval of the Laboratory Director.

Any corrective action deemed necessary based on system or performance audits, the analytical results of split samples, or the results of data review will be implemented. The corrective action may include sample re-extraction, re-preparation, re-analysis, cleanup, dilution, matrix modification, or other activities.

18. Reports to Management

18.1 General

The QAC will audit the implementation of the QAPP. Each project component will result in some type of QA report or, by its absence, will indicate that no significant QA or QC deviations occurred. Items that may result in a QA report include:

- changes or updates to the QAPP;
- deviations from QAPP or RFI Work Plan specification;
- results of system and performance audits;
- significant QA/QC problems, recommended solutions, and the results of corrective actions; and
- limitations on the use of measurement data.

18.2 Field Reports

Reporting of the quality of field sample collection and field measurements will be the responsibility of the Task Manager or designee. Information from the field logbooks will be compiled, and a summary report on field activity QA will be prepared for the project file.

18.3 Laboratory Reports

The laboratory will maintain QA records related to analyses, QC, and corrective action. This information will be made available to the Project Manager upon request. Routine reporting will include documenting all internal QC checks performed for this project.

19. Data Reduction and Review

19.1 General

After field and laboratory data are obtained, the data will be subject to the following:

- reduction, or manipulation mathematically or otherwise into meaningful and useful forms;
- review;
- organization, interpretation, and reporting; and
- data validation.

19.2 Field Data Reduction and Review

19.2.1 Field Data Reduction

Information collected in the field through visual observation, manual measurement, and/or field instrumentation will be recorded in field notebooks or data sheets, and/or on forms. Such data will be reviewed for consistency by the appropriate Task Manager. Concerns identified as a result of this review will be discussed with the field personnel; corrected if possible; and, as necessary, incorporated into the data evaluation process.

19.2.2 Field Data Review

Field data calculations, transfers, and interpretations will be conducted by the field personnel and reviewed for accuracy by the appropriate Task Manager. Logs and documents will be checked for:

- general completeness;
- readability;
- usage of appropriate procedures;
- appropriate instrument calibration and maintenance;

- reasonableness in comparison to present and past data collected;
- correct sample locations; and
- correct calculations and interpretations.

19.3 Laboratory Data Reduction and Review

19.3.1 Laboratory Data Reduction

The calculations used for data reduction will be specified in each of the analytical methods referenced previously. Whenever possible, analytical data will be transferred directly from the instrument to a computerized data system. Raw data will be entered into permanently bound laboratory notebooks. The data entered must be sufficient to document all factors used to arrive at the reported value.

Concentration calculations for chromatographic analyses will be based on response factors. Quantitation will be performed using either internal or external standards.

Inorganic analyses will be based on regression analysis. Regression analysis is used to fit a curve through the calibration standard data. The sample concentrations will be calculated using the resulting regression equations.

Nonaqueous values will be reported on a dry-weight basis. Unless otherwise specified, all values will be reported uncorrected for blank contamination.

19.4 Laboratory Data Review

Data will be subject to multi-level review by the laboratory. The Laboratory Project Manager will review all data reports prior to release for final data report generation. The QA Manager will review the final data reports prior to shipment.

If discrepancies or deficiencies are present in the analytical results, corrective action will be taken, as discussed in Section 17. Deficiencies discovered as a result of internal data review, as well as the corrective actions to be used to rectify the situation, will be documented on a Corrective Action Form provided by the Analytical Laboratory. This form will be submitted to the ARCADIS Project Manager.

19.5 Data Validation and Verification

All laboratory data generated will be subjected to the data validation and verification procedures outlined in Section 20. Data generated for disposal purposes will not be reviewed.

20. Data Validation and Verification

Data validation entails a review of the QC data and the raw data to verify that the laboratory was operating within required limits; the analytical results were correctly transcribed from the instrument read-outs; and which, if any, environmental samples were related to out-of-control QC samples. The objective of data validation is to identify any questionable or invalid laboratory measurements.

A designated data validator will validate all analytical data generated for groundwater samples and any soil samples using the versions of the USEPA's Function Guidelines (USEPA, 1999; 2002a) and USEPA Region *Innovative Approaches to Data Validation*, USEPA Region III (June 1995) for data validation available at the time of project initiation, where appropriate. A Tier I data review utilizing M-2 (organic) and IM-1 (inorganic) will be performed on 90% of the laboratory QC summary data deliverables. A Tier II data review will be performed on the remainder (10%) of the laboratory QC summary data deliverables. These procedures and criteria may be modified, as necessary, to address project-specific and method-specific criteria, control limits, and procedures. Data validation will consist of data screening, checking, reviewing, editing, and interpretation to document analytical data quality and to determine whether the quality is sufficient to meet the DQOs. Any deviation from these procedures and criteria will be identified in the data report to the MDEQ.

The ARCADIS Task Manager or Project Manager will verify that reduction of laboratory measurements and laboratory reporting of analytical parameters is in accordance with the procedures specified for each analytical method and/or as specified in this QAPP. Any deviations from the analytical method or any special reporting requirements apart from those specified in this QAPP will be detailed on COC forms.

Upon receipt of laboratory data, the following procedures will be executed by the ARCADIS Task Manager:

- evaluate completeness of data package;
- verify that field COC forms were completed and that samples were handled properly;
- verify that holding times were met for each parameter. Holding time exceedances, should they occur, will be documented. Data for all samples exceeding holding

time requirements will be flagged as either estimated or rejected. The decision as to which qualifier is more appropriate will be made on a case-by-case basis;

- verify that parameters were analyzed according to the methods specified;
- review QA/QC data (i.e., confirm that duplicates, blanks, and spikes were analyzed on the required number of samples, as specified in the method and verify that duplicate and MS recoveries are acceptable);
- investigate anomalies identified during review. When anomalies are identified, they will be discussed with the Project Manager and/or Laboratory Manager, as appropriate; and
- if data appear suspect, investigate the specific data of concern. Calculations will be traced back to raw data. If calculations do not agree, the cause will be determined and corrected.

Deficiencies discovered as a result of the data review, as well as the corrective actions implemented in response, will be documented and submitted in the form of a written report addressing the following topics, as applicable to each method:

- assessment of the data package;
- description of any protocol deviations;
- failures to reconcile reported and/or raw data;
- assessment of any compromised data;
- overall appraisal of the analytical data; and
- table of site name, sample quantities, matrix, and fractions analyzed.

Resolution of any issues regarding laboratory performance or deliverables will be handled between the laboratory and the data validator. Suggestions for reanalysis may be made by the ARCADIS Project Manager at this point.

Data validation reports will be kept in the project file.

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21. References

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Tables

TABLE 1
RACER TRUST LANSING PLANTS 2, 3 6
QUALITY ASSURNACE PPROJECT PLAN
DATA QUALITY OBJECTIVES (DQOs) FOLLOWING USEPA 7-STEP PROCESS

REVITALIZING AUTO COMMUNITIES ENVIRONMENTAL RESPONSE (RACER) TRUST
LANSING, MICHIGAN

Data Type	Problem Statement	Decision	Inputs to Decision	Boundaries	Decision Rule	Limits on Decision Errors	Design Optimization
Groundwater Level Monitoring	Determine migration of constituents of concern (COCs) in groundwater, both vertically and horizontally.	Establish a monitoring well network to define groundwater flow direction. Paired wells will be necessary if groundwater flow exhibits a vertical component of flow.	Monitoring wells will be installed and head levels measured as proposed in the Work Plan and FSP. Initially the water table will be monitored, followed by deeper wells screened preferentially within permeable zones, if present.	The monitoring will be confined to the delineated impacts.	In the event that the groundwater flow direction at the Site is other than what was anticipated (north-northwest and possibly south-southeast), additional monitoring wells may need to be installed to properly monitor contaminant migration.	Water level readings will be used directly for quantitative determination of the head levels as long as equipment is operating within acceptable calibration ranges.	Data collection procedures are described in the FSP and QAPP.
Groundwater LNAPL Monitoring	LNAPL could be present in the subsurface requiring a response action under Michigan administrative rules.	Determine whether the monitoring well network is sufficient to define LNAPL distribution on the property.	Monitoring wells will be installed and LNAPL thicknesses measured as proposed in the Work plan and FSP.	The monitoring will be confined to the delineated impacts.	In the event that LNAPL is present at the limits of the monitoring well network, additional monitoring wells may need to be installed to fully characterize LNAPL in the subsurface.	LNAPL thickness readings will be used directly for quantitative determination of the approximate volume of LNAPL on-site as long as equipment is operating within acceptable calibration ranges.	Data collection procedures are described in the FSP and QAPP.
Groundwater Chemical Sampling	Groundwater could be impacted with hazardous constituents at levels detrimental to human health and the environment and limiting future land use unless remediated.	Determine the degree to which groundwater is impacted with hazardous constituents as determined by a comparison to Michigan Part 201 cleanup criteria.	Groundwater samples will be collected and analyzed as proposed in the Work plan and FSP.	The sampling will be confined to the delineated impacts.	In the event that groundwater impacts greater than Michigan Part 201 generic cleanup criteria are present at the edge of the monitoring well network, additional monitoring wells may need to be installed to fully delineate groundwater impacts.	Groundwater chemistry laboratory results will be used for quantitative determination as long as the results are properly validated per the QAPP.	Data collection procedures are described in the FSP and QAPP.
Soil Chemical Sampling	Soil could be impacted with hazardous constituents at levels detrimental to human health and the environment and limiting future land use unless remediated.	Determine the degree to which soil is impacted with hazardous constituents as determined by a comparison to Michigan Part 201 cleanup criteria.	Soil samples will be collected and analyzed as proposed in the Work plan and FSP.	The sampling will be confined to the delineated impacts.	In the event that soil impacts greater than Michigan Part 201 generic cleanup criteria are present, additional soil borings need to be installed to fully delineate soil impacts.	Soil chemistry laboratory results will be used for quantitative determination as long as the results are properly validated per the QAPP.	Data collection procedures are described in the FSP and QAPP.

TABLE 2
RACER TRUST LANSING PLANTS 2, 3 6
QUALITY ASSURNACE PPROJECT PLAN
SAMPLE QUANTITIES AND QUALITY CONTROL FREQUENCIES

REVITALIZING AUTO COMMUNITIES ENVIRONMENTAL RESPONSE (RACER) TRUST
LANSING, MICHIGAN

Parameter	Field Quality Control Analyses						Laboratory Quality Control Sample						Total
	Trip Blank		Rinse Blank[3]		Field Duplicate		Matrix Spike		Matrix Spike Duplicate		Lab Duplicate		
	frequency	number[1]	frequency	number	frequency	number[2]	frequency	number[2]	frequency	number[2]	frequency	number[2]	
Groundwater													
VOCs and SVOCs	1/cooler	5	NC	--	1/10	1	1/20	1	1/20	1	NC	--	8
Polychlorinated Biphenyls (PCBs)	NC	--	NC	--	1/10	1	1/20	1	1/20	1	NC	--	3
Metals (arsenic, barium, cadmium, chromium, nickel, lead, silver, selenium, and zinc)	NC	--	NC	--	1/10	1	1/20	1	1/20	1	1/20	1	4
Mercury	NC	--	NC	--	1/10	1	1/20	1	1/20	1	1/20	1	4
Cyanide	NC	--	NC	--	1/10	1	1/20	1	1/20	1	1/20	1	4
General Water Quality Parameters[4]	NC	--	NC	--	1/10	1	1/20	1	1/20	1	1/20	1	4
Soil													
VOCs and SVOCs	1/cooler	5	NC	--	1/10	1	1/20	1	1/20	1	NC	--	8
Polychlorinated Biphenyls (PCBs)	NC	--	NC	--	1/10	1	1/20	1	1/20	1	NC	--	3
Metals (arsenic, barium, cadmium, chromium, nickel, lead, silver, selenium, and zinc)	NC	--	NC	--	1/10	1	1/20	1	1/20	1	1/20	1	4
Mercury	NC	--	NC	--	1/10	1	1/20	1	1/20	1	1/20	1	4
Cyanide	NC	--	NC	--	1/10	1	1/20	1	1/20	1	1/20	1	4

Notes:
1. Assuming a total of 5 coolers will be submitted to the laboratory during each sampling round.
2. Sample counts are per monitoring event assuming that groundwater samples are collected from all existing and newly installed wells, and that soil sample counts are 2 per boring.
3. It is assumed that dedicated sampling equipment will be used and rinse blanks are not required when dedicated sampling equipment is used.
4. General Water Quality Parameters - alkalinity, ammonia, chloride, nitrated/nitrite, sulfate, hardness, total dissolved solids, total organic carbon
5. NC = not collected

TABLE 3
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LANSING PLANTS 2, 3 and 6
QUALITY ASSURANCE PROJECT PLAN
SAMPLE CONTAINERS, PRESERVATION, HOLDING TIMES METHODS, AND TARGET REPORTING LIMITS
LANSING, MICHIGAN

Parameter	Analytical Method[6]	Target Detection Limit (ppb)[7]	Sample Container and Volume[8]	Preservation[9]	Maximum Holding Time[10]
GROUNDWATER SAMPLES					
Volatile Organic Compounds (VOCs)					
Acetone	8260B	50	2-40 ml VOA vials	cool to 4˚ C, HCl to pH<2 no headspace	14 days
Benzene	8260B	1	2-40 ml VOA vials	cool to 4˚ C, HCl to pH<2 no headspace	14 days
Bromodichloromethane	8260B	1	2-40 ml VOA vials	cool to 4˚ C, HCl to pH<2 no headspace	14 days
Bromoform	8260B	1	2-40 ml VOA vials	cool to 4˚ C, HCl to pH<2 no headspace	14 days
Bromomethane	8260B	5	2-40 ml VOA vials	cool to 4˚ C, HCl to pH<2 no headspace	14 days
2-Butanone	8260B	25	2-40 ml VOA vials	cool to 4˚ C, HCl to pH<2 no headspace	14 days
Carbon Disulfide	8260B	5	2-40 ml VOA vials	cool to 4˚ C, HCl to pH<2 no headspace	14 days
Carbon Tetrachloride	8260B	1	2-40 ml VOA vials	cool to 4˚ C, HCl to pH<2 no headspace	14 days
Chlorobenzene	8260B	1	2-40 ml VOA vials	cool to 4˚ C, HCl to pH<2 no headspace	14 days
Chloroethane	8260B	5	2-40 ml VOA vials	cool to 4˚ C, HCl to pH<2 no headspace	14 days
Chloroform	8260B	1	2-40 ml VOA vials	cool to 4˚ C, HCl to pH<2 no headspace	14 days
Chloromethane	8260B	5	2-40 ml VOA vials	cool to 4˚ C, HCl to pH<2 no headspace	14 days
Cyclohexane	8260B	NA	2-40 ml VOA vials	cool to 4˚ C, HCl to pH<2 no headspace	14 days
Dibromochloromethane	8260B	5	2-40 ml VOA vials	cool to 4˚ C, HCl to pH<2 no headspace	14 days
1,2-Dibromo-3-chloropropane (Dibromochloropropane)	8260B	0.2[3]	2-40 ml VOA vials	cool to 4˚ C, HCl to pH<2 no headspace	14 days
1,2-Dibromomethane (Ethylene dibromide)	8260B	0.05[3]	2-40 ml VOA vials	cool to 4˚ C, HCl to pH<2 no headspace	14 days
Dichlordifluoromethane	8260B	5	2-40 ml VOA vials	cool to 4˚ C, HCl to pH<2 no headspace	14 days
1,2-Dichlorobenzene	8260B	1	2-40 ml VOA vials	cool to 4˚ C, HCl to pH<2 no headspace	14 days
1,3-Dichlorobenzene	8260B	1	2-40 ml VOA vials	cool to 4˚ C, HCl to pH<2 no headspace	14 days
1,4-Dichlorobenzene	8260B	1	2-40 ml VOA vials	cool to 4˚ C, HCl to pH<2 no headspace	14 days
1,1-Dichloroethane	8260B	1	2-40 ml VOA vials	cool to 4˚ C, HCl to pH<2 no headspace	14 days
1,2-Dichloroethane	8260B	1	2-40 ml VOA vials	cool to 4˚ C, HCl to pH<2 no headspace	14 days
1,1-Dichloroethene	8260B	1	2-40 ml VOA vials	cool to 4˚ C, HCl to pH<2 no headspace	14 days
cis-1,2-Dichloroethene	8260B	1	2-40 ml VOA vials	cool to 4˚ C, HCl to pH<2 no headspace	14 days
trans-1,2-Dichloroethene	8260B	1	2-40 ml VOA vials	cool to 4˚ C, HCl to pH<2 no headspace	14 days
1,2-Dichloropropane	8260B	1	2-40 ml VOA vials	cool to 4˚ C, HCl to pH<2 no headspace	14 days
cis-1,3-Dichloropropene	8260B	1	2-40 ml VOA vials	cool to 4˚ C, HCl to pH<2 no headspace	14 days
trans-1,3-Dichloropropene	8260B	1	2-40 ml VOA vials	cool to 4˚ C, HCl to pH<2 no headspace	14 days
1,4-Dioxane [5]	8260B	5	2-40 ml VOA vials	cool to 4˚ C, HCl to pH<2 no headspace	14 days
Ethylbenzene	8260B	1	2-40 ml VOA vials	cool to 4˚ C, HCl to pH<2 no headspace	14 days
2-Hexanone	8260B	50	2-40 ml VOA vials	cool to 4˚ C, HCl to pH<2 no headspace	14 days
Isopropylbenzene	8260B	5	2-40 ml VOA vials	cool to 4˚ C, HCl to pH<2 no headspace	14 days
Methyl Acetate	8260B	NA	2-40 ml VOA vials	cool to 4˚ C, HCl to pH<2 no headspace	14 days
Methyl Cyclohexane	8260B	NA	2-40 ml VOA vials	cool to 4˚ C, HCl to pH<2 no headspace	14 days
4-Methyl-2-pentanone	8260B	50	2-40 ml VOA vials	cool to 4˚ C, HCl to pH<2 no headspace	14 days
Methyl tert-butyl ether (MTBE)	8260B	5	2-40 ml VOA vials	cool to 4˚ C, HCl to pH<2 no headspace	14 days
Methylene Chloride	8260B	5	2-40 ml VOA vials	cool to 4˚ C, HCl to pH<2 no headspace	14 days
Styrene	8260B	1	2-40 ml VOA vials	cool to 4˚ C, HCl to pH<2 no headspace	14 days
1,1,2,2-Tetrachloroethane	8260B	1.0	2-40 ml VOA vials	cool to 4˚ C, HCl to pH<2 no headspace	14 days
Tetrachloroethene	8260B	1	2-40 ml VOA vials	cool to 4˚ C, HCl to pH<2 no headspace	14 days

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SAMPLE CONTAINERS, PRESERVATION, HOLDING TIMES METHODS, AND TARGET REPORTING LIMITS
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Parameter	Analytical Method[6]	Target Detection Limit (ppb)[7]	Sample Container and Volume[8]	Preservation[9]	Maximum Holding Time[10]
Toluene	8260B	1	2-40 ml VOA vials	cool to 4˚ C, HCl to pH<2 no headspace	14 days
1,1,1-Trichloroethane	8260B	1	2-40 ml VOA vials	cool to 4˚ C, HCl to pH<2 no headspace	14 days
1,1,2-Trichloroethane	8260B	1	2-40 ml VOA vials	cool to 4˚ C, HCl to pH<2 no headspace	14 days
Trichloroethene	8260B	1	2-40 ml VOA vials	cool to 4˚ C, HCl to pH<2 no headspace	14 days
1,2,4-Trichlorobenzene	8260B	5	2-40 ml VOA vials	cool to 4˚ C, HCl to pH<2 no headspace	14 days
Trichlorofluoromethane	8260B	1	2-40 ml VOA vials	cool to 4˚ C, HCl to pH<2 no headspace	14 days
Trifluorotrichloroethane (Freon 113)	8260B	NA	2-40 ml VOA vials	cool to 4˚ C, HCl to pH<2 no headspace	14 days
Vinyl Chloride	8260B	1.0	2-40 ml VOA vials	cool to 4˚ C, HCl to pH<2 no headspace	14 days
m&p-Xylene	8260B	2	2-40 ml VOA vials	cool to 4˚ C, HCl to pH<2 no headspace	14 days
o-Xylene	8260B	1	2-40 ml VOA vials	cool to 4˚ C, HCl to pH<2 no headspace	14 days
Xylenes (total)	8260B	3	2-40 ml VOA vials	cool to 4˚ C, HCl to pH<2 no headspace	14 days
Semi-Volatile Organic Compounds (SVOCs)					
Acenaphthene	8270C	5	2-1 liter amber glass	cool to 4˚ C	7 days to extraction 40 days to analysis
Acenaphthylene	8270C	5	2-1 liter amber glass	cool to 4˚ C	7 days to extraction 40 days to analysis
Acetophenone	8270C	5	2-1 liter amber glass	cool to 4˚ C	7 days to extraction 40 days to analysis
Anthracene	8270C	5	2-1 liter amber glass	cool to 4˚ C	7 days to extraction 40 days to analysis
Atrazine	8270C	3.0	2-1 liter amber glass	cool to 4˚ C	7 days to extraction 40 days to analysis
1,1-Biphenyl	8270C	NA	2-1 liter amber glass	cool to 4˚ C	7 days to extraction 40 days to analysis
Benzaldehyde	8270C	NA	2-1 liter amber glass	cool to 4˚ C	7 days to extraction 40 days to analysis
Benzo(a)anthracene	8270C	1.0	2-1 liter amber glass	cool to 4˚ C	7 days to extraction 40 days to analysis
Benzo(a)pyrene	8270C	**[1]**	2-1 liter amber glass	cool to 4˚ C	7 days to extraction 40 days to analysis
Benzo(b)fluoranthene	8270C	1[4]	2-1 liter amber glass	cool to 4˚ C	7 days to extraction 40 days to analysis
Benzo(g,h,i)perylene	8270C	**[1]**	2-1 liter amber glass	cool to 4˚ C	7 days to extraction 40 days to analysis
Benzo(k)fluoranthene	8270C	**[1]**	2-1 liter amber glass	cool to 4˚ C	7 days to extraction 40 days to analysis
bis(2-Chloroethoxy)methane	8270C	5	2-1 liter amber glass	cool to 4˚ C	7 days to extraction 40 days to analysis
bis(2-Chloroethyl)ether	8270C	1.0	2-1 liter amber glass	cool to 4˚ C	7 days to extraction 40 days to analysis
bis(2-Ethylhexyl)phthalate	8270C	5	2-1 liter amber glass	cool to 4˚ C	7 days to extraction 40 days to analysis
4-Bromophenyl-phenylether	8270C	5	2-1 liter amber glass	cool to 4˚ C	7 days to extraction 40 days to analysis
Butylbenzylphthalate	8270C	5	2-1 liter amber glass	cool to 4˚ C	7 days to extraction 40 days to analysis
Caprolactam	8270C	10	2-1 liter amber glass	cool to 4˚ C	7 days to extraction 40 days to analysis
Carbazole	8270C	**[10]**	2-1 liter amber glass	cool to 4˚ C	7 days to extraction 40 days to analysis
4-Chloro-3-Methylphenol	8270C	5	2-1 liter amber glass	cool to 4˚ C	7 days to extraction 40 days to analysis
4-Chloroaniline	8270C	10	2-1 liter amber glass	cool to 4˚ C	7 days to extraction 40 days to analysis
2-Chloronaphthalene	8270C	5	2-1 liter amber glass	cool to 4˚ C	7 days to extraction 40 days to analysis
2-Chlorophenol	8270C	10	2-1 liter amber glass	cool to 4˚ C	7 days to extraction 40 days to analysis
4-Chlorophenyl-phenylether	8270C	5	2-1 liter amber glass	cool to 4˚ C	7 days to extraction 40 days to analysis
2,2'-oxybis(1-Chloropropane) [bis(2-Chloroisopropyl) ether]	8270C	5	2-1 liter amber glass	cool to 4˚ C	7 days to extraction 40 days to analysis
Chrysene	8270C	1.0	2-1 liter amber glass	cool to 4˚ C	7 days to extraction 40 days to analysis
2-Methylphenol	8270C	10	2-1 liter amber glass	cool to 4˚ C	7 days to extraction 40 days to analysis
3-Methylphenol	8270C	10	2-1 liter amber glass	cool to 4˚ C	7 days to extraction 40 days to analysis
4-Methylphenol	8270C	10	2-1 liter amber glass	cool to 4˚ C	7 days to extraction 40 days to analysis
Di-n-Butylphthalate	8270C	5	2-1 liter amber glass	cool to 4˚ C	7 days to extraction 40 days to analysis

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Parameter	Analytical Method[6]	Target Detection Limit (ppb)[7]	Sample Container and Volume[8]	Preservation[9]	Maximum Holding Time[10]
Di-n-Octylphthalate	8270C	5	2-1 liter amber glass	cool to 4˚ C	7 days to extraction 40 days to analysis
Dibenzo(a,h)anthracene	8270C	**[2]**	2-1 liter amber glass	cool to 4˚ C	7 days to extraction 40 days to analysis
Dibenzofuran	8270C	4	2-1 liter amber glass	cool to 4˚ C	7 days to extraction 40 days to analysis
3,3'-Dichlorobenzidine	8270C	**[0.3]**	2-1 liter amber glass	cool to 4˚ C	7 days to extraction 40 days to analysis
2,4-Dichlorophenol	8270C	10	2-1 liter amber glass	cool to 4˚ C	7 days to extraction 40 days to analysis
Diethylphthalate	8270C	5	2-1 liter amber glass	cool to 4˚ C	7 days to extraction 40 days to analysis
Dimethylphthalate	8270C	5	2-1 liter amber glass	cool to 4˚ C	7 days to extraction 40 days to analysis
2,4-Dimethylphenol	8270C	5	2-1 liter amber glass	cool to 4˚ C	7 days to extraction 40 days to analysis
4,6-Dinitro-2-methylphenol	8270C	**[20]**	2-1 liter amber glass	cool to 4˚ C	7 days to extraction 40 days to analysis
2,4-Dinitrophenol	8270C	25	2-1 liter amber glass	cool to 4˚ C	7 days to extraction 40 days to analysis
2,4-Dinitrotoluene	8270C	5	2-1 liter amber glass	cool to 4˚ C	7 days to extraction 40 days to analysis
2,6-Dinitrotoluene	8270C	5	2-1 liter amber glass	cool to 4˚ C	7 days to extraction 40 days to analysis
Fluoranthene	8270C	1	2-1 liter amber glass	cool to 4˚ C	7 days to extraction 40 days to analysis
Fluorene	8270C	5	2-1 liter amber glass	cool to 4˚ C	7 days to extraction 40 days to analysis
Hexachlorobenzene	8270C	0.2[3]	2-1 liter amber glass	cool to 4˚ C	7 days to extraction 40 days to analysis
Hexachlorobutadiene	8270C	0.05[3]	2-1 liter amber glass	cool to 4˚ C	7 days to extraction 40 days to analysis
Hexachlorocyclopentadiene	8270C	5.0	2-1 liter amber glass	cool to 4˚ C	7 days to extraction 40 days to analysis
Hexachloroethane	8270C	5	2-1 liter amber glass	cool to 4˚ C	7 days to extraction 40 days to analysis
Indeno(1,2,3-cd)pyrene	8270C	**[2]**	2-1 liter amber glass	cool to 4˚ C	7 days to extraction 40 days to analysis
Isophorone	8270C	5	2-1 liter amber glass	cool to 4˚ C	7 days to extraction 40 days to analysis
2-Methylnaphthalene	8270C	5	2-1 liter amber glass	cool to 4˚ C	7 days to extraction 40 days to analysis
Naphthalene	8270C	5	2-1 liter amber glass	cool to 4˚ C	7 days to extraction 40 days to analysis
2-Nitroaniline	8270C	25	2-1 liter amber glass	cool to 4˚ C	7 days to extraction 40 days to analysis
3-Nitroaniline	8270C	25	2-1 liter amber glass	cool to 4˚ C	7 days to extraction 40 days to analysis
4-Nitroaniline	8270C	25	2-1 liter amber glass	cool to 4˚ C	7 days to extraction 40 days to analysis
Nitrobenzene	8270C	3	2-1 liter amber glass	cool to 4˚ C	7 days to extraction 40 days to analysis
2-Nitrophenol	8270C	5	2-1 liter amber glass	cool to 4˚ C	7 days to extraction 40 days to analysis
4-Nitrophenol	8270C	25	2-1 liter amber glass	cool to 4˚ C	7 days to extraction 40 days to analysis
N-Nitroso-di-n-propylamine	8270C	**[5]**	2-1 liter amber glass	cool to 4˚ C	7 days to extraction 40 days to analysis
N-Nitrosodiphenylamine	8270C	5	2-1 liter amber glass	cool to 4˚ C	7 days to extraction 40 days to analysis
Pentachlorophenol	8270C	1[3]	2-1 liter amber glass	cool to 4˚ C	7 days to extraction 40 days to analysis
Phenanthrene	8270C	2.0	2-1 liter amber glass	cool to 4˚ C	7 days to extraction 40 days to analysis
Phenol	8270C	5	2-1 liter amber glass	cool to 4˚ C	7 days to extraction 40 days to analysis
Pyrene	8270C	5	2-1 liter amber glass	cool to 4˚ C	7 days to extraction 40 days to analysis
2,4,5-Trichlorophenol	8270C	5	2-1 liter amber glass	cool to 4˚ C	7 days to extraction 40 days to analysis
2,4,6-Trichlorophenol	8270C	4	2-1 liter amber glass	cool to 4˚ C	7 days to extraction 40 days to analysis
Polychlorinated Biphenyls (PCBs)					
Total PCBs	8082A	0.2	2-1 liter amber glass	cool to 4˚ C	7 days to extraction 40 days to analysis
Metals					
Antimony	1631E	2	2-40 ml VOA vials	cool to 4˚ C	28 days
Arsenic	6020	5	125 ml plastic	cool to 4˚ C, HNO_3 to pH<2	6 months
Barium	7196A	100	125 ml plastic	cool to 4˚ C	24 hours
Beryllium	6020	**[1]**	125 ml plastic	cool to 4˚ C, HNO_3 to pH<2	6 months
Boron	6020	**10**	125 ml plastic	cool to 4˚ C, HNO_3 to pH<2	6 months
Cadmium	6020	1	125 ml plastic	cool to 4˚ C, HNO_3 to pH<2	6 months

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Parameter	Analytical Method[6]	Target Detection Limit (ppb)[7]	Sample Container and Volume[8]	Preservation[9]	Maximum Holding Time[10]
Chromium	6020	10	125 ml plastic	cool to 4˚ C, HNO_3 to pH<2	6 months
Copper	6020	4	125 ml plastic	cool to 4˚ C, HNO_3 to pH<2	6 months
Cyanide	4500-CN-E	NA	125 ml plastic	cool to 4˚ C, HNO_3 to pH<2	6 months
Lead	6020	3	125 ml plastic	cool to 4˚ C, HNO_3 to pH<2	6 months
Manganese	6020	50	125 ml plastic	cool to 4˚ C, HNO_3 to pH<2	6 months
Mercury	7471a	NA	125 ml plastic	cool to 4˚ C, HNO_3 to pH<2	6 months
Low-Level Mercury	1631	0.001[3]	125 ml plastic	cool to 4˚ C, HNO_3 to pH<2	6 months
Nickel	6020	20	125 ml plastic	cool to 4˚ C, HNO_3 to pH<2	6 months
Selenium	6020	5	125 ml plastic	cool to 4˚ C, HNO_3 to pH<2	6 months
Silver	6020	**[0.2]**	125 ml plastic	cool to 4˚ C, HNO_3 to pH<2	6 months
Thallium	6020	2.0	125 ml plastic	cool to 4˚ C, HNO_3 to pH<2	6 months
Vanadium	6020	4	125 ml plastic	cool to 4˚ C, HNO_3 to pH<2	6 months
Zinc	6020	50	125 ml plastic	cool to 4˚ C, HNO_3 to pH<2	6 months
Inorganics and General Water Quality Parameters					
Chloride	300.0	1 mg/l	1 L plastic	cool to 4˚ C	28 days
Sulfate	300.0	1 mg/l	1 L plastic	cool to 4˚ C	28 days
Nitrate	300.0	0.1 mg/l	1 L plastic	cool to 4˚ C	48 hours
Nitrite	300.0	0.1 mg/l	1 L plastic	cool to 4˚ C	48 hours
Hardness	2340 Std Mtd	2 mg/l	125 ml plastic	cool to 4˚ C, HNO_3 to pH<2	6 months
Alkalinity	2320B	1 mg/l	1 L plastic	cool to 4˚ C	14 days
Ammonia	4500-NH3 D	0.02 mg/l	250 ml plastic	cool to 4˚ C, H_2SO_4 to pH<2	28 days
Total Dissolved Solids	2540C	1 mg/l	1 L plastic	cool to 4˚ C	7 days
Total Organic Carbon	EPA 415.1	1 mg/l	2-40 ml VOA vials	cool to 4˚ C, H_2SO_4 to pH<2	28 days
Cyanide	335.4/4500-CN-E	5	125 ml plastic	cool to 4˚ C, NaOH to pH>12	14 days

Notes:

[ ] The TDLs in bold type and enclosed with [ ] brackets indicate that the contaminant's TDL is higher than the most restrictive criteria.

(1) The TDLs for groundwater and soil are based on the TDLs defined in Michigan Department of Environmental Quality (MDEQ) Remediation and Redevelopment Division Memorandum No. 2 (February 2, 2005).

(2) The MDLs and PQLs listed are current as of March 2005 and may differ slightly during future data reporting.

(3) In some instances, the TDL is below the MDL, indicating that the MDEQ TDL is not currently achievable by the lab. If it is necessary to achieve the TDL, a selective ion mass spectrometry (SIM) test can be performed.

(4) Target Detection Limits and Designated Analytical Methods are based on MDEQ RRD Operational Memo No. 2 - Attachment 1, dated October 22, 2004.

(5) When analyses of these compounds are requested using GC/MS, SIM analyses must be conducted on all samples with no detects found in the full scan. Positive detects in the mode should then be appropriately coded to indicate SIM analyses were conducted.SIM

(6) United States Environmental Protection Agency. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, Edition 3 (SW-846), Office of Solid Waste & Emergency Response.

(7) Michigan Department of Environmental Quality (MDEQ) Remediation and Redevelopment Division (RRD) Operational Memorandum No. 2 - Attachment 1, October 22, 2004. The target detection limit (TDL) for each parameter in the VOC and Base/Neutral/Acid groups varies. Refer to the Operational Memorandum to determine the TDL for each compound included in those groups.

(8) Sample container will be new, precleaned, and certified by manufacturer.

(9) Whenever possible, pre-preserved bottles will be used.

(10) Holding time measured from date of collection.

(11) For response activities under Part 201 and Part 213, if the GSI has been appropriately documneted to not be a relevant pathway, then a water reporting limit of 10 ug/l and soil reporting limit of 330 ug/kg is sufficient to valuate the most restrictive criteria for Hexachlorobutadiene.

(12) For response activities under Part 201 and Part 213, if the GSI and the drinking water have been documented to not be relevant pathways, then water and soil reporting limits of 20 ug/l and 800 ug/kg will be sufficient to evaluate the most restrictive criteria for pentachlorophenol.

NL = not listed in the Operational Memorandum No. 2

ml = milliliters

˚ C = degrees Celsius

ug/l = micrograms per liter

ug/kg = micrograms per kilogram

The table applies to initial investigations to characterize the Site. Additions to this table may be required depending upon results used to characterize the Site and future sample collection. Any such additions will be made in accordance with the MDEQ Operational Memorandum no. 2, Sampling and Analysis, dated October 22, 2004.

TABLE 4
RACER TRUST LANSING PLANTS 2, 3 6
QUALITY ASSURNACE PPROJECT PLAN
ANALYTICAL QUALITY CONTROL LIMITS(1)

REVITALIZING AUTO COMMUNITIES ENVIRONMENTAL RESPONSE (RACER) TRUST
LANSING, MICHIGAN

Parameter [2]	Accuracy - % Recovery			Precision - RPD		
	Surrogate	MS/MSD	LCS	MS/MSD	Lab Duplicate	Field Duplicate
Groundwater / Soil						
Volatile Organic Compounds (VOCs)	70-130	60-145	70-140	20	--	50
SVOCs	20-140	20-130	40-120	40	--	50
Polychlorinated Biphenyls (PCBs)	30-120	40-130	50-140	20	--	50
Metals (As, Ba, Cd, Total Cr, Ni, Pb, Hg, Ag, Se, Zn)	--	75- 125	75- 125	--	30	50
Cyanide, Available	--	75- 125	75- 125	--	30	50
Chromium (hexavalent)	--	65-121	70-130	--	30	50
Alkalinity	--	70-130	70-130	--	30	50
Ammonia	--	70-130	70-130	--	30	50
BOD	--	70-130	70-130	--	30	50
Chloride	--	70-130	70-130	--	30	50
MBAS	--	70-130	70-130	--	30	50
Nitrate/Nitrite	--	70-130	70-130	--	30	50
Oil and Grease	--	70-130	70-130	--	30	50
Sulfate	--	70-130	70-130	--	30	50
Sulfide	--	70-130	70-130	--	30	50
Hardness	--	70-130	70-130	--	30	50
Total Dissolved Solids (TDS)	--	70-130	70-130	--	30	50
TKN	--	70-130	70-130	--	30	50
Total Organic Carbon (TOC)	--	70-130	70-130	--	30	50

Notes:

1 The listed QC limits are based on SW-846 guidance and are advisory. The actual limits are determined based on laboratory performance. Frequent failure to meet the QC limits however, warrant investigation of the laboratory.

2. Analysis for groundwater pH, groundwater conductivity, and oxidation/reduction potential will be analyzed using field methods only.
3. LCS - Laboratory Control Sample
4. RPD - Relative Percent Deviation
5. MS - Matrix Spike
6. MSD - Matrix Spike Duplicate

Appendix A

Standard Operating Procedures: Chain of Custody, Packaging and Shipping

ARCADIS
Infrastructure, environment, buildings

Imagine the result

Chain-of-Custody, Handling, Packing and Shipping

Rev. #: 2

Rev Date: March 6, 2009

Approval Signatures

Prepared by: _____ Date: 3/6/09
Caron Koll

Reviewed by: _____ Date: 3/6/09
Jane Kennedy(Technical Expert)

I. Scope and Application

This Standard Operating Procedure (SOP) describes the chain-of-custody, handling, packing, and shipping procedures for the management of samples to decrease the potential for cross-contamination, tampering, mis-identification, and breakage, and to insure that samples are maintained in a controlled environment from the time of collection until receipt by the analytical laboratory.

II. Personnel Qualifications

ARCADIS field sampling personnel will have current health and safety training, including 40-hour HAZWOPER training, Department of Transportation (DOT) training, site supervisor training, and site-specific training, as needed. In addition, ARCADIS field sampling personnel will be versed in the relevant SOPs and possess the skills and experience necessary to successfully complete the desired field work.

III. Equipment List

The following list provides materials that may be required for each project. Project documents and sample collection requirements should be reviewed prior to initiating field operations:

- indelible ink pens (black or blue);
- polyethylene bags (resealable-type);
- clear packing tape, strapping tape, duct tape;
- chain of custody
- DOT shipping forms, as applicable
- custody seals or tape;
- appropriate sample containers and labels,;
- insulated coolers of adequate size for samples and sufficient ice to maintain 4°C during collection and transfer of samples;
- wet ice;
- cushioning and absorbent material (i.e., bubble wrap or bags);

- temperature blank
- sample return shipping papers and addresses; and
- field notebook.

IV. Cautions

Review project requirements and select appropriate supplies prior to field mobilization.

Insure that appropriate sample containers with applicable preservatives, coolers, and packing material have been supplied by the laboratory.

Understand the offsite transfer requirements for the facility at which samples are collected.

If overnight courier service is required schedule pick-up or know where the drop-off service center is located and the hours of operation. Prior to using air transportation, confirm air shipment is acceptable under DOT and International Air Transport Association (IATA) regulation

Schedule pick-up time for laboratory courier or know location of laboratory/service center and hours of operation.

Understand DOT and IATA shipping requirements and evaluate dangerous goods shipping regulations relative to the samples being collected (i.e. complete an ARCADIS shipping determination). Review the ARCADIS SOPs for shipping, packaging and labeling of dangerous goods. Potential samples requiring compliance with this DOT regulation include:

- Methanol preservation for Volatile Organic Compounds in soil samples
- Non-aqueous phase liquids (NAPL)

V. Health and Safety Considerations

Follow health and safety procedures outlined in the project/site Health and Safety Plan (HASP).

Use caution and appropriate cut resistant gloves when tightening lids to 40 mL vials. These vials can break while tightening and can lacerate hand. Amber vials (thinner glass) are more prone to breakage.

Some sample containers contain preservatives.

- The preservatives must be retained in the sample container and should in no instance be rinsed out.
- Preservatives may be corrosive and standard care should be exercised to reduce potential contact to personnel skin or clothing. Follow project safety procedures if spillage is observed.
- If sample container caps are broken discard the bottle. Do not use for sample collection.

VI. Procedure

Chain-of-Custody Procedures

1. Prior to collecting samples, complete the chain-of-custody record header information by filling in the project number, project name, and the name(s) of the sampling technician(s) and other relevant project information. Attachment 1 provides an example chain-o- custody record

2. Chain-of-custody information MUST be printed legibly using indelible ink (black or blue).

3. After sample collection, enter the individual sample information on the chain-of-custody:

    a. Sample Identification indicates the well number or soil location that the sample was collected from. Appropriate values for this field include well locations, grid points, or soil boring identification numbers (e.g., MW-3, X-20, SB-30). When the depth interval is included, the complete sample ID would be “SB-30 (0.5-1.0) where the depth interval is in feet. Please note it is very important that the use of hyphens in sample names and depth units (i.e., feet or inches) remain consistent for all samples entered on the chain-of-custody form. DO NOT use the apostrophe or quotes in the sample ID. Sample names may also use the abbreviations “FB,” “TB,” and “DUP” as prefixes or suffixes to indicate that the sample is a field blank, trip blank, or field duplicate, respectively. NOTE: The sample

nomenclature may be dictated by the project database and require unique identification for each sample collected for the project. Consult the project data management plan for additional information regarding sample identification.

b. List the date o sample collection. The date format to be followed should be mm/dd/yy (e.g., 03/07/09) or mm/dd/yyyy (e.g. 03/07/2009).

c. List the time that the sample was collected. The time value should be presented using military format. For example, 3:15 P.M. should be entered as 15:15.

d. The composite field should be checked if the sample is a composite over a period of time or from several different locations and mixed prior to placing in sample containers.

e. The “Grab”. field should be marked with an “X” if the sample was collected as an individual grab sample. (e.g. monitoring well sample or soil interval).

f. Any sample preservation should be noted.

g. The analytical parameters that the samples are being analyzed for should be written legibly on the diagonal lines. As much detail as possible should be presented to allow the analytical laboratory to properly analyze the samples. For example, polychlorinated biphenyl (PCB) analyses may be represented by entering “PCBs” or “Method 8082.” Multiple methods and/or analytical parameters may be combined for each column (e.g., PCBs/VOCs/SVOCs or 8082/8260/8270). These columns should also be used to present project-specific parameter lists (e.g., Appendix IX+3 target analyte list. Each sample that requires a particular parameter analysis will be identified by placing the number of containers in the appropriate analytical parameter column. For metals in particular, indicate which metals are required.

h. Number of containers for each method requested. This information may be included under the parameter or as a total for the sample based on the chain of custody form used.

i. Note which samples should be used for site specific matrix spikes.

j. Indicate any special project requirements.

k. Indicate turnaround time required.

l. Provide contact name and phone number in the event that problems are encountered when samples are received at the laboratory.

m. If available attach the Laboratory Task Order or Work Authorization forms

n. The remarks field should be used to communicate special analytical requirements to the laboratory. These requirements may be on a per sample basis such as “extract and hold sample until notified,” or may be used to inform the laboratory of special reporting requirements for the entire sample delivery group (SDG). Reporting requirements that should be specified in the remarks column include: 1) turnaround time; 2) contact and address where data reports should be sent; 3) name of laboratory project manager; and 4) type of sample preservation used.

o. The “Relinquished By” field should contain the signature of the sampling technician who relinquished custody of the samples to the shipping courier or the analytical laboratory.

p. The “Date” field following the signature block indicates the date the samples were relinquished. The date format should be mm/dd/yyyy (e.g., 03/07/2005).

q. The “Time” field following the signature block indicates the time that the samples were relinquished. The time value should be presented using military format. For example, 3:15 P.M. should be entered as 15:15.

r. The “Received By” section is signed by sample courier or laboratory representative who received the samples from the sampling technician or it is signed upon laboratory receipt from the overnight courier service.

3. Complete as many chain-of-custody forms as necessary to properly document the collection and transfer of the samples to the analytical laboratory.

4. Upon completing the chain-of-custody forms, forward two copies to the analytical laboratory and retain one copy for the field records.

5. If electronic chain-of-custody forms are utilized, sign the form and make 1 copy for ARCADIS internal records and forward the original with the samples to the laboratory.

Handling Procedures

1. After completing the sample collection procedures, record the following information in the field notebook with indelible ink:

   - project number and site name;
   - sample identification code and other sample identification information, if appropriate;
   - sampling method;
   - date;
   - name of sampler(s);
   - time;
   - location (project reference);
   - location of field duplicates and both sample identifications;
   - locations that field QC samples were collected including equipment blanks, field blanks and additional sample volume for matrix spikes; and
   - any comments.

2. Complete the sample label with the following information in indelible ink:

   - sample type (e.g., surface water);
   - sample identification code and other sample identification information, if applicable;
   - analysis required;
   - date;
   - time sampled; and
   - initials of sampling personnel;

- sample matrix; and
- preservative added, if applicable.

3. Cover the label with clear packing tape to secure the label onto the container and to protect the label from liquid.

4. Confirm that all caps on the sample containers are secure and tightly closed.

5. In some instances it may be necessary to wrap the sample container cap with clear packing tape to prevent it from becoming loose.

6. For some projects individual custody seals may be required. Custody seal evidence tape may be placed on the shipping container or they may be placed on each sample container such that the cooler or cap cannot be opened without breaking the custody seal. The custody seal should be initialed and dated prior to relinquishing the samples.

Packing Procedures

Following collection, samples must be placed on wet ice to initiate cooling to 4°C immediately. Retain samples on ice until ready to pack for shipment to the laboratory.

1. Secure the outside and inside of the drain plug at the bottom of the cooler being used for sample transport with "Duct" tape.

2. Place a new large heavy duty plastic garbage bag inside each cooler

3. Place each sample bottle wrapped in bubble wrap inside the garbage bag. VOC vials may be grouped by sample in individual resealable plastic bags). If a cooler temperature blank is supplied by the laboratory, it should be packaged following the same procedures as the samples. If the laboratory did not include a temperature blank, do not add one. Place 1 to 2 inches of cushioning material (i.e., vermiculite) at the bottom of the cooler.

4. Place the sealed sample containers upright in the cooler.

5. Package ice in large resealable plastic bags and place inside the large garbage bag in the cooler. Samples placed on ice will be cooled to and maintained at a temperature of approximately 4°C.

6. Fill the remaining space in the cooler with cushioning material such as bubble wrap. The cooler must be securely packed and cushioned in an upright position and be surrounded (Note: to comply with 49 CFR 173.4, filled cooler must not exceed 64 pounds).

7. Place the completed chain-of-custody record(s) in a large resealable bag and tape the bag to the inside of the cooler lid.

8. Close the lid of the cooler and fasten with packing tape.

9. Wrap strapping tape around both ends of the cooler.

10. Mark the cooler on the outside with the following information: shipping address, return address, “Fragile, Handle with Care” labels on the top and on one side, and arrows indicating “This Side Up” on two adjacent sides.

11. Place custody seal evidence tape over front right and back left of the cooler lid, initial and date, then cover with clear plastic tape.

Note: Procedure numbers 2, 3, 5, and 6 may be modified in cases where laboratories provide customized shipping coolers. These cooler types are designed so the sample bottles and ice packs fit snugly within preformed styrofoam cushioning and insulating packing material.

Shipping Procedures

1. All samples will be delivered by an express carrier within 48 hours of sample collection. Alternatively, samples may be delivered directly to the laboratory or laboratory service center or a laboratory courier may be used for sample pickup.

2. If parameters with short holding times are required (e.g., VOCs [EnCore™ Sampler], nitrate, nitrite, ortho-phosphate and BOD), sampling personnel will take precautions to ship or deliver samples to the laboratory so that the holding times will not be exceeded.

3. Samples must be maintained at 4°C+2°C until shipment and through receipt at the laboratory

4. All shipments must be in accordance with DOT regulations and ARCADIS dangerous goods shipping SOPs.

5. When the samples are received by the laboratory, laboratory personnel will complete the chain-of-custody by recording the date and time of receipt of samples, measuring and recording the internal temperature of the shipping container, and checking the sample identification numbers on the containers to ensure they correspond with the chain-of-custody forms.

Any deviations between the chain-of-custody and the sample containers, broken containers, or temperature excursions will be communicated to ARCADIS immediately by the laboratory.

VII. Waste Management

Not applicable

VIII. Data Recording and Management

Chain-of-custody records will be transmitted to the ARCADIS PM or designee at the end of each day unless otherwise directed by the ARCADIS PM. The sampling team leader retains copies of the chain-of-custody forms for filing in . the project file. Record retention shall be in accordance with project requirements.

IX. Quality Assurance

Chain-of-custody forms will be legibly completed in accordance with the applicable project documents such as Sampling and Analysis Plan (SAP), Quality Assurance Project Plan (QAPP), Work Plan, or other project guidance documents. A copy of the completed chain-of-custody form will be sent to the ARCADIS Project Manager or designee for review.

X. References

Not Applicable

Attachment 1

ARCADIS
Infrastructure, environment, facilities

ID#:

CHAIN OF CUSTODY & LABORATORY ANALYSIS REQUEST FORM

Page ___ of ___

Lab Work Order #

Send Results to:

Contact & Company Name: | Telephone:

Address: | Fax:

City | State | Zip | E-mail Address:

Project Name/Location (City, State): | Project #:

Sampler's Printed Name: | Sampler's Signature:

Sample ID	Collection Date	Collection Time	Type (✓) Comp	Type (✓) Grab	Matrix

Preservative													
Filtered (✓)													
# of Containers													
Container Information													

PARAMETER ANALYSIS & METHOD

Keys

Preservation Key:
A. H_2SO_4
B. HCL
C. HNO_3
D. NaOH
E. None
F. Other: _____
G. Other: _____
H. Other: _____

Container Information Key:
1. 40 ml Vial
2. 1 L Amber
3. 250 ml Plastic
4. 500 ml Plastic
5. Encore
6. 2 oz. Glass
7. 4 oz. Glass
8. 8 oz. Glass
9. Other: _____
10. Other: _____

Matrix Key:
SO - Soil | SE - Sediment | NL - NAPL/Oil
W - Water | SL - Sludge | SW - Sample Wipe
T - Tissue | A - Air | Other: _____

REMARKS

Special Instructions/Comments:

☐ Special QA/QC Instructions(✓):

Laboratory Information and Receipt		Relinquished By	Received By	Relinquished By	Laboratory Received By
Lab Name:	Cooler Custody Seal (✓)	Printed Name:	Printed Name:	Printed Name:	Printed Name:
☐ Cooler packed with ice (✓)	☐ Intact ☐ Not Intact	Signature:	Signature:	Signature:	Signature:
Specify Turnaround Requirements:	Sample Receipt:	Firm:	Firm/Courier:	Firm/Courier:	Firm:
Shipping Tracking #:	Condition/Cooler Temp: _____	Date/Time:	Date/Time:	Date/Time:	Date/Time:

20730826 CofC AR Form 01.12.2007

Distribution: **WHITE – Laboratory returns with results** **YELLOW – Lab copy** **PINK – Retained by BBL**

Appendix B

Standard Operating Procedures:
Field Log Book

ARCADIS
Infrastructure, environment, facilities

Imagine the result

Field Log Book Entries

Rev. #: 0

Rev Date: 11 August 2009

Approval Signatures

Prepared by: Andrew Kanik Date: 8/11/09

Reviewed by: Michael J. Hefferon Date: 8/11/09
(Technical Expert)

I. Scope and Application

This ARCADIS Standard Operating Procedure covers the entries needed in a field log book for environmental investigations.

This SOP does not address all of the entries that may be needed for a specific project, and does not address health and safety, equipment decontamination, field parameter measurements, sample preservation, chain-of-custody, or laboratory analysis. For direction on requirements in these areas, refer to other ARCADIS SOPs, the project work plans including the quality assurance project plan, sampling plan, and health and safety plan, as appropriate.

II. Personnel Qualifications

ARCADIS personnel participating in fieldwork and making entries into the field log book should have a minimum of one (1) year of field experience (or be under the supervision and accompanied in the field by someone who does) and current health and safety training including 40-hour HAZWOPER training, site supervisor training, site-specific training, first aid, and CPR, as needed. Field personnel will also be compliant with client-specific training requirements. In addition, ARCADIS field sampling personnel will be versed in the relevant SOPs and posses the required skills and experience necessary to successfully complete the desired field work.

III. Equipment List

- Field Log Book
- Ball point (medium point) pen with blue or black ink (black preferred). A fine point Sharpie pen may be used if the ink does not bleed through the page and become visible on back side of the page. If weather conditions prevent the use of a pen, indicate so in the log and use an alternate writing instrument .
- Zip-lock baggie or other weather-proof container to protect the field log book from the elements.

IV. Cautions

All entries in the field log must be legible and archivable. Do not leave the field log book exposed to the elements or other conditions that might moisten the pages and smear/dissolve the entries. When not in the field, the log book should be stored in a location that is easily accessible to field crews.

V. Health and Safety Considerations

ARCADIS field personnel will be familiar and compliant with Client-specific health and safety requirements.

VI. Procedure

- Print legibly. Do not use cursive writing.
- The name of the project, project number and project location should be written in indelible ink on the outside of the field log book.
- On the inside of the front cover, write "If Found, Please Return to ARCADIS" and include the appropriate address and phone number, the name of the person to which the book is assigned, and the name of the project manager.
- Reserve the first page of the book for a Table of Contents.
- Reserve the last five (5) pages of the book for important contacts, notes, reminders, etc.
- Each day of field work, the following should be recorded in the field log book as applicable:

    a) Project Name

    b) Date and time arrived

    c) Work Site Location

    d) Names of people on-site related to the project including ARCADIS employees, visitors, subcontractor employees, agency personnel, client representative, etc.

    e) Describe the work to be performed briefly, and list the equipment on-site

    f) Indicate the health and safety (H&S) level to be used

    g) Record instrument calibrations and checks

    h) Record time and general content of H&S briefing

    i) Describe the weather conditions, including temperature, precipitation, and wind speed and direction

    j) List periodic time entries in the far left hand column of each page

    k) Minimize unused space on each page

- The tailgate meeting must be recorded in the log book and the tailgate form completed. If H&S monitoring is performed, record the time and results of initial and followup monitoring.

- Note factual observations including collection of QA/QC samples, delays, well damage, accidents, work plan deviations, instrument problems, and problem resolutions.
- Describe work performed and how documented such as photographs, sample core logs, water sampling logs, etc.
- Describe bases for field decisions including pertinent conversations with visitors, regulators, or project personnel.
- Note final instrument calibrations and checks.
- Sign the log book at the end of each day at a minimum. Draw a line to the end of the page to indicate no further entries on that page. Sign the bottom of each page if possible.
- If an entry to the log book is changed, strike out the deleted text or item with a single line such that the entry remains legible, and initial and date the change. Such changes should only be made by the same person that made the initial entry.
- Field log book entries must be made in the field at the site, not at a later time at a different location. Supplemental entries to the log book may be made at a later date. The supplemental entry must be clearly identified as such and the entry must be signed and dated as described in this SOP.
- Problems noted in the field log book must be brought to the attention of the project manager and task manager in a timely fashion. Problems may be reported in person, on the telephone, or in a written daily log form. If daily logs are prepared and you will not be able to personally give the daily log to the project manager, send the daily log via FAX or overnight courier to the project manager and task manager.

VII. Waste Management

Investigation-derived waste will be managed as described in the Investigation-Derived Waste Handling and Storage SOP. A drum/waste inventory should be maintained on a pre-designated page in the field log book.

VIII. Data Recording and Management

Each page of the field log book should be scanned for electronic/digital archiving at periodic intervals. This will ensure that copies of the field notes are available in the event the field book is lost or damaged, and that field data can be easily disseminated to others without the risk of physically sending the field log book. Field log books that are full should be archived with the project files, and readily retrievable.

IX. Quality Assurance

Be mindful that the field log book may be produced in court. All entries should be legible (as discussed above). Entries should also be in English, unless working in a country where English is not the predominant language or you are directed otherwise by the project manager.

X. References

Not Applicable

Appendix C

Laboratory Standard Operating Procedures and Quality Assurance – Merit Laboratories (on CD)

ARCADIS

Appendix C

Laboratory Standard Operating Procedures and Quality Assurance

Trace Analytical Laboratories, Inc. and Pace Analytical Services, Inc.

1. VOCs
2. SVOCs
3. PCBs
4. Extractions for SVOCs
5. Extractions for PCBs
6. Metals
7. Metals Digestions for metals
8. Mercury (with digestions)
9. Anions (Chloride, Sulfate, NO2, NO3)
10. Hardness
11. Alkalinity
12. Ammonia
13. TDS
14. TOC
15. pH
16. Conductivity
17. Temperature
18. Turbidity/Oxydation Reduction Potential (ORP)
19. List of SOPs (Prepared By: Merit Laboratories, Inc.)

Location: QA Director's Office
SOP Files
Analyst's work bench Conventional Laboratory #103-7

1.0 SCOPE

1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.

1.2 The method is suitable for all concentration ranges; however, appropriate aliquots should be used to avoid a titration volume greater than 50-mL.

2.0 SUMMARY OF THE METHOD

2.1 This SOP is a procedure for evaluating Alkalinity in liquid samples.

3.0 INTERFERENCES

3.1 N/A

4.0 APPARATUS AND MATERIALS

4.1 Digital titrator

4.2 Stir plate

4.3 Clear plastic cups

5.0 REAGENTS

5.1 Deionized (DI) water

5.2 0.1600 sulfuric acid titration cartridge

5.3 Bromcresol Green-Methyl Red indicator pillow packets

5.4 25,000-mg/L alkalinity standard

6.0 SAMPLE HANDLING AND PRESERVATION

6.1 Alkalinity is best analyzed as soon as possible from the time the sample is collected. Maximum holding time for **water samples from the time of sampling is 14 days** refrigerated at $4^{o}C \pm 2^{o}C$

6.2 Samples should be provided in unpreserved, clear plastic bottles.

7.0 PROCEDURE [1], [2]

7.1 COLOR DEVELOPMENT AND MEASUREMENT (TOTAL)

7.1.1 Pour 100-mL of DI water in a clear plastic cup to make a Blank sample. Place a magnetic stirring bar in the cup and place the cup on a stir plate. Turn on stir place so that the sample is stirred well, but its color is still clearly visible.

7.1.2 Pour one powder pillow in the cup.

7.1.3 Using a digital titrator set up with a 0.1600 sulfuric acid titration cartridge, place its tip in the sample so that the acid may be released into the sample. Slowly turn the endpiece clockwise until the water just turns from its original green color to pink/purple.

7.1.4 The number of digits used to do this is the value for the Blank. This value will be subtracted from the digit values of all other samples.

7.1.5 Rinse off magnetic stir bar.

7.1.6 Place 5-mL of a sample in another cup and add 95-mL DI water to it. Repeat the same procedure to find the number of digits needed to titrate the sample. If this value is exceedingly small or large, the dilution of the sample may be adjusted.

7.2 CARBONATE AND BICARBONATE MEASUREMENT

7.2.1 Place 5-mL of sample in cup, add the contents of a Phenolpthalein Indicator Powder pillow and swirl to mix.

7.2.1.1 If there is no color change, dilute and titrate exactly like a Total Alkalinity sample.

---

[1] *Standard Methods*, twentieth edition, Method 2320B, Alkalinity.

[2] Hach Digital Titrator Model 16900-01 Manual. Alkalinity.

7.2.1.2 If there is a color change to pink, dilute and titrate to a colorless endpoint. Record the number of digits required as the Phenolpthalein Alkalinity. (Do not reset digit counter!) Continue titration same as Total Alkalinity, adding the contents Bromcresol Green-Methyl Red indicator pillow packet to the sample. Record the number of digits required.

8.0 CALCULATIONS

8.1 Total Alkalinity, $\frac{mg}{L}$ $CaCO_3$ = $\frac{D*100mL*M}{S}$

Where: D = number of digits used in titration of sample
M = multiplier number specified by concentration of cartridge (in this case, 0.1)
S = mL of sample used

8.2 Bicarbonate Alkalinity, $\frac{mg}{L}$ = Total Alkalinity ($\frac{mg}{L}$) – (2 * Phenolpthalein Alkalinity)

8.3 Carbonate Alkalinity, $\frac{mg}{L}$ = 2 * Phenolpthalein Alkalinity

9.0 QUALITY CONTROL

9.1 See Table 1

9.2 Samples are analyzed in batches of thirty or less per QC set. The QC samples that are analyzed per batch are:

- Standard Check
- MS
- LCS
- DUP
- MSD (optional)
- Method Blank

10.0 DOCUMENTATION

10.1 Bench book for digestion and analysis

10.2 Work sheets

11.0 METHOD PERFORMANCE

1.1 Precision and accuracy studies are performed on as needed basis. (Ex. new instrument, etc.)

1.2 Method Detection limit studies are performed annually.

Table 1. Quality Control Requirements (Sample Set = 20 samples)

QC Analysis	Required/ Frequency	Limits	Corrective Action	Corrective Action after Reanalyzing
Method (preparation) Blank	Yes One each set	<MDL or 1/10 Regulatory limit	Remove contamination and rerun	
Laboratory Control Sample (LCS) Soluble or insoluble	Yes One every 20 samples	85%-115%	Rerun	
Matrix Duplicate	Yes One each set	RPD<20%	Rerun entire set	
Matrix Spike	Yes One each set	85%-115%	Analyze by Method of Standard Additions	
Matrix Spike Duplicate	Yes One every 20 samples			
Dilution & Rerun	No except if result indicates suppressive interference	Does interference persist?	Yes. Rerun with Method of Standard Additions	

12.0 APPROVAL & ISSUE:

12.1 The following personnel have read, accepted and approved this standard operating practice.

_____

Analyst Date

_____

Andy Ball, QA Officer Date

_____

Maya V. Murshak, QA Director Date

Location: QA Director's Office
SOP Files
Analyst's work bench Conventional Laboratory #103-7

1.0 SCOPE

1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.

1.2 The method is suitable for all concentration ranges; however, appropriate aliquots should be used to avoid a titration volume greater than 50-mL.

2.0 SUMMARY OF THE METHOD

2.1 This SOP is a procedure for evaluating Alkalinity in liquid samples.

3.0 INTERFERENCES

3.1 N/A

4.0 APPARATUS AND MATERIALS

4.1 Digital titrator

4.2 Stir plate

4.3 Clear plastic cups

5.0 REAGENTS

5.1 Deionized (DI) water

5.2 0.1600 sulfuric acid titration cartridge

5.3 Bromcresol Green-Methyl Red indicator pillow packets

5.4 25,000-mg/L alkalinity standard

6.0 SAMPLE HANDLING AND PRESERVATION

6.1 Alkalinity is best analyzed as soon as possible from the time the sample is collected. Maximum holding time for **water samples from the time of sampling is 14 days** refrigerated at $4^{o}C \pm 2^{o}C$

6.2 Samples should be provided in unpreserved, clear plastic bottles.

7.0 PROCEDURE [1], [2]

7.1 COLOR DEVELOPMENT AND MEASUREMENT (TOTAL)

7.1.1 Pour 100-mL of DI water in a clear plastic cup to make a Blank sample. Place a magnetic stirring bar in the cup and place the cup on a stir plate. Turn on stir place so that the sample is stirred well, but its color is still clearly visible.

7.1.2 Pour one powder pillow in the cup.

7.1.3 Using a digital titrator set up with a 0.1600 sulfuric acid titration cartridge, place its tip in the sample so that the acid may be released into the sample. Slowly turn the endpiece clockwise until the water just turns from its original green color to pink/purple.

7.1.4 The number of digits used to do this is the value for the Blank. This value will be subtracted from the digit values of all other samples.

7.1.5 Rinse off magnetic stir bar.

7.1.6 Place 5-mL of a sample in another cup and add 95-mL DI water to it. Repeat the same procedure to find the number of digits needed to titrate the sample. If this value is exceedingly small or large, the dilution of the sample may be adjusted.

7.2 CARBONATE AND BICARBONATE MEASUREMENT

7.2.1 Place 5-mL of sample in cup, add the contents of a Phenolpthalein Indicator Powder pillow and swirl to mix.

7.2.1.1 If there is no color change, dilute and titrate exactly like a Total Alkalinity sample.

---

[1] *Standard Methods*, twentieth edition, Method 2320B, Alkalinity.

[2] Hach Digital Titrator Model 16900-01 Manual. Alkalinity.

7.2.1.2 If there is a color change to pink, dilute and titrate to a colorless endpoint. Record the number of digits required as the Phenolpthalein Alkalinity. (Do not reset digit counter!) Continue titration same as Total Alkalinity, adding the contents Bromcresol Green-Methyl Red indicator pillow packet to the sample. Record the number of digits required.

8.0 CALCULATIONS

8.1 Total Alkalinity, $\frac{mg}{L}$ $CaCO_3$ = $\frac{D*100mL*M}{S}$

Where: D = number of digits used in titration of sample
M = multiplier number specified by concentration of cartridge (in this case, 0.1)
S = mL of sample used

8.2 Bicarbonate Alkalinity, $\frac{mg}{L}$ = Total Alkalinity ($\frac{mg}{L}$) – (2 * Phenolpthalein Alkalinity)

8.3 Carbonate Alkalinity, $\frac{mg}{L}$ = 2 * Phenolpthalein Alkalinity

9.0 QUALITY CONTROL

9.1 See Table 1

9.2 Samples are analyzed in batches of thirty or less per QC set. The QC samples that are analyzed per batch are:

- Standard Check
- MS
- LCS
- DUP
- MSD (optional)
- Method Blank

10.0 DOCUMENTATION

10.1 Bench book for digestion and analysis

10.2 Work sheets

11.0 METHOD PERFORMANCE

1.1 Precision and accuracy studies are performed on as needed basis. (Ex. new instrument, etc.)

1.2 Method Detection limit studies are performed annually.

Table 1. Quality Control Requirements (Sample Set = 20 samples)

QC Analysis	Required/ Frequency	Limits	Corrective Action	Corrective Action after Reanalyzing
Method (preparation) Blank	Yes One each set	<MDL or 1/10 Regulatory limit	Remove contamination and rerun	
Laboratory Control Sample (LCS) Soluble or insoluble	Yes One every 20 samples	85%-115%	Rerun	
Matrix Duplicate	Yes One each set	RPD<20%	Rerun entire set	
Matrix Spike	Yes One each set	85%-115%	Analyze by Method of Standard Additions	
Matrix Spike Duplicate	Yes One every 20 samples			
Dilution & Rerun	No except if result indicates suppressive interference	Does interference persist?	Yes. Rerun with Method of Standard Additions	

12.0 APPROVAL & ISSUE:

12.1 The following personnel have read, accepted and approved this standard operating practice.

_____

Analyst Date

_____

Andy Ball, QA Officer Date

_____

Maya V. Murshak, QA Director Date

SOP #033503: NITROGEN, AMMONIA (NH_3)
POTENTIOMETRIC, ION SELECTIVE ELECTRODE

Revision: 7
Date: 05/12/10

Location: Analyst's Bench
QA Director's Office
SOP Files

1.0 SCOPE AND APPLICATION

1.1 This method is applicable to the measurement of ammonia-nitrogen in drinking, surface and saline waters, domestic and industrial wastes.

1.2 This method covers the range from 0.02 to 15 mg NH_3 -N/L. Color and turbidity has no effect on the measurements, thus, distillation may not be necessary.

Nitrogen CAS # N 7727-37-9
Ammonia, NH_3 CAS # 7664-41-7

2.0 SUMMARY OF METHOD

2.1 The ammonia is determined potentiometrically using an ion selective ammonia electrode and a pH meter having an expanded millivolt scale or a specific ion meter.

2.2 The ammonia electrode uses a hydrophobic gas-permeable membrane to separate the sample solution from an ammonium chloride internal solution. Ammonia in the sample diffuses through the membrane and alters the pH of the internal solution, which is sensed by a pH electrode. The constant level of chloride in the internal solution is sensed by a chloride selective ion electrode which acts as the reference electrode.

3.0 SAMPLE HANDLING AND PRESERVATION

3.1 Liquid samples must be collected in 250 mL polyethylene plastic bottle pre-preserved with 2 mL of concentrated H_2SO_4 and stored at 4±2°C. Soil samples are collected in glass jars without preservative and stored at 4±2°C. The holding time for water and soil ammonia samples is 28 days from sampling.

4.0 INTERFERENCES

4.1 Volatile amines act as a positive interference.

4.2 Mercury interferes by forming a strong complex with ammonia. Thus the samples cannot be preserved with mercuric chloride.

5.0 APPARATUS AND MATERIALS

5.1 Electrometer (pH meter) with expanded mV scale

5.2 Ammonia selective electrode, VWR Symphony 14002/794.

5.3 Magnetic stirrer, thermally insulated, and Teflon-Coated stirring bar.

5.4 Plastic cups

6.0 REAGENTS

6.1 Deionized water: Special precautions must be taken to insure that the deionized water is free of ammonia. This is accomplished by passing deionized water through an ion exchange column containing a strongly acidic cation exchange resin mixed with a strongly basic anion exchange resin.

6.2 Sodium hydroxide(NaOH), 10N: Dissolve 200 g of sodium hydroxide in 400 mL of deionized water. Cool and dilute to 500 mL with deionized water.

6.3 Environmental Resource Associates quality control nutrients standards

6.4 Ammonium chloride, standard: Hach solutions 1000mg/l, Cat.#23541-53

6.5 Concentrated Sulfuric Acid (H_2SO_4)

7.0 PROCEDURE

7.1 Samples need to be brought to room temperature before samples can be run.

7.2 Probe is rinsed with 100 mL deionized water containing 2 mL of NaOH at the beginning of the procedure and between samples.

7.3 Preparation of standards: Hach pre-prepared Standards

7.4 Calibration of electrometer: Place 100 mL of each standard solution in clean plastic cups. Immerse electrode into standard of lowest concentration and add 1mL of 10N sodium hydroxide solution while mixing. Keep electrode in the solution until a stable reading is obtained.

NOTE 1: *The pH of the solution after the addition of NaOH must be above 11. Caution: sodium hydroxide must not be added prior to electrode immersion, for ammonia may be lost from a basic solution.*

7.5 Repeat this procedure with the remaining standards, going from lowest to highest concentration. Plot the concentration of ammonia in mg NH_3-N/L on the log axis vs. the electrode potential developed in the standard on the linear axis, starting with the lowest concentration at the bottom of the scale.

7.6 Calibration of a specific ion meter: Follow the directions of the manufacturer for the operation of the instrument.

7.7 Sample measurement: Follow the procedure in Section 7.2 for 100 mL of sample in plastic cups. Record the stabilized potential of each unknown sample and convert the potential reading to the ammonia concentration using the standard curve.

7.8 Note: All samples analyzed under NELAC projects must be distilled prior to analysis. This includes QC samples.

8.0 QUALITY CONTROL

8.1 All set standards must include:

- 8.1.1 2 standards (1 ppm and 10 ppm) to establish a curve.
- 8.1.2 1 method blank (Deionized water)
- 8.1.3 Calibration Check (5ppm)
- 8.1.4 Laboratory Control Sample (LCS) (2.5 ppm) at a mid-point concentration
- 8.1.5 Known addition standard, ERA, from a different source than the calibration curve
- 8.1.6 Matrix Spike (MS) per 20 samples
- 8.1.7 Sample duplicate (DUP) per 20 samples
- 8.1.8 Extra standards to include concentrations of sample set (0.02ppm, 0.1 ppm, 10 – 15 ppm)

8.2 Table 1. Quality Control Requirements (Sample Set = 20 samples)

QC Analysis	Required/ Frequency	Limits	Corrective Action	Corrective Action after Reanalyzing
Method (preparation) Blank	Yes One each set	<MDL or 1/10 Regulatory limit	Remove contamination and rerun	Notify client. Flag data.
Laboratory Control Sample (LCS)	Yes One each set	90%-110%	Rerun	Notify client. Flag data.
Matrix Duplicate	Yes One each set	RPD<20%	Rerun	Notify client. Flag data.
Matrix Spike	Yes One each set	80%-120%	Rerun	Notify client. Flag data.
Dilution & Rerun	No, unless sample out of calib curve range	Is sample now in range?	Yes. Report.	Notify client. Flag data.

9.0 DATA ANALYSIS

9.1 Calculations:

$$HN3\text{-}N/L=(A)(B)$$

Where:

A = dilution factor
B = concentration of NH_3-N mg/l from curve

10.0 DOCUMENTATION

10.1 Ammonia Bench Sheet

- 10.1.1 Analyst
- 10.1.2 Method
- 10.1.3 Date Run
- 10.1.4 Detection Limit
- 10.1.5 ID
- 10.1.6 Merit #
- 10.1.7 Dilution
- 10.1.8 Concentration (mg/L)
- 10.1.9 % S
- 10.1.10 Mv
- 10.1.11 Result (mg/L)
- 10.1.12 Spike (mg/L)
- 10.1.13 % Recovery
- 10.1.14 Notes

11.0 METHOD PERFORMANCE

11.1 Method detection limit studies are performed annually.

12.0 REFERENCES

12.1 *Standard Methods*, twentieth edition, Method 4500NH_3D, Nitrogen (Ammonia).

13.0 SAFETY

13.1 Every Laboratory area has eyewash, emergency shower, and fire extinguisher. The metals lab also has dust masks available for use with dust samples.

13.2 The air system through out the laboratory area is on a 100% fresh air exchange system, this system exchanges 100% the air in the laboratory area with air from outside 6 times per hour and 30 times per hour when the emergency purge button is hit.

13.3 A reference file of material safety data sheets (MSDSs) is available to all personnel.

13.4 Specific attention be paid (but not limited) to

- 13.4.1 Concentrated sulfuric acid is toxic and damaging to skin and mucus membranes. If eye or skin contact occurs, flush with large volumes of water. Always wear safety glasses or a shield for eye protection when working with these reagents.
- 13.4.2 Sodium hydroxide is corrosive, causes burns to any area of contact, can slowly pick up moisture from air and react with carbon dioxide from air to form sodium carbonate, and in contact with acids and organic halogen compounds, especially trichloroethylene, sodium hydroxide may causes violent reactions.

14.0 WASTE DISPOSAL AND POLLUTION PREVENTION

14.1 All laboratory waste must be managed, stored, and disposed in accordance with all federal and state laws and regulations.

14.2 Additional information can be found in the Sample Disposal SOP and Merit's Waste Management Plan and Handbook.

14.3 Sample waste is made acidic by adding concentrated sulfuric acid, neutralized with baking soda, and then disposed of down the drain.

15.0 APPROVAL & ISSUE:

15.1 This section indicates which personnel have read, accepted and approved the SOP. All analysts involved with the SOP must acknowledge their comprehension of the SOP with a signature and a date.

_____

Analyst Date

_____

Andy Ball, QA Officer Date

_____

Maya V. Murshak, Technical Director Date

SOP #033000: ION CHROMATOGRAPHY FOR ANALYZING ANIONS (CHLORIDE, FLUORIDE, NITRATE, NITRITE, BROMIDE & SULFATE) USING THE DX-100 DIONEX ION CHROMATOGRAPH

Revision: 6
Date: 5/12/10

Location: QA Officer's Office
Wet Chemistry Laboratory

1.0 SCOPE

0.1 This method is applicable to drinking, surface, ground waters, treated mixed wastewater and some industrial process waters, such as boilerwater and cooling water as long as samples are filtered through a 0.5 micron filter. (Metrigard, Glass Fiber Filter, 47mm /GE Water & Process Technologies)

2.0 SUMMARY OF THE METHOD

2.1 This SOP is a procedure for evaluating Anions, (Chloride, Sulfate, Nitrate-N, Nitrite-N, Fluoride & Bromide) in liquid samples.

2.2 A water sample is injected into a stream of cabonate-bicarbonate eluent and passed through a series of ion exchangers. The anions of interest are separated on the basis of their relative affraction for a low capacity, strongly basic anion exchanger (guard & separator columns). The separated anions are directed onto a strongly acidic cation exchanger (suppressor). The anions are then converted to their highly conductive acid forms and the eluent is converted to weakly conductive carbonic acid. The separated anions are then measured by conductivity. They are identified on the basis of retention time as compared to standards. Quantitation is by measurement of peak area or peak height.

3.0 INTERFERENCES

3.1 Any substance that has a retention time coinciding with that of any anions to be determined will cause interferences. Some low-molecular-weight organic acids interfere with chloride and fluoride. High concentration of any one ion also interferes with the resolution of others. Sample dilution overcomes many interferences. To resolve uncertainties of identification use the method of known addition.

4.0 REAGENTS

4.1 Deionized (DI) water

4.2 Stock Eluent, sodium bicarbonate – sodium carbonate: Dissolve 1.908g Na2CO3 and 1.428g NaHCO3 in water and dilute to 100ml. Prepared every 2 monthsor when stock eluent bottle starts running low.

4.3 Working eluent: Pipet 10ml of stock eluent to a 1 L volumetric flask and dilute to volume. Made up fresh when eluent bottle runs low.

4.4 Control ERA

4.5 Standard Anion solutions:

- 4.5.1 Chloride (Hach Std) 1,000ppm. Cat # 183-49. Expiration listed on standard bottle.
- 4.5.2 Sulfate (Hach Std) 1,000ppm Cat # 21757-49. Expiration listed on standard bottle.
- 4.5.3 Fluoride (Hach Std) 100ppm Cat # 232-49. Expiration listed on standard bottle.
- 4.5.4 Nitrate-N (Hach Std) 100ppm Cat # 1947-49. Expiration listed on standard bottle.
- 4.5.5 Bromide (KBr) (Hach) 1,000ppm Cat # 11270-34 Dissolve: 0.1489g KBr in water and dilute to 100ml, *See stock solutions prep log*, Prepared fresh every 3 months. KBr shelf life is 5 years.
- 4.5.6 Nitrite-N (NaNO2) (Hach) 100ppm Cat # 2452-01 Disslove: 0.0498g NaNO2 in water and dilute to 100ml, *See stock solutions prep log.* Prepared fresh every 48 hours as need. NaNO2 shelf life is 5 years.

5.0 APPARATUS & MATERIALS

5.1 Ion Chromatograph (DX-100 Dionex)

5.2 Anion separator column, resolves Br-; Cl-; SO4; NO3-; NO2-; F- and PO4 (not run with this method)

5.3 Guard column, protects separator column.

5.4 Self-Regenerating suppressor, converts eluent and separated anions to their acid forms.

5.5 5ml polyvials with filtercaps
5.6 50ml centrifuge tubes with screw caps
5.7 Filtering apparatus & 0.5 micron filters (Metrigard, Glass Fiber Filter, 47mm /GE Water & Process Technologies)
5.8 Auto-pipettors (.05 – 1mL)

6.0 SAMPLE HANDLING AND PRESERVATION

6.1 Samples should be collected in unpreserved high-density polyethylene containers. All bottles purchased by Merit are pre-cleaned certified.
6.2 Analyze samples needing Nitrite and/or Nitrate as soon as possible, not exceeding 48 hours. Maximum holding time for water samples from the time of sampling is 28 days for Chloride, Sulfate, Fluoride, & Bromide. Sample must be refrigerated at 4±2 degrees C.

7.0 PROCEDURE

7.1 System Startup and Test

7.1.1 Turn the system power on and set the *Control* button on the system Panel to Relay. Make sure computer, printer and autosampler are also on.
7.1.2 Confirm system air is working and pressure is between 50 and 60 psi.
7.1.3 Comfirm that the eluent container is at least half full before a run. If not, make up working eluent: Add new working eluent by the following
7.1.3.1 Turn eluent pressure switch to off (should be set at 5psi).
7.1.3.2 Take cap off eluent container and slowly add working eluent, replace cap and swirl to mix.
7.1.3.3 Re-pressurize eluent container by turning eluent switch to on.
7.1.3.4 Open valve below Pulse Damper and alow to bleed for 1 minute.
7.1.4 Ensure pump flow rate adjustment is correct (180 = 1.8ml/min).
7.1.5 Make sure detector range is set to operating range 30 uS.
7.1.6 Check waste container, if close to full empty before startup.
7.1.7 Open Run program. Click on Load / Method / norm.met. Instrument will begin startup. After approximately 20 seconds, open up valve below pulse damper again to rid any air and to reprime pump. Close valve again before system pressure drops to zero (around 8 seconds).
7.1.8 Let system equilibrate for at least 45 minutes before running samples (Conductivity reading should be between 15 and 17).
7.1.9 Set Low Limit pressure switch to on.

7.2 Running the Analysis

7.2.1 All samples must be filtered through 0.5 micron filters prior to being analyzed.
7.2.2 All Anion runs begin with a Blank, Blank Spike, ERA Control and LCS.
7.2.3 Fill polyvial with 5ml of sample to be tested.
7.2.4 Place filtercap on polyvial and push to top of vial with filtercap tool.
7.2.5 The sample can now be placed in autosampler tray.
7.2.6 Open schedule program; Double-click to setup IC run.
7.2.7 Type in sample ID under **Sample Name**; Norm.met under **Method**; the date of run under **Data File**, ex.(090501); & dilution factor under **Dil**.
7.2.8 Click on **File; Save As** (type in date); click **ok.**
7.2.9 Go to Run program, click on **Load**; **Schedule,** scroll through to find schedule just set and click **ok.**
7.2.10 Push **Run** button on autosampler the 1st tray will then load.
7.2.11 Push green **Run** button on Computer Interface. The scheduled run will now begin.

7.3 Calibration

7.3.1 Inject calibration standards containing a mixture of all anions and determine approximate retention times. Approximate times: Fluoride (0.97min), Chloride

(1.53min), Nitrite-N (1.85min), Bromide (2.87min), Nitrate-N (3.30min), and Sulfate (6.80min). This is always the order of retention.

7.3.2 Next, prepare 5 different calibration standards for each anion all in one mixture, (See Section 5.4).

7.3.3 Run these 5 calibration standards with a blank proceeding the run, following the procedure in 7.2.2 through 7.2.10

7.3.4 A calibration coefficient of 0.999 or greater is necessary for working calibration curve. If less than 0.999, then rerun.

7.3.5 A calibration curve can now be plotted in the **Cal Plot / Norm.Meth** program. Open the Cal Plot program by double clicking on icon, click on **File**, double-click on **norm.meth,** click on **Edit,** click on **component table**.

7.3.6 From the component table each anions calibration curve can now be plotted by entering the peak height and area against the concentration.

7.3.7 Recalibration must be done when changing columns, changing any detector settings, when retention times begin to shift, when QC samples begin to fall outside the methods limits, or every 6 months.

8.0 CALCULATIONS

7.1 Equation $C = H \times F \times D$

where:

C = mg anion / L
H = peak area,
F = response factor = concentration of standard / area of standard, and
D = dilution factor for those samples requiring dilution.

Note: This calculation is automatically performed by software when sample is run, so the result on chromatograph for each anion is final result as long as dilution factor was entered before run.

9.0 QUALITY CONTROL

9.1 See Table 1

9.2 A sample batch will consist of 20 samples unless noted below. The QC samples that are analyzed per batch are:

- Method Blank
- Blank Spike
- Control (ERA or another outside known)
- LCS (every 10 samples for drinking water matrix)
- Matrix Spike (every 10 samples for drinking water matrix)
- Matrix Spike Dup (every 10 samples for Level 3)
- Matrix Duplicate (every 10 samples for drinking water matrix)

Table 1. Quality Control Requirements (Sample Set = 20 samples)

QC Analysis	Required/ Frequency	Limits	Corrective Action	Corrective Action after Reanalyzing
Method (preparation) Blank	Yes One each set	<MDL or 1/10 Regulatory limit	Remove contamination and rerun	Notify client. Flag data.
Laboratory Control Sample (LCS) Soluble or insoluble	Yes Every 10 drinking Water / One every sample set	90%-110%	Rerun	Notify client. Flag data.
Matrix Duplicate	Yes Every 10 drinking Water / One every sample set	RPD<15%	Rerun entire set	Notify client. Flag data.
Matrix Spike	Yes Every 10 drinking Water / One every sample set	80%-120%	Analyze by Method of Standard Additions	Notify client. Flag data.
Matrix Spike Duplicate	Level 3 One every 10 samples			Notify client. Flag data.
Dilution & Rerun	No except if result indicates suppressive interference	Does interference persist?	Yes. Rerun with Method of Standard Additions	Notify client. Flag data.

10.0 DOCUMENTATION

10.1 Ion Chromatograph raw data

10.2 Ion Chromatograph schedule log

11.0 METHOD PERFORMANCE

11.1 Precision and accuracy studies are performed on as needed basis.

11.2 Method Detection Limit studies are performed every 6 months.

12.0 SAFETY

12.1 Every Laboratory area has eyewash, emergency shower, and fire extinguisher. The metals lab also has dust masks available for use with dust samples.

12.2 The air system through out the laboratory area is on a 100% fresh air exchange system, this system exchanges 100% the air in the laboratory area with air from outside 6 times per hour and 30 times per hour when the emergency purge button is hit.

12.3 A reference file of material safety data sheets (MSDSs) is available to all personnel.

13.0 WASTE DISPOSAL AND POLLUTION PREVENTION

13.1 All laboratory waste must be managed, stored, and disposed in accordance with all federal and state laws and regulations.

13.2 Additional information can be found in the Sample Disposal SOP and Merit's Waste Management Plan and Handbook.

14.0 REFFERENCES

14.1 Method 300.0, Revision 2.2, 1999

15.0 APPROVAL & ISSUE:

15.1 The following personnel have read, accepted and approved this standard operating practice.

_____

Analyst Date

_____

Andy Ball, QA Officer Date

_____

Maya Murshak, Technical Director Date

Location: QA Officer's Office
SOP Files
Wet Chemistry Laboratory

1.0 SCOPE

1.1 This SOP is applicable to drinking, surface, and saline water, domestic and industrial wastes, and acid rain (atmospheric deposition). Conductivity is run by EPA Method 120.1.

2.0 SUMMARY OF THE METHOD

2.1 This SOP is a procedure for evaluating Conductivity in liquid samples.
2.2 The specific conductance of a sample is measured by use of a self-contained conductivity meter.
2.3 Samples are preferably analyzed at 25°C.
2.4 Field measurements with comparable instruments are reliable.

3.0 INTERFERENCES

3.1 N/A

4.0 APPARATUS AND MATERIALS

4.1 Hach Conductivity/TDS Meter
4.2 1 L Volumetric flask
4.3 Plastic 50 mL Centrifuge tubes
4.4 Clean plastic cup
4.5 Pipette
4.6 Graduated Cylinder
4.7 Analytical Balance, 0.03 g – 100 g capacity

5.0 REAGENTS

5.1 Deionized (DI) water
5.2 Sodium Chloride (NaCl)
5.3 ERA Standard (2nd Source), see Certified Reference Material for preparation and concentration

6.0 SAMPLE HANDLING AND PRESERVATION

6.1 Conductivity is best analyzed as soon as possible from the time the sample is collected. Maximum holding time for water samples is 14 days when refrigerated at $4^{o}C \pm 2^{o}C$.
6.2 Samples must be provided in unpreserved, clear plastic bottles.
6.3 Analyses can be preformed either in the field or laboratory.

7.0 PROCEDURE

7.1 PREPARATION OF STANDARD SOLUTIONS, PREPARED FRESH EVERY 2 MONTHS

7.1.1 For a 180-µmhos/cm standard, dissolve 0.0214 g NaCl in 250 mL of DI water. The 180-µmhos/cm standard is used for blank spike.
7.1.2 For a 1,990-µmhos/cm standard, dissolve 0.25 g NaCl in 250 mL of DI water. The 1,990-µmhos/cm standard is used for Laboratory Control Sample (LCS).

7.2 MEASUREMENT

7.2.1 Turn on meter and place probe in a plastic cup filled with DI water.
7.2.2 For a blank, pour 10 mL DI water in a centrifuge tube.
7.2.3 Rinse off probe then place in tube. Make sure to eliminate all air bubbles around the tube. Press the 2 key for the most sensitive reading possible.
7.2.4 Place probe back in cup containing clean DI water.
7.2.5 Pour 10 mL of Blank Spike into centrifuge tube and read conductivity by following Section 7.2.3. Rinse off probe between each sample.
7.2.6 Pour 10 mL of LCS into centrifuge tube and read conductivity by following Section 7.2.3. Rinse off probe between each sample.
7.2.7 Pour 10 mL of Control, ERA standard, into centrifuge tube and read conductivity by following Section 7.2.3. Rinse off probe between each sample.
7.2.8 Pour 10 mL sample in another tube. Rinse off probe and place in this tube just as before. Adjust settings if the meter is reading too sensitively by pressing the 20 key.

If the meter still reads a value too high, press the 200 key. The meter gives values in µmhos/cm.

8.0 QUALITY CONTROL

8.1 See Table 1

8.2 Samples are analyzed in batches of twenty (20) or less per QC set. The QC samples that are analyzed per batch are:

- Control
- LCS
- Duplicate
- Method Blank
- Blank Spike

9.0 DOCUMENTATION

9.1 Conductivity Bench sheet

9.1.1 Analyst
9.1.2 Date Run
9.1.3 Method #
9.1.4 Detection Limit
9.1.5 Program #
9.1.6 Wavelength
9.1.7 Merit #
9.1.8 Dilution
9.1.9 Umhos/cm
9.1.10 ABS
9.1.11 %S
9.1.12 Result (umhos/cm)
9.1.13 Spike (umhos/cm)
9.1.14 % Recovery
9.1.15 Lot/ Source
9.1.16 Run Time

10.0METHOD PERFORMANCE

10.1 Precision and accuracy studies are performed on as needed basis. (Ex. new instrument, etc.)

Table 1. Quality Control Requirements (Sample Set = 20 samples)

QC Analysis	**Required/ Frequency**	**Limits**	**Corrective Action**	**Corrective Action after Reanalyzing**
Method (preparation) Blank	Yes One each set	1/10 Regulatory limit	Remove contamination and rerun	Notify client. Flag data.
Blank Spike	Yes One every 10 samples	90%-110%	Rerun	Notify client. Flag data.
Control	Yes One every 10 samples	90%-110%	Rerun	Notify client. Flag data.
Laboratory Control Sample (LCS)	Yes One each set	90%-110%	Rerun	Notify client. Flag data.
Matrix Duplicate	Yes One each set	RPD<20%	Rerun entire set	Notify client. Flag data.

11.0 REFERENCES

11.1 EPA Water NPDES, Method 120.1, EPA Test Methods, Revision 1982, Conductance (Specific Conductance, µmhos at 25°C).

12.0 SAFETY

12.1 Every Laboratory area has eyewash, emergency shower, and fire extinguisher. The metals lab also has dust masks available for use with dust samples.

12.2 The air system through out the laboratory area is on a 100% fresh air exchange system, this system exchanges 100% the air in the laboratory area with air from outside 6 times per hour and 30 times per hour when the emergency purge button is hit.

12.3 A reference file of material safety data sheets (MSDSs) is available to all personnel.

13.0 WASTE DISPOSAL AND POLLUTION PREVENTION

13.1 All laboratory waste must be managed, stored, and disposed in accordance with all federal and state laws and regulations.

13.2 Additional information can be found in the Sample Disposal SOP and Merit's Waste Management Plan and Handbook.

14.0 APPROVAL & ISSUE:

14.1 This section indicates which personnel have read, accepted and approved the SOP. All analysts involved with the SOP should acknowledge their comprehension of the SOP with a signature and a date.

_____

Analyst Date

_____

Andy Ball, QA Officer Date

_____

Maya V. Murshak, Technical Director Date

MICROWAVE ASSISTED ACID DIGESTION OF SOLID SAMPLES

Location:
SOP Files
Metals Laboratory

1.0 SCOPE AND APPLICATION

1.1 This digestion procedure is used for the preparation of soils and solid samples for analysis, by inductively coupled plasma mass spectrometry (ICP-MS). The procedure is a hot acid leach for determining available metals. The method referenced within this SOP is the EPA SW-846 Method 3050B. This SOP is for use on all samples that do not require Ohio VAP certification.

1.2 This method is not a total digestion technique for most samples. The method is a very strong acid digestion that will dissolve almost all elements that could become environmentally available. By design, elements bound in silicate structures are not normally dissolved by this procedure, as they are not usually mobile in the environment.

1.3 Samples prepared by using nitric acid digestion are analyzed by ICP-MS for the following metals:

Metal (Symbol)	CAS#:
Aluminum (Al)	7429-90-5
Antimony (Sb)	7440-36-0
Arsenic (As)	7440-38-2
Barium (Ba)	7440-39-3
Beryllium (Be)	7440-41-7
Boron (B)	7440-42-8
Cadmium (Cd)	7440-43-9
Calcium (Ca)	7440-70-2
Chromium (Cr)	7440-47-3
Cobalt (Co)	7440-48-4
Copper (Cu)	7440-50-8
Iron (Fe)	7439-89-6
Lead (Pb)	7439-92-1
Lithium (Li)	7439-93-2
Magnesium (Mg)	7439-95-4
Manganese (Mn)	7439-96-5
Molybdenum (Mo)	7439-95-4
Nickel (Ni)	7440-02-0
Potassium (K)	7440-09-7
Selenium (Se)	7782-49-2
Silver (Ag)	7440-22-4
Sodium (Na)	7440-23-5
Strontium (Sr)	7440-24-6
Thallium (Th)	7440-28-0
Titanium (Ti)	7440-32-6
Vanadium (V)	7440-62-2
Zinc (Zn)	7440-66-6

2.0 SUMMARY OF METHOD

2.1 For the digestion of samples, a representative 0.05-2.0 gram (wet weight) sample is digested with nitric acid (HNO_3) using microwave heating. The resultant digestate is diluted to a final volume of 50 ml. After the digestion process, the sample is cooled, and then filtered, centrifuged, or allowed to settle prior to analysis.

2.2 If required, a separate sample aliquot is reserved for the determination of percent total solids.

3.0 INTERFERENCES

3.1 Addition of nitric acid to samples that contain organics could result in a violent reaction and splattering (loss) of the sample, leading to loss of analytes and/or sample, which must be avoided. Sludge samples can contain diverse matrix types, each of which can present its own analytical challenge. Spiked samples and any relevant standard reference material must be processed in accordance with the quality control requirements given in Sec. 8.0.

4.0 APPARATUS AND MATERIALS

4.1 Microwave Digestion System CEM–Model MDS-81D and MARSX Model # 907600

4.1.1 The MDS-81D consists of a microwave drying system with an operator selectable power output of 0-600 watts in 1% increments, a microwave cavity with a variable speed exhaust fan, a programmable microprocessor based digital computer, Teflon® coated cavity, exhaust tubing and standard screen rotating turntable, rotated at 6 rpm to ensure uniform microwave heating

4.1.2 The MARSX consists of a microwave drying system with an operator selectable power output of 0 – 1200 watts, a microwave cavity with a variable speed exhaust fan, a programmable microprocessor based digital computer, Teflon® coated cavity, exhaust tubing and standard rotating turntable, and self calibration features.

4.1.3 Microwave Digestion System Specifications:

MDS-81D		MARSX	
Power	600 Watts	Power	1200 Watts
Pressure	0 - 200 psi	Pressure	0 - 200 psi
Temperature	0 - 200°C	Temperature	0 - 200°C
Capacity	26 samples	Capacity	50 samples

4.2 Glass Fiber Filter paper, 0.45 µm.
4.3 Membrane Filter paper, 0.45 µm.
4.4 Analytical balances, 510 g capacity, minimum accuracy ± 0.001 g, and 250g capacity, minimum accuracy ±0.0001g.
4.5 Filter funnel, glass, or disposable polypropylene.
4.6 Digital bottle top dispenser capable of dispensing volumes of 0-5 ml in 0.02 ml increments.
4.7 Disposable Polypropylene vessels, 50 ml, compatible with centrifuge.
4.8 Plastic containers to support minimum of 200 ml.
4.9 Disposable tongue depressors for sample handling.
4.10 Disposable Pasteur pipettes.
4.11 Eppendorf automatic pipette with disposable combitips ranging from 2.50 ml to 50 ml capable of pipetting volumes ranging from 50 µl to 5,000 µl.
4.12 Centrifuge (IEC Centra GP8)

5.0 REAGENTS

5.1 Trace metal grade chemicals are used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, if applicable.

5.2 Deionized (DI) Water (Type I) is used which meets the specifications of the ASTM standard criteria.

5.3 Concentrated nitric acid, HNO_3, Trace Metal Grade. Acid purity is monitored by analysis of the laboratory reagent blank (LRB).

5.4 Standards added to digestion:

5.4.1 Spiking Solutions:

5.4.1.1 Multi-element standard solution **WS**, containing 10 µg/ml each of Al, Sb, As, Ba, Be, B, Cd, Cr, Co, Cu, Fe, Pb, Li, Mo, Mn, Ni, Se, Ag, Tl, Ti, V, and Zn. From this solution, 0.50 ml is added to the QC samples (*i.e.* MS/MSD samples), and 0.25 ml to the laboratory control sample (LCS), using the Eppendorf automatic pipette.

5.4.1.2 Multi-element standard solution **HM** (see Appendix 1), containing 100 µg/ml each of Ca, K, Mg, and Na. From this solution, 1.0 ml is added to the QC samples (*i.e.* MS/MSD samples), and 0.50 ml to the laboratory control sample (LCS), using the Eppendorf automatic pipette or by weighing the amounts (1.0 g or 0.50 g) on the scale.

5.4.2 Internal Standards (after digestion):

5.4.2.1 Lithium 6, 1000 µg/ml stock solution.
5.4.2.2 Scandium, 1000 µg/ml stock solution.
5.4.2.3 Yttrium, 1000 µg/ml stock solution.
5.4.2.4 Rhodium, 1000 µg/ml stock solution.
5.4.2.5 Rhenium, 1000 µg/ml stock solution.

NOTE: The manufacturer provides the stock solutions with a certificate of analyses and MSDS sheets.

5.4.2.6 Internal Standard working solution (**IS-WS**): From the above stock solution, 2.5 g of each is transferred to a 1000 ml plastic bottle, along with 10 ml of concentrated HNO_3 and brought to a final volume of 1000 ml (by weight). The concentration in the flask will be 2.5 µg/ml. This represents the internal standards working solution from which 1 ml will be added to all samples (*i.e.* samples, QC samples, blanks, etc.) prior to the analysis by the ICP/MS.

5.4.3 Spiking Solutions:

5.4.3.1 Spiking solutions are prepared according to the Standard Prep Log. The formula, date source solutions, lot numbers, expiration date of stock standards, expiration date standard made, expiration and unique ID of any working standards used.
5.4.3.2 All standards are NIST traceable.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Soil samples are collected without preservation, usually in glass containers with Teflon lined caps. Non-aqueous samples must be refrigerated at 4±2 degrees Celsius.

6.2 Holding times for metals are 6 months from the date of sampling, with the exception of Mercury which is not covered in this SOP.

7.0 PROCEDURE[1]

7.1 Calibration of Microwave Equipment.

7.1.1 Microwaves are calibrated once a year according to the manufacturer's instructions

7.2 All digestion vessels are disposable and are used only once. This allows for better sample control and prevents cross contamination.

[1] "Microwave digestion for metals", EPA SW 846 Method 3050B, Update III, 1998 for calibration of the microwave and Method 3051 for the digestion of solid samples.

7.3 Sample Digestion[2]

CAUTION: -Toxic nitrogen oxide fumes may be evolved, therefore all work must be performed in a properly operating ventilation system.
- Loss of sample through splattering inside the microwave system needs to be avoided. Physical observation is sufficient to determine if this is the case, therefore the batch of samples needs to be inspected at the end of the digestion cycle. If splattering has occurred, the samples are to be discarded, and a new batch is to be prepared.

7.3.1 Mix the sample thoroughly to achieve homogeneity. Transfer 0.2 to 0.3 grams sample (wet weight) for a soil matrix or 0.05 to 2 grams sample (wet weight) for liquidy sludges and other various solid matrices to a digestion vessel, and record the weight on the preparation sheet, to a minimum of 0.001 g. Ten milliliters DI water is used for LCS and LRB.

7.3.2 Add 1 ml of concentrated HNO_3 to each sample vessel, mixing the slurry, then wait 5-10 minutes for any reaction to occur.

7.3.3 After the acid has had some time to react add 10ml DI water.

7.3.4 With every batch of samples, pipette 1 ml of concentrated HNO_3 into a vessel labeled Laboratory Reagent Blank (LRB), which is carried through the entire digestion procedure, similar to an analytical sample. For every 20, samples pipette 1 ml of concentrated HNO_3 into a vessel labeled Laboratory Control Sample (LCS), which is carried through the entire digestion procedure, similar to an analytical sample. For every 20 samples measured, as described at 7.3.1 and 7.3.2, a sample is designated for analysis as a Matrix Spike (MS) and Matrix Spike Duplicate (MSD) or Duplicate (Dp).

7.3.5 For all metals, except Ca, Mg, K, and Na, add 0.50 ml of the QC spiking solution to the LCS, and 1.0 ml to the MS/MSD samples. For Ca, Mg, K and Na, add 1.0 ml of the **HM** solution to the LCS, and 1.0 ml to the MS/MSD samples. The spike concentration and the Lot # of the stock solution used is recorded in the digestion log. The spike solution for MS/MSD is added before digestion. For samples prepared for use with method 6020or 6020A a post-digestion spike is employed if the regular spike fails to meet the QC criteria.

7.3.6 Samples are slowly ramped in the microwave to 95±4 degrees Celsius over the course of a few minutes and maintained at this temperature for 5 minutes without boiling.

7.3.7 Allow samples to set for 5 minutes then repeat step 7.3.6.

7.3.8 After the temperature program is completed, leave the vessels 5-10 minutes in the microwave, to cool down, and then move them into the hood. Add 1 ml of the Internal Standard working solution using an Eppendorf automatic pipettor and dilute to the 50 ml mark with DI Water, into a calibrated (per lot) digestion vessel.

7.3.9 A post-digestion spike is performed as necessary and prepared as follows: take a 25 ml aliquot of the sample designated for MS/MSD and add to it 0.50 ml of the QC spiking solution (for all elements except Ca, Mg, K, and Na). For Ca, Mg, K, and Na add 1.0 ml of the **HM** solution.

7.3.10 If the digested sample contains particulate matter, which may clog the nebulizer, the sample may be centrifuged, allowed to settle over night, or filtered.

7.3.10.1 Centrifugation: Centrifugation at 4500 rpm for 3 minutes is usually sufficient to clear the supernatant.

7.3.10.2 Settling: Allow the sample to stand until the supernatant is clear. Allowing a sample to stand overnight will usually accomplish this. If it does not, centrifuge or filter the sample.

7.3.10.3 Filtering: The filtering apparatus (flask and funnel) must be thoroughly rinsed with a 10% v/v nitric acid solution and copious amounts of DI Water. Filter the sample through a 0.45 µm filter paper and transfer the liquid to a new vessel. Glass fiber filters are acceptable for all metals except Zn and Ba, for which membrane filters are required, due to the presence of these elements in the glass fiber filters.

7.3.11 Calculate the dilution factor(DF) by the formula:

$$DF = \frac{Final\ Volume\ (50)}{Sample\ amount} x \frac{100}{\%\ Total\ solids}$$

7.3.12 This is recorded in the sample preparation log and is used in the determination of the final result by the ICP/MS.

8.0 QUALITY CONTROL

8.1 For each analytical batch of 20 samples processed, one laboratory reagent blank (LRB) must be carried throughout the entire sample preparation and analytical process. The LRB will be used in determining if the samples are being contaminated during preparation or from reagents.

8.2 For each analytical batch of 20 samples processed, one laboratory control sample (LCS) must be carried throughout the entire sample preparation and analytical process. The LCS will be used in determining the performance of the method for that particular batch.

8.3 Spiked samples (MS) must be employed to determine accuracy. A spiked sample must be included with each batch of 20 samples processed.

8.4 Duplicate (Dp) samples or Matrix Spike Duplicate (MSD) must be processed for every 20 samples or less.

9.0 WASTE DISPOSAL

9.1 Samples

9.1.1 All digested samples are neutralized with baking soda and diluted before being disposed of with the normal laboratory waste water.

9.1.2 As a "small generator" of metals, Merit Laboratories has been approved for this type of disposal from the local government.

9.2 Acid bottles

9.2.1 Acid bottles are rinsed out and neutralized with baking soda before being disposed of with the normal laboratory waste.

10.0 DOCUMENTATION

9.1 Metals digestion log sheet must contain the following information:

- Date.
- Analyst initials.
- Method reference.
- Sample #.
- Sample weight or volume.
- MS/MSD/LCS spike concentration.
- Total solids (if applicable)

- Acid Lot #
- Spike Lot #
- Dilution Factor
- Prep batch
- Final volume of sample

11.0 METHOD PERFORMANCE

11.1 The precision and accuracy of the method will depend upon the overall performance of the sample preparation and analysis.

12.0 REFERENCES

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12.3 Tan, S.H., and Horlick, G., Appl. Spectrosc. 40, 445 (1986).
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12.6 Hinners, T.A., Heithmar, E., Rissmann, E., and Smith, D., Winter Conference on Plasma Spectrochemistry, Abstract THP18; p. 237, San Diego, CA (1994).
12.7 Lichte, F.E., et al., Anal. Chem. 59, 1150 (1987).
12.8 Evans E.H., and Ebdon, L., J. Anal. At. Spectrom. 4, 299 (1989).
12.9 Beauchemin, D., et al., Spectrochim. Acta 42B, 467 (1987).
12.10 Houk, R.S., Anal. Chem. 58, 97A (1986).
12.11 Thompson, J.J., and Houk, R.S., Appl. Spectrosc. 41, 801 (1987).
12.12 SW-846, Method 6020 Revision 0, 1994.
12.13 Method 200.8, Revision 5.4, 1998.
12.14 SW-846, Method 6020A Revision 1, 2007
12.15 SW-846, Method 8000C Revision 3, 2003
12.16 SW-846, Method 3050B Revision 2, 1996
12.17 1985 Annual Book of ASTM Standards, Vol.11.01; “Standard Specification for Reagent Water”
12.18

13.0 SAFETY

13.1 Every Laboratory area has eyewash, emergency shower, and fire extinguisher. The metals lab also has dust masks available for use with dust samples.

13.2 The air system through out the laboratory area is on a 100% fresh air exchange system, this system exchanges 100% the air in the laboratory area with air from outside 4 times per hour and 6 times per hour when the emergency purge button is hit.

13.3 A reference file of material safety data sheets (MSDSs) is available to all personnel.

13.4 Specific attention be paid (but not limited) to

13.4.1 Nitric acid is a corrosive, not combustible, but substance is a strong oxidizer and its heat of reaction with reducing agents or combustibles may cause ignition, and can react with metals to release flammable hydrogen gas.

13.4.2 Many metal salts are extremely toxic if inhaled or swallowed. Extreme care must be taken to ensure that samples and standards are handled properly and that all exhaust gases are properly vented. Wash hands thoroughly after handling.

13.4.3 The acidification of samples containing reactive materials may result in the release of toxic gases, such as cyanides or sulfides. For this reason, the acidification and digestion of samples should be performed in an approved fume hood.

14.0 APPROVAL & ISSUE:

14.1 This section indicates which personnel have read, accepted and approved the SOP. All analysts involved with the SOP must acknowledge their comprehension of the SOP with a signature and a date.

_____

Analyst Date

_____

Andy Ball, QA Officer Date

_____

Maya V. Murshak, Technical Director Date

Location: SOP Files
QA Officer's Office
Wet Chemistry Laboratory

1.0 SCOPE

1.1 This SOP is applicable to drinking, surface, and saline water, domestic and industrial wastes.

1.2 The SOP is suitable for all concentration ranges of hardness; however, in order to avoid large titration volumes, use a sample aliquot containing not more than 25-mg $CaCO_3$.

2.0 SUMMARY OF THE METHOD

2.1 This SOP is a procedure for evaluating Total Hardness as $CaCO_3$ in liquid samples.

2.2 Calcium and magnesium ions in the sample are sequestered upon the addition of disodium ethylenediamine tetraacetate (Na_2EDTA). The end point of the reaction, using indicator, has a red color in the presence of Ca and Mg and a blue color when they're sequestered.

3.0 INTERFERENCES

3.1 When in excessive amounts, some heavy metal ions interfere by causing fading or indistinct end points.

4.0 APPARATUS AND MATERIALS

4.1 Digital titrator
4.2 Stir plate
4.3 Clear plastic cups
4.4 Stir Bar
4.5 Graduated Cylinder
4.6 Pipette
4.7 Analytical Balance

5.0 REAGENTS

5.1 Deionized (DI) water
5.2 0.080 EDTA tetrasodium titration cartridge
5.3 0.800 EDTA tetrasodium titration cartridge, used for samples of known or suspected high concentration
5.4 Hach Buffer Solution Hardness 1
5.5 Hach ManVer® 2 Hardness indicator powder pillows
5.6 10,000 mg/L calcium, total hardness as $CaCO_3$ standard
5.7 5N Sodium Hydroxide (NaOH)

6.0 SAMPLE HANDLING AND PRESERVATION

6.1 Hardness is best analyzed as soon as possible from the time the sample is collected. Holding time for water samples is 180 days refrigerated at 4 ± 2^oC

6.2 Samples must be provided in unpreserved, clear plastic bottles. When samples are received in Nitric acid preserved bottles, samples must be neutralized with NaOH before analysis.

7.0 PROCEDURE

7.1 Color Development and Measurement

7.1.1 Pour 100 mL of DI water in a clear plastic cup to make a Blank sample.

7.1.2 Place a magnetic stirring bar in the cup and place the cup on a stir plate. Turn on stir place so that the sample is stirred well, but its color is still clearly visible.

7.1.3 Add 1.0 mL buffer solution to sample.

7.1.4 Pour one Hach ManVer® 2 Hardness indicator powder pillow in the cup.

7.1.5 Using a digital titrator set up with a 0.080 EDTA tetrasodium titration cartridge, place its tip in the sample so that the acid may be released into the sample. Slowly turn the end piece clockwise until the water just turns from its original pink color to blue.

7.1.6 The number of digits used to do this is the value for the Blank. This value will be subtracted from the digit values of all other samples.

7.1.7 Rinse off magnetic stir bar.

7.1.8 Analyze quality control samples by following Sections 7.1.2 to 7.1.7.

7.1.9 Place 10 mL of a sample in another cup and add 90 mL DI water to it. Repeat Sections 7.1.2 to 7.1.7 to find the number of digits needed to titrate the sample. If this value is exceedingly small or large, the dilution of the sample may be adjusted

8.0 CALCULATIONS

8.1 Hardness mg $CaCO_3$/L = $\frac{D*100mL}{S}\times M$

Where D = number of Digits used in titration of sample
M = multiplier number specified by concentration of cartridge (in this case, 1.0)
S = mL of sample used

9.0 QUALITY CONTROL

9.1 See Table 1

9.2 Samples are analyzed in batches of twenty or less per QC set. The QC samples that are analyzed per batch are:

- Control
- MS
- LCS
- DUP
- MSD (optional if set is not Level 3)
- Method Blank
- Blank Spike

Table 1. Quality Control Requirements (Sample Set = 20 samples)

QC Analysis	Required/ Frequency	Limits	Corrective Action	Corrective Action after Reanalyzing
Method (preparation) Blank	Yes One each set	<MDL or 1/10 Regulatory limit	Remove contamination and rerun	Notify Client. Flag Data.
Laboratory Control Sample (LCS)	Yes One each set	90%-110%	Rerun	Notify Client. Flag Data.
Blank Spike	Yes One each set	90%-110%	Rerun	Notify Client. Flag Data.
Control	Yes One each set	90%-110%	Rerun	Notify Client. Flag Data.
Matrix Duplicate	Yes One each set	RPD<20%	Rerun entire set	Notify Client. Flag Data.
Matrix Spike	Yes One each set	80%-120%	Analyze by Method of Standard Additions	Notify Client. Flag Data.
Matrix Spike Duplicate	Level 3 One each set	80%-120%	Analyze by Method of Standard Additions	Notify Client. Flag Data.

10.0 DOCUMENTATION

10.1 Hardness Bench Sheet

10.1.1 Analyst
10.1.2 Date Run
10.1.3 Method #
10.1.4 Detection Limit
10.1.5 Program #
10.1.6 Wavelength

10.1.7 Titrant
10.1.8 Merit #
10.1.9 Dilution
10.1.10 Digit Multiplier
10.1.11 Digits
10.1.12 Total Solids %
10.1.13 Final Concentration (mg/L)
10.1.14 Spike (mg/L)
10.1.15 % Recovery
10.1.16 Source/Lot #
10.1.17 Run Time

11.0 METHOD PERFORMANCE

11.1 Precision and accuracy studies are performed on as needed basis. (Ex. new instrument, etc.)
11.2 Method Detection limit studies are performed annually.

12.0 REFERENCES

12.1 EPA Water NPDES, Method 130.2, EPA Test Methods, Revision 1982, Hardness, Total (mg/L as $CaCO_3$, Titrimetric, EDTA)
12.2 Standard Methods, Method 2340, 20th Edition.

13.0 SAFETY

13.1 Every Laboratory area has eyewash, emergency shower, and fire extinguisher. The metals lab also has dust masks available for use with dust samples.
13.2 The air system through out the laboratory area is on a 100% fresh air exchange system, this system exchanges 100% the air in the laboratory area with air from outside 6 times per hour and 30 times per hour when the emergency purge button is hit.
13.3 A reference file of material safety data sheets (MSDSs) is available to all personnel.
13.4 Specific attention be paid (but not limited) to
13.4.1 Sodium hydroxide is corrosive, causes burns to any area of contact, can slowly pick up moisture from air and react with carbon dioxide from air to form sodium carbonate, and in contact with acids and organic halogen compounds, especially trichloroethylene, sodium hydroxide may causes violent reactions.

14.0 WASTE DISPOSAL AND POLLUTION PREVENTION

14.1 All laboratory waste must be managed, stored, and disposed in accordance with all federal and state laws and regulations.
14.2 Additional information can be found in the Sample Disposal SOP and Merit's Waste Management Plan and Handbook.

15.0 APPROVAL & ISSUE:

15.1 This section indicates which personnel have read, accepted and approved the SOP. All analysts involved with the SOP should acknowledge their comprehension of the SOP with a signature and a date.

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Analyst Date

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Andy Ball, QA Officer Date

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Maya V. Murshak, Technical Director Date

MERCURY IN WATERS, SOLIDS, AND WASTES (COLD-VAPOR TECHNIQUE)

1.0 SCOPE AND APPLICATION

1.1 Cold-vapor atomic absorption (CVAA) procedure is used for determining the concentration of mercury in mobility-procedure extracts, aqueous wastes, and ground waters, soils, solid and sludge-type wastes.

2.0 SUMMARY OF METHOD

2.1 Prior to analysis, the samples are prepared according to the procedure discussed in this SOP.

2.2 The cold-vapor atomic absorption technique is based on the absorption of radiation at 253.7-nm by mercury vapor. The mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height or peak area) is measured as a function of mercury concentration. Method references include SW846 7470A and 7471A, and 245.1.

2.3 Typical detection limit for this method is 0.2 µg/L. This range may be extended above or below the normal range by increasing or decreasing sample size or by optimizing instrument sensitivity. With the operating conditions and parameters stated in this SOP, a detection limit as low as 0.005 µg/L, with a practical quantitation limit of 0.05 µg/L can be obtained without difficulty. Solid reporting limits range from 0.005 mg/kg to 0.10 mg/kg.

3.0 INTERFERENCES

3.1 Potassium permanganate is added to eliminate possible interference from sulfide. Concentrations as high as 20 mg/L of sulfide as sodium sulfide do not interfere with the recovery of added inorganic mercury from reagent water.

3.2 Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/L had no effect on recovery of mercury from spiked samples.

3.3 Seawaters, brines, and industrial effluents high in chlorides require additional permanganate (as much as 7.5 ml) because, during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation of 253.7 nm. Both inorganic and organic mercury spikes have been quantitatively recovered from seawater by using this technique.

3.4 Certain volatile organic materials that absorb at this wavelength may also cause interference. The indication that an organic interference is present is usually suggested by peak broadening with increase in the retention approximately 0.4-0.5 min more than the retention time of the calibration standards.

3.5 For qualitative purposes, ICP/MS verification is possible to confirm the presence of mercury.

4.0 APPARATUS AND MATERIALS

4.1 Quick Trace Mercury Analyzer M-7500 consisting of the following components:

4.1.1 Computer-controlled 4-channel high-performance peristaltic pump (12-roller pump head).

4.1.2 Computerized thermally ozone-free Hg lamp with a thermally controlled Hg lamp housing (for a stabilized Hg vapor lamp).

4.1.3 Stable high performance Gas-Liquid Separator (GLS). Non-foaming/non-bubbling “thin liquid film” GLS design, which allows trouble-free direct analysis of blood, urine, and fish tissue digests as well as standard water and waste analysis.

4.1.4 Integrated ASX-510 Auto Sampler for accommodation of calibration standards and up to 360 samples.

4.2 Digestion block
4.3 Polypropylene digestion vessels.
4.4 VWR Brand Digital Pipettor dispensing variable volumes from 100 to 1000 µl.
4.5 Pipette Dispenser Bottles with adjustable volume 0 - 5 ml in 0.2 ml increments.
4.6 Graduated cylinder 100 ml, 1000 ml or equivalent.
4.7 Disposable Pasteur pipettes.
4.8 Disposable Serological pipettes, 0-10 ml in 0.1 ml increments, 0-5 ml in 0.1 ml increments, and 0-1 ml in 0.01 ml increments.
4.9 Disposable plastic cups.
4.10 Analytical balance, 300 g capacity, minimum accuracy ± 0.01 g.
4.11 Filter funnel, glass or disposable polypropylene.
4.12 Glass-fiber filter paper, 0.45 µm.

5.0 REAGENTS

5.1 Reagent water (Deionized water): All references to reagent water in the method refer to ASTM Type I water (ASTM D1193), unless otherwise specified.

5.2 Sulfuric acid (H_2SO_4), concentrated: Trace metal grade, indefinite shelf live.

5.3 Sulfuric acid, 10% (v/v): Measure 900 g reagent water on the scale and add to it 100 ml of concentrated sulfuric acid in the hood. Prepare as needed, indefinite shelf live.

5.4 Nitric acid (HNO_3), concentrated: Trace metal grade, indefinite shelf live.

5.5 Stannous chloride: Add 25 g stannous chloride ($SnCl_2$) and 25 g sodium chloride (NaCl) to 500 ml of 10% H_2SO_4. Prepare as needed, can be stored for 30 days.

5.6 Hydroxylamine hydrochloride solution ($NH_2OH{\cdot}HCl$): Dissolve 120 g of sodium chloride and 120 g of Hydroxylamine hydrochloride in 1000 g reagent water. Prepare as needed, indefinite shelf live.

5.7 Potassium permanganate ($KMnO_4$), 5% solution (w/v): Dissolve 50 g of potassium permanganate in 1000 g of reagent water. Prepare as needed, indefinite shelf live.

5.8 Potassium persulfate ($K_2S_2O_8$), 5% solution (w/v): Dissolve 50 g of potassium persulfate in 1000 ml of reagent water. Prepare as needed, indefinite shelf live.

5.9 Stock mercury solutions: 10 ppm mercury solutions from SPEX CertiPrep (**SPEX**) and High Purity Standards (**HPS**).

5.10 Mercury working standard: Dilute of the stock mercury solution to obtain a working standard containing 100 µg/L mercury (1 g of the stock solution to 100 g reagent water, on the scale). The HPS stock solution is used for preparing calibration standards; the SPEX stock solution is used for preparing the initial calibration verification (ICV) standard. The working solutions should be prepared fresh before making standards or preparing samples. Acidity of the working standard should be maintained at 1% HCl (v/v). This acid (1 ml) should be added immediately after measuring the standard aliquot, and before dilution to final volume (100 g).

Note: All reagents purchased for Mercury analyses are of high purity (ACS Reagent Grade or better). Verification is done by the laboratory through the analysis of the reagent blank (LRB).

Note: The stock solutions are NIST traceable, and provided with a certificate of analyses and MSDS sheets by the vendor.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples are collected in appropriate containers. For water samples, the samples are collected in HNO_3 pre-preserved plastic container, ensuring acidification to pH of < 2. Soil samples are collected without preservation, usually in glass containers with Teflon lined caps.

6.2 Holding times for Mercury is 28 days. Refrigerate soil samples @ 4°C.

7.0 PROCEDURE

7.1 Sample Preparation:

7.1.1 Liquids

7.1.1.1 In a polypropylene vessel measure (with a disposable serological pipette) 25 ml/g sample or a smaller amount, if the sample is expected to foam or if it is not aqueous, and dilute to 25 ml (g) with reagent water. The amount of sample used is recorded in the preparation log.

7.1.1.2 Repeat this procedure for a batch of 20 samples. If the batch does not have 20 samples, fill the rest of the tubes with reagent water.

7.1.1.3 With each batch include a matrix duplicate and a matrix spike for every 10 samples, a Laboratory Control Sample (LCS), and a Laboratory Reagent Blank (LRB).

7.1.1.4 Add 1.25 ml concentrated H_2SO_4, 0.66 ml concentrated HNO_3, and 3.75 ml $KMnO_4$, to all vessels, and 0.5 ml of the 100 ppb HPS working standard solution to the QC samples (i.e. MS/MSD, etc.). The LCS is prepared the exact same way, but instead of sample, uses DI water plus 0.05 ml of the HPS working standard.

7.1.2 Solids:

7.1.2.1 In a polypropylene tube weigh out approximately 0.5 g sample, and dilute to 25 ml (g) with reagent water.

7.1.2.2 The amount of sample used is recorded in the preparation log. Repeat this procedure for a batch of 20 samples. If the batch does not have 20 samples, fill the rest of the tubes with reagent water.

7.1.2.3 With each batch include a matrix duplicate and a matrix spike for every 10 samples, a Laboratory Control Sample (LCS), and a Laboratory Reagent Blank (LRB). Add 1.25 ml concentrated H_2SO_4, 0.66 ml concentrated HNO_3, and 3.75 ml $KMnO_4$, to all vessels, and 0.5 ml of the 100 ppb HPS working standard solution to the QC samples (i.e. LCS, MS/MSD, etc.). The LCS is prepared the exact same way, but instead of sample, uses DI water plus 0.05 ml of the HPS working standard.

7.1.3 Wait 15 min. Check if $KMnO_4$ is still in solution. If the purple color is gone, add more $KMnO_4$ (Section 3.3), record the amount added, and make corrections to the dilution factor for that particular sample (see Section 7.1.10 for correction to the dilution factor). If the solution is still purple, proceed to step 7.1.3.

7.1.4 Add 2 ml $K_2S_2O_8$.

7.1.5 Place the vessels in block digester

7.1.5.1 heat water samples at 95°C for 2 hours

7.1.5.2 heat soil samples at 95°C for 30 minutes.

7.1.6 Let the vessels cool and add 1.5 ml of Hydroxylamine hydrochloride solution.

7.1.7 If the digested sample contains particulate matter, which may clog some of the valves of the mercury analyzer, the sample may be centrifuged or filtered.

7.1.8 Centrifugation: Centrifugation at 4500 rpm for 5 minutes is usually sufficient to clear the supernatant.

7.1.9 Filtering: The filtering apparatus (flask and funnel) must be thoroughly washed with warm water and soap, and rinsed with a 10% v/v nitric acid solution and copious amounts of DI Water. Filter the sample through a 1.0 µm filter paper and transfer the liquid to a new vessel.

7.1.10 Calculate the dilution factor (*DF*) by the formula:

$$DF = \frac{Final\ \ Volume\ \ (25)}{Sample\ \ amount} x \frac{100}{\%\ Total\ \ solids} xCF$$

If needed, calculate the correction factor (*CF*) due to additional $KMnO_4$ (*x*):

$$CF = \frac{35.16 + x}{35.16}$$

This is recorded in the sample preparation log, and is used in the determination of the mercury result by the CVAA analyzer.

7.2 Calibration Procedure:

7.2.1 Prepare 5 point calibration curve: From the HPS working standard solution weigh out aliquots of 0.0 ml, 0.1 ml, 0.2 ml, 0.5 ml, 1.0ml, 2.0 ml, 4.0ml,and 10.0 ml to 8 Teflon bottles (125 ml) and dilute to 100 ml (g). Follow the steps described in the sample preparation above, adding 4x of each reagent, and without heating. This will provide a calibration curve of 0.0, 0.1, 0.2, 0.5,1.0, 2.0, 4.0, 10.0 µg/L. The minimum acceptable correlation coefficient is 0.997.

7.2.2 Prepare in a similar manner an Initial Calibration Verification (ICV) standard made from a different source (from the SPEX stock solution) at a concentration of 5.0 µg/L, to verify the calibration. In addition, for verifying the calibration solution, an optional ERA standard can be used. The ERA standard comes with performance acceptance limits established by ERA, and is prepared according to the instructions provided by ERA, by taking 1 ml (g) of the concentrate, dilution to 100 ml (g) with reagent water, followed by the steps described in section 7.2.1.

7.2.3 Continuing Calibration Verification (CCV) standard is also prepared as in 7.2.1 from the HPS working standard, to a concentration of 2.0 µg/L. An optional Upper Limit standard of 30 µg/L can be included with the analytical run.

7.2.4 The standard solutions described above must be kept in sealed Teflon bottles, and are to be prepared every 4 weeks, although they are stable for at much longer when kept as above. Usually, the CCV standard is prepared more often because it is used more frequent than the other solutions. The LCS is used to evaluate the performance of the method and is to be prepared with every batch, form fresh mercury working standard.

7.3 Sample Analysis:

7.3.1 Turn on the Mercury Analyzer and allow it to warm up for one hour to be able to analysis ppb's and three hours to be able to analysis ppt's.

7.3.2 Transfer the appropriate standards and samples to the labeled vials, and load the auto-sampler starting with the calibration standards, calibration verification samples, and the batch of samples to be analyzed (QC samples included).

7.3.3 Once the analyzer is warmed up turn on the gas flow to the instrument.

7.3.4 Start the Quick Trace program.

7.3.4.1 Click on the instrument button then the analyzer button
7.3.4.2 Set the pump to 50% and the gas to 100 ml/minute

7.3.5 Check to make sure the reagent has a smooth segmented flow. Once this has be established se the pump speed to 100% and the gas flow to 300 ml/minute.

7.3.5.1 Disconnect the GLS exhaust tubing and crimp the waste tubing just before the mixing tee.
7.3.5.2 This will wet the GLS center post after this is done reset the pump speed to 50% and the gas flow to 100 ml/minute.
7.3.5.3 Wait for the water to drain out of the GLS and then attach the GLS exhaust tubing.

7.3.6 Place the reagent capillary in the reagent bottle and appropriate tubing in to the rinse solution.

7.3.7 Type in the number of samples that you are running. The go into method editor and click read sample to zero mercury analyzer and pick a standard

7.3.8 Verify the baseline and peak are correct for the standard.

7.3.9 Exit method editor and press start to analyze samples

7.4 Data Reporting: The instrument reports final mercury concentrations as µg/L for aqueous samples, and mg/Kg dry weight (where appropriate) for solid samples.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Initial Demonstration of Performance.

8.2.1 The initial demonstration of performance is used to characterize instrument performance (determination of linear dynamic range) and laboratory performance (determination of method detection limit) prior to analyses conducted by this method.

8.2.2 Linear calibration ranges - The upper limit of the linear calibration range should be established for mercury by determining the signal responses from a minimum of three different concentration standards, one of which is close to the upper limit of the linear range. Linear calibration ranges should be determined initially, and whenever a significant change in instrument response is observed.

8.2.3 A mercury MDL (Method Detection Limit) is established using reagent water (blank) fortified at a concentration of two to five times the estimated detection limit. To determine MDL values, take seven replicate aliquot of the fortified reagent water and process through the entire analytical method. Perform all calculations defined in the method and report the concentration values in the appropriate units. Calculate the MDL as follows:

$$MDL = (t) \times (S)$$

where *t* is student's t value for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom (t = 3.14 for seven replicates), and *S* is the standard deviation of the replicate analyses. A MDL is determined annually or whenever a significant change in background or instrument response is expected (e.g. detector change).

8.3 Assessing Laboratory Performance.

8.3.1 The laboratory must analyze at least one LRB with each batch of 20 samples of samples. LRB data is used to assess contamination from the laboratory environment and to characterize spectral background from the reagents used in sample processing. If a mercury value in a LRB exceeds 2.2 x MDL or the reporting limit for liquid samples, whichever is greater, laboratory or reagent contamination is suspected. Any determined source of contamination should be eliminated and the batch re-digested and re-analyzed.

8.3.2 The laboratory must analyze at least one LCS with each batch of 20 samples. Calculate accuracy as percent recovery. If recovery of mercury falls outside control limits (85-115%), the method is judged out of control. The source of the problem should be identified and resolved and new aliquots of the samples redigested and reanalyzed.

8.3.3 Instrument performance:

8.3.3.1 The calibration curve correlation coefficient should be ≥ 0.997. If this is not achieved prepared fresh standards and re-analyze.

8.3.3.2 Check instrument calibration by analyzing the initial calibration verification solution (ICV), made from a source different than the calibration standards (Section 5.10), and the initial calibration blank (ICB). Corrective action listed in Section 8.3.3.4.

8.3.3.3 Verify calibration at a frequency of every 10 analytical samples with the CCV standard and the continuing calibration blank (CCB). These solutions must also be analyzed at the beginning of the analysis and after the last sample.

8.3.3.4 The results of the ICV and CCV must agree within ± 10% of the expected value. If not, terminate the analysis, correct the problem, and recalibrate the instrument. Reanalyze the samples if the last CCV was outside ±15% of expected value.

8.3.3.5 The results of the ICB and CCB's must be less than 2.2 times the current MDL or less than the reporting limits for liquid samples, whichever is greater. If this is not the case, the reason for the out-of-control condition must be found and corrected, and affected samples must be reanalyzed.

8.4 Assessing Analyte Recovery and Data Quality.

8.4.1 The laboratory must a analyze matrix spike (MS) with every 10 samples. Calculate the percent recovery of each analyte, corrected for background concentrations measured in the unfortified (original) sample. Percent recovery may be calculated in units appropriate to the matrix, using the following equation:

$$R = \frac{C_s - C}{S} x100$$

where: R = percent recovery.
C_s = spiked sample concentration.
C = sample background concentration.
S = concentration equivalent of analyte added to fortify the sample.

The recovery limits for MS samples are 70-130%. If the recovery falls outside the designated range, and the laboratory performance is shown to be in control (ICV/ICB, CCV/CCB, and LCS/LRB within the limits), the recovery problem encountered with the spiked sample is judged to be matrix related, not system related. The data user should be informed that the result for the unspiked sample is suspect due to matrix interference. Recovery is not required if the concentration of the mercury added is less than 30% of the concentration of mercury in the original sample.

8.4.2 Analyze one matrix duplicate (Dp) sample for every 10 samples. In some cases, a matrix spike duplicate (MSD) can be used instead of the matrix duplicate, especially if the analyte in the sample is of low concentration. A control limit of 20% RPD should not be exceeded for measured mercury concentration greater than 100 times the MDL. If this limit is exceeded and laboratory performance for that analyte is shown to be in control (ICV/ICB, CCV/CCB, and LCS/LRB within the limits), the problem encountered is judged to be matrix related. The data user should be informed that the result for that analyte is suspect due to the heterogeneous nature of the sample. If the performance of the laboratory is not in control (ICV/ICB, CCV/CCB, and LCS/LRB outside the limits), the reason for the out-of-control situation must be found and corrected, and any samples analyzed during the out-of-control condition for that analyte must be reanalyzed.

8.4.3 Summary of Quality Control Criteria:

QC Item	Frequency	QC Limits
ICV	Following calibration.	90-110%
ICB	Following calibration	<RL liquid samples.
CCV	Before and after each batch. Every 10 samples.	90-110%
CCB	Before and after each batch. Every 10 samples.	<RL liquid samples.
LCS	Every batch of 20 samples.	85-115%
LRB	Every batch of 20 samples.	<RL liquid samples.
Dp	Every 10 samples.	0-20%
MS	Every 10 samples.	70-130%
MSD	Every 10 samples.	0-20%

Note: RL = Reporting Limit.

9.0 METHOD PERFORMANCE

9.1 The precision and accuracy of the method will depend upon the overall performance of the sample preparation and analysis.

9.2 Performance Evaluation samples are analyzed periodically in order to prove the performance of the method.

10.0 APPROVAL & ISSUE:

_____

Analyst Date

_____

Andy Ball, QA Officer Date

_____

Maya V. Murshak, Technical Director Date

1.0 SCOPE AND APPLICATION

1.1 Inductively coupled plasma-mass spectrometry (ICP-MS) is applicable to the determination of sub-µg/L concentrations of a large number of elements in water samples and in waste extracts or digests. When dissolved constituents are required, samples are filtered through 0.45 µm membrane filters and acid-preserved prior to analysis. No digestion is needed prior to analysis for dissolved elements in water samples. Acid digestion prior to filtration and analysis is performed for groundwater, aqueous samples, industrial wastes, soils, sludges, sediments, and other solid wastes for which total (acid-leachable) elements are needed. Acid digestion is also needed prior to analysis to dissolve elements in drinking water samples with turbidity <1 NTU. This SOP follows the guidelines of the EPA Methods 200.8 and 6020.

1.2 The metals that can be determined by using this SOP are listed bellow. Elements specific to each method (*i.e.* 6020, 6020A, 200.8) and reporting limits are listed in Table 1.

Metal (Symbol)	CAS#:
Aluminum (Al)	7429-90-5
Antimony (Sb)	7440-36-0
Arsenic (As)	7440-38-2
Barium (Ba)	7440-39-3
Beryllium (Be)	7440-41-7
Boron (B)	7440-42-8
Cadmium (Cd)	7440-43-9
Calcium (Ca)	7440-70-2
Chromium (Cr)	7440-47-3
Cobalt (Co)	7440-48-4
Copper (Cu)	7440-50-8
Iron (Fe)	7439-89-6
Lead (Pb)	7439-92-1
Lithium (Li)	7439-93-2
Magnesium (Mg)	7439-95-4
Manganese (Mn)	7439-96-5
Molybdenum (Mo)	7439-95-4
Nickel (Ni)	7440-02-0
Potassium (K)	7440-09-7
Selenium (Se)	7782-49-2
Silver (Ag)	7440-22-4
Sodium (Na)	7440-23-5
Strontium (Sr)	7440-24-6
Tin (Sn)	7440-31-5
Titanium (Ti)	7440-32-6
Thallium (Tl)	7440-28-0
Vanadium (V)	7440-62-2
Zinc (Zn)	7440-66-6

1.3 If this SOP is used to determine any analyte not listed in the table above, it is the responsibility of the analyst to demonstrate the accuracy and precision of the Method in the samples to be analyzed. The analyst is always required to monitor potential sources of interferences and take appropriate action to ensure data of known quality.

1.4 Use of this method is restricted to analysts who are knowledgeable in the recognition and in the correction of spectral, chemical and physical interferences in ICP-MS.

2.0 SUMMARY OF METHOD

2.1 Prior to analysis, samples which require total ("acid-leachable") values are digested using appropriate sample digestion procedures (see SOP 3015dig and 3051dig).

2.2 This SOP describes the measurement of ions produced by radio-frequency inductively coupled plasma. Analyte species originating in a liquid are nebulized and the resulting aerosol transported by argon gas into the plasma torch. The ions produced are entrained in the plasma gas and introduced, by means of an interface, into a mass spectrometer. The ions produced in the plasma are sorted according to their mass-to-charge ratios, and quantified with a channel electron multiplier. Potential interference from isobaric elements and polyatomic ions are corrected for by the use of elemental interference equations based on natural isotope abundance. Interference corrections include compensation for background ions contributed by the plasma gas, reagents, and constituents of the sample matrix. Instrument drift and matrix induced signal suppressions and enhancements are compensated for by the use of internal standardization.

3.0 INTERFERENCES

There are three fundamentally different sources of interference in ICP-MS: spectroscopic interferences, physical, and memory interferences.

3.1 **Spectroscopic Interferences** are interferences caused by the presence of compounds or elements entering the mass spectrometer which have the same nominal mass to charge (m/z ratio as the analyte elements. They can be isobaric elemental and isobaric molecular interferences (polyatomic, refractory oxide, and doubly charged ions).

3.1.1 Isobaric elemental interferences in ICP-MS are caused by isotopes of different elements forming atomic ions with the same nominal mass-to-charge ratio (m/z) as the analyte element. These can be managed by the selection of an alternate isotope for analysis or by the use of elemental interference equations. These equations use the naturally occurring isotope ratios of most elements to estimate and allow for the subtraction of isobaric interferences. An example of an elemental isobaric interference is ^{40}Ar on ^{40}Ca. In this case, the use of ^{43}Ca or ^{44}Ca is recommended. The appropriate elemental interference equations are incorporated in the methods (or parameter) used for calibration and data acquisition.

3.1.2 Isobaric molecular and doubly-charged ion interferences in ICP-MS are caused by ions consisting of more than one atom or charge, respectively. Most isobaric interferences that affect ICP-MS determinations have been identified. Examples include $ArCl^+$ ions on the ^{75}As signal and MoO^+ ions on the cadmium isotopes. While the approach used to correct for molecular isobaric interferences is demonstrated below using the natural isotope abundance, the most precise coefficients for an instrument can be determined from the ratio of the net isotope signals observed for a standard solution at a concentration providing suitable (<1%) counting statistics.

3.1.2.1 Example for As is as follows: Because the ^{35}Cl natural abundance of 75.77 % is 3.13 times the ^{37}Cl abundance of 24.23 %, the chloride correction for arsenic can be calculated (approximately) as follows (where the $^{38}Ar^{37}Cl^+$ contribution at m/z 75 is a negligible 0.06 % of the $^{40}Ar^{35}Cl^+$ signal): Corrected arsenic signal (using natural isotopes abundance for coefficient approximations) = (m/z 75 signal) - (3.13) (m/z 77 signal) + (2.73) (m/z 82 signal), (where the final term adjusts for any selenium contribution at 77 m/z).

NOTE: Arsenic values can be biased high by this type of equation when the net signal at m/z 82 is caused by ions other than $^{82}Se^+$, (e.g., $^{81}BrH^+$ from bromine wastes[6]).

3.1.2.2 Example for Cd is as follows: corrected cadmium signal (using natural isotopes abundance for coefficient approximations) = (m/z 114 signal) - (0.027)(m/z 118

signal) - (1.63)(m/z 108 signal), (where last 2 terms adjust for any tin or MoO^+ contributions at m/z 114).

NOTE: Cadmium values will be biased low by this type of equation when $^{92}ZrO^+$ ions contribute at m/z 108, but use of m/z 111 for Cd is even subject to direct ($^{94}ZrOH^+$) and indirect ($^{90}ZrO^+$) additive interferences when Zr is present.

NOTE: Since there is a certain degree of uncertainty as to which equation is better to use, and in what cases, it is up to the analyst to determine how the interference will be corrected, upon the evaluation of data. It is suggested that the elemental isobaric interference equations be included in all methods (parameters) from the beginning, but potential polyatomic species (masses) that could interfere be only monitored (except for $^{40}Ar^{35}Cl^+$ on As). When species monitored indicate that an isobaric molecular interference is present, the equations can be adjusted to correct for such interference, and data be reprocessed to produce an interference free summary report. Generally, an interference is easy to spot when multiple isotopes of an element show different results. Since the interference is additive, the use of the isotope with the lowest result is suggested for data reporting, providing that all other QC criteria are met.

3.1.3 Abundance sensitivity is a property defining the degree to which the wings of a mass peak contribute to adjacent masses. Wing overlap interference may occur when a small ion peak is being measured adjacent to a large one. The potential for these interferences should be recognized, and the spectrometer resolution adjusted to minimize them. Although this type of interference is uncommon, it is not easily corrected, and samples exhibiting a significant problem of this type could require matrix separation, or analysis using another verified and documented isotope.

3.2 **Physical Interferences** are associated with the physical processes, which govern the transport of sample into the plasma, sample conversion process within the plasma and the transmission of ions through the plasma-mass spectrometer interface. These interferences may result in differences between instrument responses for the samples and 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 effects), during the atomization and ionization process within the plasma itself, or during the transfer of ions through the interface and mass spectrometer (space charge effects). To minimize some of these effects, acid composition and concentration should be matched for all standards, blanks, and samples. Total solid levels below 0.2% (2,000 mg/L) have been currently recommended to minimize solid deposition. Internal standardization may be effectively used to compensate for many physical interference effects. Internal standards should ideally display similar analytical behavior to the elements being determined. Generally, an internal standard should be no more than 50 amu removed from the analyte. Recommended internal standards include ^{6}Li, ^{45}Sc, ^{89}Y, ^{103}Rh, ^{115}In, ^{159}Tb, ^{169}Ho, ^{185}Re, and ^{209}Bi.

3.3 **Memory Interferences** result when elements in a previous sample contribute to signals measured in a subsequent sample. Memory effects can result from the deposition of sample on various components of the sample introduction system, including sample and peristaltic pump tubing, spray chamber, torch, and interface cones. The site(s) where deposition may occur is dependent on the sample and may need to be minimized through the use of a rinse blank between samples. Routine maintenance (cleaning and/or replacement) of sample introduction components is necessary for long-term minimization of memory effects. The possibility of memory interferences within an analytical run should be recognized and suitable rinse times should be used to reduce them. Memory effects are evaluated by using a minimum of three replicate integrations for data acquisition. High relative standard deviation (%RSD) of the three replicates caused by a consecutive drop in signal intensity is indicative of carryover from the previous sample. If a memory interference is suspected, the sample should be reanalyzed after analysis of a blank indicates that the carryover has been eliminated

4.0 APPARATUS AND MATERIALS

4.1 Inductively coupled plasma-mass spectrometers:

4.1.1 **Perkin Elmer (PE) Elan 9000 ICP-MS:** :
- Windows XP Operating System
- Elan 3.0 Software
- Cetac Asx510 Autosampler

4.1.2 **Hewlett-Packard (HP) 4500 ICP-MS**:
- Windows 95 operating system.
- Chem Station Software.
- Cetac ASX150 Autosampler.

4.2 Argon gas supply: liquid argon cylinders.
4.3 Analytical balance, 510gcapacity, minimum accuracy ± 0.001g.
4.4 Digital bottle top dispenser capable of dispensing volumes of 0-5 ml in 0.02 ml increments.
4.5 Eppendorf automatic pipette with disposable combitips ranging from 2.50 ml to 50 ml capable of pipetting volumes ranging from 50 µl to 5,000 µl.
4.6 Disposable Pasteur pipettes.
4.7 Polypropylene vessels, 50 mL.
4.8 Plastic cups to support minimum of 200 ml.
4.9 Plastic bottles.

5.0 REAGENTS

5.1 Nitric Acid (HNO_3), concentrated, Trace Metal Grade. Acids used in the preparation of standards and for sample processing must be of high purity. Trace metal grade (also known as re-distilled) acids are recommended because of the high sensitivity of ICP-MS. Nitric acid at 2% (v/v) or less in the solution to be analyzed is required for ICP-MS, in order to minimize damage to the interface.

5.2 Hydrochloric Acid (HCl), concentrated, Trace metal Grade. Several polyatomic ion interferences result when HCl is used. However, its use is recommended to maintain stability in solutions containing high concentrations of antimony and silver. When used, corrections for the chloride polyatomic ion interference must be applied to all data.

5.3 Reagent water (Deionized water): All references to reagent water in the method refer to ASTM Type I water (ASTM D1193), unless otherwise specified.

5.4 Internal Standard stock solutions:

5.4.1 Lithium 6, 1000 µg/ml stock solution.
5.4.2 Scandium, 1000 µg/ml stock solution.
5.4.3 Yttrium, 1000 µg/ml stock solution.
5.4.4 Rhodium, 1000 µg/ml stock solution.
5.4.5 Rhenium, 1000 µg/ml stock solution.

5.4.6 Internal Standard working solution (**IS-WS**): From the above stock solution, 5 g of each is transferred to a 1000 ml plastic bottle, along with 20 ml of concentrated HNO_3 and brought to a final volume of 1000 ml (by weight). The concentration in the flask will be approximately 5.0 µg/ml. This represents the internal standards working solution from which 1 ml (for a 50 ml final volume) will be added to all calibration standards and blanks. This will provide a 0.10 ppm of internal standard concentration in all calibration standards, similar to analytical samples.

Note: The stock solutions are NIST traceable, and provided with a certificate of analyses and MSDS sheets by the vendor.

5.5 Multielement standard stock solution from three different vendors:

5.5.1 Inorganic Venture (IV), 100mg/L each of Ag, Al, B, Ba, As, Be, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sb, Se, Ti, Tl, V, Zn.. This solution is used for the preparation of standards.

5.5.2 High Purity Standards (**HM**), 100 µg/ml each of Ca, Mg, K, Na. This solution is used for the preparation of the calibration standards and for the minerals standard.

5.5.3 SPEX Industries (**S**), 100 µg/ml each of Al, Sb, As, Ba, Be, B, Cd, Ca Cr, Co, Cu, Fe, Pb, Li, Mg, Mn, Mo, Ni, K, Se, Si, Ag, Na, Sr, Sn, Ti, Tl, V, Zn. This solution is used for the preparation of the initial calibration verification (ICV) standards.

5.5.2 Environimental Resourse Associates (ERA), concentration varies by lot number and element but contains all of the following Al, Sb,As,Ba, Be, B Cd, Cr, Co, Cu, Fe, Pb, Mn, Mo, Ni, Se, Ag, Zn, V, Th, S. This solution is used as a third source of verification

Note: The stock solutions are NIST traceable, and provided with a certificate of analyses and MSDS sheets by the vendor. See Appendix 1 for standard preparation.

5.6 Multielement calibration standard solutions are prepared by diluting the stock standard solutions to levels in the linear range for the instrument in a solvent consisting of 2% (v/v) HNO_3 in reagent water. The calibration standard solutions must contain a suitable concentration of an appropriate internal standard for each analyte. The calibration standards are kept in plastic bottles, and prepared every two weeks or as needed. They must be verified using a quality control standard (ICV). Table 2 and Table 3 can be used as guidance, when preparing standards.

5.7 Blanks: Three types of blanks are required for the analysis. The calibration blank (std-0.00) is used in establishing the calibration curve. The preparation blank (LRB) is used to monitor possible contamination resulting from the sample preparation procedure. The rinse blank (also called optional rinse or autosampler wash) is used to flush the system between all samples and standards.

5.7.1 The calibration blank (std-0.00) and the continuing calibration blank (CCB) consists of the same concentration(s) of the same acid(s) used to prepare the calibration standards, along with the appropriate concentration of internal standard.

5.7.2 The preparation (or reagent) blank must be carried through the complete preparation procedure and contain the same volumes of reagents as the sample solutions.

5.7.3 The rinse blank consists of 2% HNO_3 (v/v) in reagent water. Prepare a sufficient quantity to flush the system between standards and samples.

5.8 The interference check solution (ICS) is prepared to contain known concentrations of interfering elements that will demonstrate the magnitude of interferences and provide an adequate test of any corrections. Chloride in the ICS provides a means to evaluate software corrections for chloride-related interference such as $^{35}Cl^{16}O^{+}$ on $^{51}V^{+}$ and $^{40}Ar^{35}Cl^{+}$ on $^{75}As^{+}$. Iron is used to demonstrate adequate resolution of the spectrometer for the determination of manganese. Molybdenum serves to indicate oxide effects on cadmium isotopes. The other components are present to evaluate the ability of the measurement system to correct for various molecular isobaric interferences. The ICS is used to verify that the interference levels are corrected by the data system within quality control limits.

5.8.1 Interference check stock solution A, containing 1000 µg/ml each of Al, Ca, Fe, Mg, Na, P, K, S, 2000 µg/ml of C, 10000 µg/ml of Cl, and 20.0 µg/ml each of Mo and Ti. The ICS-A solution is prepared by weighing 10.0 g of the stock solution in a plastic cup, addition of 2 ml IS-WS, 2ml HNO_3, and dilution to 100 g on the scale with reagent water.

5.8.2 Interference check stock solution AB, containing 2.0 µg/ml each of As, Cd, Cr, Co, Cu, Mn, Ni, Ag, and Zn. The ICS-AB solution is prepared by weighing 1.00 g of the stock solution in a plastic cup, addition of 2 ml IS-WS, 2ml HNO_3, and dilution to 100 g on the scale with reagent water.

5.8.3 The final concentration of the elements in ICS-A and ICS-AB is listed in Table 5. These solutions are prepared fresh every two weeks or as needed.

5.9 The quality control standard is the initial calibration verification solution (ICV), which must be prepared in the same acid matrix as the calibration standards. This solution must be an independent standard near the midpoint of the linear range at a concentration other than that used for instrument calibration. An independent standard is defined as a standard from a source different from those used in the standards for instrument calibration.

5.10 Mass spectrometer tuning solution. A solution containing elements representing all of the mass regions of interest must be prepared to verify that the resolution and mass calibration of the instrument are within the required specifications (see Section 7.5). This solution is also used to verify that the instrument has reached thermal stability (See Section 7.4).

5.10.1 Tuning solution for HP 4500 ICP-MS: 10 µg/ml each of Li, Y, Ce, and Tl. Take 1.00 g of this solution in a plastic bottle, add 20 ml HNO_3, and dilute to 1000 g on the scale with reagent water (or add 979 g reagent water to the bottle with standard and acid). This will result in a 10.0 ppb solution of the above elements, used to tune the instrument according to the manufacturer instructions.

5.10.2 Tuning solution for PE Elan 9000 Tune Solution 6020-Li Co In Tl (10 ppb) Tune Solution 200.8- Be Mg Co In Pb (10ppb)This is used to tune the instrument according to the manufacturer instructions.

5.11 Drinking water working standards are prepared every two weeks

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples are collected in appropriate containers. For water samples, the samples are collected in HNO_3 pre-preserved plastic container (approximately 125 ml volume), and are acidified to pH of <2.

6.2 Soil samples are collected without preservation, usually in glass containers with Teflon lined caps. Non-aqueous samples should be refrigerated upon receipt and analyzed as soon as possible.

6.3 Holding times for metals are 6 months from the date of sampling.

7.0 PROCEDURE

7.1 Solubilization and digestion procedures are presented in the Sample Preparation SOP's (e.g., 3015dig, 3051dig).

7.2 Initiate appropriate operating configuration of the instrument's computer according to the instrument manufacturer's instructions.

7.3 Set up the instrument with the proper operating parameters according to the instrument manufacturer's instructions (Table 4).

7.4 Operating conditions: The analyst should follow the instructions provided by the instrument manufacturer. Allow at least 30 minutes for the instrument to equilibrate before analyzing any samples. This must be verified by analyzing a tuning solution (Section 5.10.1 and 5.10.2).

7.5 Tune the instrument according to the instrument manufacturer's instructions. For drinking water samples the tuning requirements are listed in the 200.8 method. The tuning should include beryllium, magnesium, cobalt, indium, and lead. Conduct mass calibration and resolution checks in the mass regions of interest. The mass calibration and resolution parameters are required criteria that must be met prior to any samples being analyzed. If the mass calibration differs more than 0.1 amu from the true value, then the mass calibration must be adjusted to the correct value. The resolution must also be verified to be within 0.5-0.9 amu full width at 10 percent peak height.

NOTE: Precautions must be taken to protect the channel electron multiplier from high ion currents. The channel electron multiplier suffers from fatigue after being exposed to high ion currents. This fatigue can last from several seconds to hours depending on the extent of exposure. During this time period, response factors are constantly changing, which invalidates the calibration curve, causes instability, and invalidates sample analyses.

7.6 Calibrate the instrument for the analytes of interest (recommended isotopes for the elements in Section 1.2 are provided in Table 6a and Table 6b), using the calibration blank and at least a single initial calibration standard according to the instrument manufacturer's procedure. Table 2 and Table 3 (Section 5.6) provides information as to what calibration standards to use. Flush the system with the rinse blank (Section 5.7.3) between each standard solution. Use the average of at least three integrations for both calibration and sample analyses.

7.7 All masses that could affect data quality should be monitored to determine potential effects from matrix components on the analyte peaks. The recommended isotopes to be monitored are listed in Table 6a, and Table 6b).

7.8 Immediately after the calibration has been established, the calibration must be verified and documented for every analyte by the analysis of the calibration verification solution (ICV, Section 5.9). When measurements exceed ± 10% of the accepted value, the analyses must be terminated, the problem corrected, the instrument re-calibrated, and the new calibration verified. During the course of an analytical run, the instrument may be "re-sloped" or re-calibrated to correct for instrument drift. A re-calibration must then be followed immediately by a new analysis of a ICV and ICB before any further samples may be analyzed. Corrective actions for specific situations are summarized in Table 7.

7.9 An optional Blank Spike (BS) of low concentration can be used to verify the linearity of the calibration curve near the lower end. When such standard is used, recalibrate the instrument if the recovery of the BS is outside 70-130% of true concentration.

7.10 Flush the system with the rinse blank solution (Section 5.7.3) until the signal levels return to the method's levels of quantitation (usually about 30 seconds) before the analysis of each sample. Nebulize each sample until a steady-state signal is achieved (usually about 30 seconds) prior to collecting data. Analyze the calibration verification solution (CCV), and the continuing calibration blank (CCB) at a frequency of at least once every 10 analytical samples.

7.11 Dilute and reanalyze samples that are more concentrated than the linear range (LDR Section 8.2.2.) for an analyte or measure an alternate less-abundant isotope. The linearity at the alternate mass must be confirmed by appropriate calibration (see Sec. 7.6 and 7.8).

7.12 Calculations: The quantitative values shall be reported in appropriate units, such as milligrams per liter (mg/L) for aqueous samples and milligrams per kilogram (mg/kg) for solid samples.

7.12.1 The appropriate dilution factor (DF) resulted from sample preparation (see 3015dig and 3051B SOP's) is entered in the data system for each sample at the time of programming the

sequence to be analyzed. If additional dilutions are performed, the appropriate corrections must be applied to the dilution factor.

7.12.2 Generally, for solid samples, DF includes the correction necessary for the determination of a dry weight result. If this is not the case or if a dry weight result is requested at a later time, calculate results for solids on a dry-weight basis as follows:

(1) A separate determination of percent solids must be performed.
(2) A new DF can be calculated, based on the original wet weight of the sample (from the preparation log) and the percent total solids. The sequence is updated with the new DF, data reprocessed, and a new quantitation report is generated by the data system.
(3) Manual calculation of the dry weight concentration (DWC) by the formula:

$$DWC\ (mg\ /\ kg) = \frac{CxV}{WxS}$$

Where, C = Digest Concentration (mg/L).
V = Final volume in liters after sample preparation.
W = Weight in kg of wet sample.
S = (% Total Solids)/100.

7.12.3 Calculations performed by the data system include appropriate interference corrections, internal-standard normalization, and the summation of signals at 206, 207 and 208 m/z for lead (to compensate for any differences in the abundances of these isotopes between samples and standards).

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and be available for easy reference or inspection.

8.2 Initial Demonstration of Performance.

8.2.1 The initial demonstration of performance is used to characterize instrument performance (determination of linear calibration ranges) and laboratory performance (determination of method detection limits) prior to analyses conducted by this method.

8.2.2 Linear calibration ranges: Linear calibration ranges are primarily detector limited. The upper limit of the linear calibration range should be established by determining the signal responses from a minimum of three different concentration standards, one of which is close to the upper limit of the linear range. Care should be taken to avoid potential damage to the detector during this process. The linear calibration range, which may be used for the analysis of samples, should be judged by the analyst from the resulting data. The upper LDR is defined as the maximum concentration for which the measured concentration is within ±10% of the true value. Determined sample analyte concentrations that are greater than the upper LDR limit must be diluted and reanalyzed. The LDR should be verified whenever, in the judgement of the analyst, a change in analytical performance caused by either a change in instrument hardware or operating conditions would dictate they be redetermined.

8.2.3 Method detection limits (MDL) should be established for all analytes, using reagent water (blank) fortified at a concentration of two to five times the estimated detection limit. To determine MDL values, take seven 7 replicate aliquots of the fortified reagent water and process through the entire analytical method. Perform all calculations defined in the method and report the concentration values in the appropriate units. Calculate the MDL as follows:

MDL = (t) x (S)

Where: t = student's t value for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom (t = 3.14 for seven replicates);
S = standard deviation for the replicate analyses.

MDL's should be determined annually, when a new operator begins work or whenever, in the judgement of the analyst, a change in the instrument hardware or operating conditions would dictate they be redetermined.

8.3 To obtain analyte data of known quality, it is necessary to measure more than the analytes of interest in order to apply corrections or to determine whether interference corrections are necessary. If the concentrations of interference sources (such as C, Cl, Mo, Zr, W) are such that, at the correction factor, the analyte is less than the limit of quantification or the concentration of interferents are insignificant, then the data may go uncorrected. Note that monitoring the interference sources does not necessarily require monitoring the interferant itself, but that a molecular species may be monitored to indicate the presence of the interferent. The monitored masses must include those elements whose hydrogen, oxygen, hydroxyl, chlorine, nitrogen, carbon, and sulfur molecular ions could impact the analytes of interest. Unsuspected interferences may be detected by adding pure major matrix components to a sample to observe any impact on the analyte signals. If an interference source is present, and can not be corrected, the sample elements impacted must be flagged. When correction equations are used, all QC criteria must also be met.

8.4 The intensities of all internal standards must be monitored for every analysis. When the intensity of any internal standard fails to fall outside limits as compared with the first calibration standard (Calibration Blank or std-0.00), the following procedure is followed. The sample must be diluted at least fivefold (1+4) and reanalyzed with the addition of appropriate amounts of internal standards. This procedure must be repeated until the internal-standard intensities fall within the prescribed window. The intensity levels of the internal standards for the ICV/ICB, CCV/CCB, LCS/LRB must also be within the specified acceptance limits (refer to Section 8.9.1.3 and 8.9.2.4 for limits). If they are not, terminate the analysis, correct the problem, recalibrate, verify the new calibration, and reanalyze the affected samples.

8.5 Check the instrument calibration by analyzing appropriate quality control solutions as follows:

8.5.1 Check instrument calibration by analyzing the initial calibration verification solution (ICV) and the initial calibration blank (ICB).

8.5.2 Verify calibration at a frequency of every 10 analytical samples with the CCV standard and the continuing calibration blank (CCB). These solutions must also be analyzed for each analyte at the beginning of the analysis and after the last sample.

8.5.3 The results of the ICV and CCV must agree within ± 10% of the expected value. If not, terminate the analysis, correct the problem, and recalibrate the instrument.

8.5.4 The results of the ICB and CCB's must be less than the current RDL for each element or less than the reporting limits for sample, whichever is greater. If this is not the case, the reason for the out-of-control condition must be found and corrected, and affected samples must be reanalyzed.

8.6 A Laboratory Control Sample (LCS) should be analyzed for each analyte using the same sample preparations, analytical methods, and QA/QC procedures employed for the test samples. One LCS should be prepared and analyzed for each sample batch at a frequency of one LCS for each 20 samples or less. The recovery limits for the LCS are 85-115% of the true value (stated in the preparation log).

8.7 Analyze one matrix spike (MS) sample for every 10 analytical water samples or every 20 analytical soil samples. For majority of the elements, the aqueous samples are spiked at levels similar to the LCS (0.05 ppm in the analysis solution). For solid samples, the concentration added is approximately 20 mg/Kg equivalent (0.10 ppm in the analysis solution). The acceptable limits for performance are summarized in Section 8.10.

8.7.1 Calculate the percent recovery of each analyte, corrected for background concentrations measured in the unfortified (original) sample. Percent recovery may be calculated in units appropriate to the matrix, using the following equation:

$$R = \frac{C_s - C}{S} x100$$

where: R = percent recovery.
C_s = spiked sample concentration.
C = sample background concentration.
S = concentration equivalent of analyte added to fortify the sample.

8.8 Analyze one matrix duplicate (Dp) sample for every 10 water samples or every 20 soil samples. In some cases, a matrix spike duplicate (MSD) can be used instead of the matrix duplicate, especially if the analytes in the sample are of low concentration. A control limit of 20% RPD should not be exceeded for analyte values greater than 100 times the MDL. If this limit is exceeded and laboratory performance for that analyte is shown to be in control (ICV/ICB, CCV/CCB, and LCS/LRB within the limits), the problem encountered is judged to be matrix related. The data user should be informed that the result for that analyte is suspect due to the heterogeneous nature of the sample. If the performance of the laboratory is not in control (ICV/ICB, CCV/CCB, and LCS/LRB outside the limits), the reason for the out-of-control situation must be found and corrected, and any samples analyzed during the out-of-control condition for that analyte must be reanalyzed.

8.8.1 The relative percent difference (RPD) between duplicate determinations must be calculated as follows:

$$RPD = \frac{\left| D_1 - D_2 \right|}{\frac{D_1 + D_2}{2}} x\,100$$

where: RPD = relative percent difference.
D_1 = first sample value.
D_2 = second sample value (duplicate).

8.9 The Quality Control requirements and limits vary slightly, based upon the method referenced in the analytical report (i.e. 6020 vs. 200.8). For both methods, the calibration is verified by the analysis of ICV/ICB and CCV/CCB. Recalibration is required when either one falls outside the limits. The performance of the method is evaluated by the analysis of the LCS/LRB pair for every batch of 20 samples, and MS/MSD/Dp for every 10 samples.

8.9.1 Method 200.8 specific requirements:

8.9.1.1 When the recovery for ICV/CCV falls outside ±10% terminate the analysis and recalibrate the instrument. If the last CCV was within 15% of the true concentration, the results for the samples are still acceptable. If this is not the case, the only acceptable results are the once corresponding to samples analyzed before the last CCV that was within 15% of the true concentration. All other samples are to be analyzed again, after recalibration of the instrument.

8.9.1.2 The recovery limits for MS samples are 70-130%. If the recovery of any analyte falls outside the designated range and the laboratory performance is shown to be in control (ICV/ICB, CCV/CCB, and LCS/LRB within the limits), the recovery problem encountered with the spiked sample is judged to be matrix related, not system related. The data user should be informed that the result for the analyte in the unspiked sample is suspect due to an uncorrected matrix effect. Recovery is not required if the concentration of the analyte added is less than 30% of the concentration of the analyte in the original sample.

8.9.1.3 The absolute response of any one internal standard must not deviate by more than 60 to 125% of the original response in the first calibration standard (Calibration Blank or std-0.00). If deviations greater than these are observed flush the instrument with rinse blank, than analyze a CCB. If the responses of the internal standards are now within the limit proceed with sample dilution as described in Section 8.4. If the responses of the internal standards are not within the limit, terminate the analysis, recalibrate the instrument, and reanalyze the samples from the last CCB with acceptable internal standard recoveries.

8.9.2 Method 6020 specific requirements:

8.9.2.1 When the recovery for ICV/CCV falls outside ±10% terminate the analysis and recalibrate the instrument. The samples from the last CCV that was within limits are to be re-analyzed, after recalibration of the instrument.

8.9.2.2 The MS is represented by a spiked sample, before digestion, and a Post-Digestion Spike, if the recovery of the regular spike fails to meet QC criteria. An analyte spike added to a portion of a prepared sample, or its dilution, should be recovered to within 75 to 125 percent of the known value. The spike addition should be based on the indigenous concentration of each element of interest in the sample. If the spike is not recovered within the specified limits, the original sample must be diluted to compensate for the matrix effect, and reanalyzed, after a new post-digestion spike is added. The same recovery limits apply to the spiked dilution.

8.9.2.3 The MSD is represented by a spiked duplicate sample, before digestion, and a Post-Digestion Spike, if the recovery of the regular duplicate spike fails to meet QC criteria. The evaluation of the MSD is similar to the evaluation of the duplicate analysis described in Section 8.8.

8.9.2.4 When the intensity of any internal standard in the sample to falls outside 30-120% of the intensity of that internal standard in the initial calibration standard (Calibration Blank or std-0.00), follow the procedure described in Section 8.4. The intensity levels of the internal standards for the ICV/ICB and CCV/CCB must agree within ± 20 percent of the intensity level of the initial calibration standard (Calibration Blank or std-0.00). If they do not agree, terminate the analysis, correct the problem, recalibrate, verify the new calibration, and reanalyze the affected samples.

8.9.2.5 Dilution Test: If the analyte concentration is within the linear dynamic range of the instrument and sufficiently high (minimally, a factor of at least 100 x MDL), an analysis of a fivefold (1+4) dilution must agree within ± 10% of the original determination. If not, an interference effect must be suspected, and the results flagged. One dilution test must be included with every batch of twenty samples.

8.9.2.6 Verify the magnitude of elemental and molecular-ion isobaric interferences and the adequacy of any corrections at the beginning of an analytical run or once every 12 hours, whichever is more frequent. Do this by analyzing the interference check solutions ICS-A and ICS-AB. The recovery of the elements of interest in ISC-AB (listed in Table 5 at a concentration of 0.02 ppm) should be between 70-135%.

8.10 Summary of the QC requirements and performance acceptance limits are shown in the following table:

QC Type	Method 6020 (%)	Method 200.8 (%)
ICV	90-110	90-110
BS	70-130	70-130
CCV	90-110	90-110*

Dp	0-20	0-20
MS	75-125	70-130
MSD	0-20	0-20
ICS-AB	70-135	n.a.
Internal Standard	80-120 for CCV/CCB 30-120 for samples	80-120 for CCV/CCB 60-125 for samples

*NOTE: *Sample results still acceptable if CCV between 85-115%.*

9.0 METHOD PERFORMANCE

9.1 The precision and accuracy of the method will depend upon the overall performance of the sample preparation and analysis.

9.2 Performance Evaluation samples are analyzed periodically in order to prove the performance of the method.

9.3 In an EPA multi-laboratory study, laboratories applied the ICP-MS technique to both aqueous and solid samples. The results are listed at the end of methods 200.8 and 6020.

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11.0 APPROVAL & ISSUE:

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Paul Roettger, Senior Analyst Date

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Andrew Ball, QA Officer Date

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Maya V. Murshak, Technical Director Date

12.0 LIST OF TABLES

Table 1. List of elements analyzed.

Element	Symbol	CAS#	Reporting Limits		Method 6020	Method 200.8
			mg/L	mg/Kg		
Aluminum	(Al)	7429-90-5	0.05	0.5	Aluminum	Aluminum
Antimony	(Sb)	7440-36-0	0.002	0.3	Antimony	Antimony
Arsenic	(As)	7440-38-2	0.001	0.1	Arsenic	Arsenic
Barium	(Ba)	7440-39-3	0.01	1.0	Barium	Barium
Beryllium	(Be)	7440-39-3	0.001	0.50	Beryllium	Beryllium
Boron	(B)	7440-42-8	0.01	1.0	-	-
Cadmium	(Cd)	7440-43-9	0.0005	0.2	Cadmium	Cadmium
Calcium	(Ca)	7440-70-2	0.05	10.0	Calcium	-
Chromium	(Cr)	7440-47-3	1.0	2.0	Chromium	Chromium
Cobalt	(Co)	7440-48-4	0.005	2.0	Cobalt	Cobalt
Copper	(Cu)	7440-50-8	0.01	0.5	Copper	Copper
Iron	(Fe)	7439-89-6	0.004	1.0	Iron	-
Lead	(Pb)	7439-92-1	0.1	1.0	Lead	Lead
Lithium	(Li)	7439-93-2	0.003	1.0	-	-
Magnesium	(Mg)	7439-95-4	0.01	1.0	Magnesium	-
Manganese	(Mn)	7439-96-5	1.0	4.0	Manganese	Manganese
Molybdenum	(Mo)	7439-98-7	0.02	1.0	-	Molybdenum
Nickel	(Ni)	7440-02-0	0.005	0.50	Nickel	Nickel
Potassium	(K)	7440-09-7	0.005	1.0	Potassium	-
Selenium	(Se)	7782-49-2	1.0	5.0	Selenium	Selenium
Silver	(Ag)	7440-22-4	0.005	0.2	Silver	Silver
Sodium	(Na)	7440-23-5	0.0002	0.1	Sodium	-
Strontium	(Sr)	7440-24-6	0.05	10.0	-	-
Tin	(Sn)	7440-31-5	0.005	0.50	-	-
Titanium	(Ti)	7440-32-6	0.02	1.0	-	-
Thallium	(Tl)	7440-28-0	0.005	1.0	-	-
Vanadium	(V)	7440-62-2	0.001	0.50	Thallium	Thallium
Zinc	(Zn)	7440-66-6	0.004	1.0	Vanadium	Vanadium
			0.01	1.0	Zinc	Zinc

Table 2. Standard preparation for all elements except Ca, Mg, K, Na.

STANDARD PREPARATION

Inorganic Stock Solution IV-7 + IV-19 (100 ppm)

I. Working Stock Solution 1 (WS1)

10 mls IV-7 + 10 mls IV-19 + 2 mls HNO_3; Bring to a final volume of 100 mls = 10 ppm

II. Working Stock Solution 2 (WS2)

1ml of WS1 to a final volume of 100 mls = 0.100 ppm

III. Standards

Standards	Volume Working Stock Solution	Internal Standard 5.0 ppm	HNO_3	1.1. Final Volume
0.20 ppm	2.00 mls WS1	2 mls	2 mls	100 mls
0.10 ppm	1.00 ml WS1	2 mls	2 mls	100 mls
0.05 ppm	0.50 ml WS1	2 mls	2 mls	100 mls
0.02 ppm	20.0 mls WS2	2 mls	2 mls	100 mls
0.01 ppm	10.0 mls WS2	2 mls	2 mls	100 mls
0.005 ppm	5.00 mls WS2	2 mls	2 mls	100 mls
0.002 ppm	2.00 mls WS2	2 mls	2 mls	100 mls
0.0005 ppm	0.50 mls WS2	2 mls	2 mls	100 mls

Table 3. Standard preparation for Ca, Mg, K, Na.

Standards **Ppm**	**Volume of Working Stock**	**Source and Lot # of Working Stock (100ppm)**	**Internal Standard 5.0 ppm**	**HNO_3**	Final Volume
0.50	**0.5**	**High Purity - 620719**	**2 mls**	**2 mls**	**100 mls**
1.0	**1.0**	**High Purity - 620719**	**2 mls**	**2 mls**	**100 mls**
2.0	**2.0**	**High Purity - 620719**	**2 mls**	**2 mls**	**100 mls**
5.0	**5.0**	**High Purity - 620719**	**2 mls**	**2 mls**	**100 mls**
10.0	**10.0**	**High Purity - 620719**	**2 mls**	**2 mls**	**100 mls**
ICV- 5.0	**5.0**	**Spex – 5-59JB**	**2 mls**	**2 mls**	**100 mls**

Table 4. ICS Components and Concentration.

Solution Component	**ICS-A (ppm)**	**ICS-AB (ppm)**
Al	100.0	100.0
Ca	100.0	100.0
Fe	100.0	100.0
Mg	100.0	100.0
Na	100.0	100.0
P	100.0	100.0
K	100.0	100.0
S	100.0	100.0
C	200.0	200.0
Cl	1000.0	1000.0
Mo	2.0	2.0
Ti	2.0	2.0
As	0.0	0.020
Cd	0.0	0.020
Cr	0.0	0.020
Co	0.0	0.020
Cu	0.0	0.020
Mn	0.0	0.020
Ni	0.0	0.020
Ag	0.0	0.020
Zn	0.0	0.020

Table 5a. Recommended analytical isotopes (underlined) and additional masses to be monitored.

Mass	**Element**	**I.S. Used**	**Elemental Correction**	**Potential interferences**
19	K	Sc, Rh		
23	Na	Sc, Rh		

24	Mg	Sc, Rh		
43	Ca	Sc, Rh		
44	Ca	Sc, Rh	$(-0.0271)(^{88}C)$	Sr^{++}

Notes:
- † Recommended for PE instrument.
- ‡ Recommended for HP instrument.
- C = Counts at specified mass.
- When the concentration of Na in the samples is high, the ionization of Sc is suppressed leading to positive bias of the results, therefore Rh should be used as the internal standard, even if more than 50 amu removed from the element of interest.

Table 5b. Recommended analytical isotopes (underlined) and additional masses to be monitored.

Mass	Element	I.S. Used	Elemental Correction	Potential interferences
6	Li	**I.S.**	-(0.0813)(^{7}C)	
7	Li	^{6}Li, Sc		
9	Be	^{6}Li, Sc		
10	B	^{6}Li, Sc		
11	B	^{6}Li, Sc		
27	Al	^{6}Li, Sc		
45	Sc	**I.S.**		CO_2H^+
47	Ti	^{6}Li, Sc		
49	Ti	^{6}Li, Sc		
51	V	^{6}Li, Sc	-(3.127)(^{53}C)+(0.352)(^{52}C)	$^{35}ClO^+$, $^{34}SOH^+$
52†	Cr	Sc, Y, Rh		ArC^+, ArO^+, $^{35}ClHO^+$
53‡	Cr	Sc, Y, Rh		$^{37}ClHO^+$
54†	Fe	Sc, Y, Rh	-(0.0284)(^{52}C)	
55	Mn	Sc, Y, Rh		$ArNH^+$
56	Fe	Sc, Y, Rh		
57‡	Fe	Sc, Y, Rh		
58†	Ni	Sc, Y, Rh		
59	Co	Sc, Y, Rh		
60	Ni	Sc, Y, Rh		
62	Ni	Sc, Y, Rh		TiO
63†	Cu	Sc, Y, Rh		$^{31}PO_2^+$, $^{40}ArNa^+$, TiO
65‡	Cu	Sc, Y, Rh		TiO
66	Zn	Sc, Y, Rh		TiO
68	Zn	Sc, Y, Rh		
75	As	Y, Rh	-(3.132)(^{77}C)+(2.736)(^{83}C)	$^{40}Ar^{35}Cl^+$
76	$^{40}Ar^{36}Ar^+$	Y, Rh		$^{40}Ar^{37}Cl^+$
77	Se	Y, Rh		
78†	Se	Y, Rh	-(0.1869)(^{76}C)‡	$^{40}Ar^{38}Ar^+$
82‡	Se	Y, Rh		$^{81}BrH^+$
83	Kr	Y, Rh		
88	Sr	Y, Rh		
89	Y	**I.S.**		
90	Zr	Y, Rh		
95	Mo	Y, Rh		$^{79}BrO^+$
98	Mo	Y, Rh	-(0.146)(^{99}C)	$^{79}BrHO^+$
99	Ru	Y, Rh		
103	Rh	**I.S.**		
105	Pd	Rh		
106	Pd, Cd	Rh		ZrO,
107	Ag	Rh		ZrO
108	MoO	Rh		ZrO, MoO
109	Ag	Rh		ZrO, MoO
111	Cd	Rh		ZrO, MoO
112	Cd	Rh	-(0.040)(^{118}C)	ZrO, MoO
114	Cd	Rh	-(0.0269)(^{118}C)	MoO
118	Sn	Rh		
119	Sn	Rh		
120	Sn	Rh	-(0.0127)(^{125}C)	
121	Sb	Rh	-(0.124)(^{125}C)	$^{40}Ar^{81}Br^+$
123	Sb	Rh		
125	Te	Rh		
137	Ba	Rh		
138	Ba	Rh	-(8.91E-04)(^{139}C)-(2.82E-04)(^{140}C)	
139	La	Rh		
140	Ce	Rh		
185	Re	**I.S.**		
203	Tl	Re		
205	Tl	Re		
206	Pb	Re		
207	Pb	Re		
208	Pb	Re	+(1.0)(^{206}C)+(1.0)($^{2.07}$C)	

Notes:
- † Recommended for the PE instrument.
- ‡ Recommended for the HP instrument.

Table 6. Quality Control Items, Frequency, and Corrective Action.

QC Item	Frequency	Acceptance Criteria	Corrective Action
Tuning	After warm-up. Every 12 hours.	Manufacturer specifications	Check operating parameters, clean cones, replace malfunctioning components if necessary. Reevaluate the tuning.
ICV	After initial calibration.	90-110%	Verify that method parameters are valid, check calibration tables, replace calibration standards if necessary, and recalibrate the instrument.
ICB	Following ICV.	<RL for water samples	Prepare fresh calibration blank and/or increase the rinse time between analyses; reanalyze ICB; if within limits, continue the run; if still outside limits, determine the source of the problem, make the necessary corrections, and start from the beginning with a new calibration.
BS	After initial calibration.	70-130%	Verify that method parameters are valid, check calibration tables, replace calibration standards if necessary, prepare a fresh calibration blank, and recalibrate the instrument.
CCV	Before and after each batch. Every 10 sample. After re-calibration.	90-110%	Recalibrate the instrument. Follow method specific requirements (6020 or 200.8) as to what data prior to the CCV can be used.
CCB	Following CCV.	<RL for water samples	Prepare fresh calibration blank; reanalyze CCB; if within limits, continue the run; if still outside limits, eliminate the source of the contamination, clean the sample introduction system if necessary, and recalibrate the instrument. Reanalyze all samples from the last good CCB.
LCS	Every batch of 20 samples.	85-115%	Re-digest the entire sample batch and reanalyze.
LRB	Every batch of 20 samples.	<RL for water samples	Re-digest the entire sample batch and reanalyze.
Dp	Every 10 samples.	0-20%	If all other QC acceptable continue the run; sample result should be flagged; otherwise recalibrate instrument and reanalyze samples.
MS	Every 10 samples, prior to digestion.	70-130% with 200.8 75-125% with 6020	For 200.8 flag data if all other QC met; otherwise recalibrate instrument and reanalyze affected samples. For 6020 dilute original sample, re-spike this dilution, and reanalyze until within limits.
MSD†	Every 10 samples, prior to digestion.	0-20%	Same as for duplicate.
Dil‡	Every batch of 20 samples.	0-10%	If concentration analyzed >100 x MDL, flag data for possible matrix interference.
ICS-A‡	Every 12 hours.	<RL for water samples	Reevaluate the equations used for corrections, make the necessary adjustments, and recalibrate the instrument.
ICS-AB‡	Every 12 hours.	70-135%	Reevaluate the equations used for corrections, make the necessary adjustments, and recalibrate the instrument.
IS	With every analysis.	60-125% with 200.8 30-120% samples with 6020 80-120% for CCB with 6020	For samples, dilute 4+1 and reanalyze until in control. For CCV/CCB's recalibrate the instrument and reanalyze the affected samples.

NOTE:
- RL = Reporting Limit.
- Dil = Dilution Test.
- † MSD optional instead of duplicate sample.
- ‡ When Method 6020 referenced in the analytical report.

Appendix 1.

ICP/MS STANDARDS PREP LOG

Date	Standards	**IS id**	**ExpIRATION Date**	Analyst

Source: Inorganic Venture (IV-7 + IV-19)

Lot #: _____

Exp. Date:_____

ICP/MS INITIAL CALIBRATION VERIFICATION (ICV) PREP LOG

Date	ICV ID	IS id	**EXPIRATION DATE**	Analyst

Source ID **Lot#** **Expiration Date**

S = Spex _____ _____ _____

H = High Purity _____

E = ERA _____

APPENDIX 2. METALS DIGESTION

DATE _____

ANALYST _____

PREP BATCH MTD_____

2. SAMPLE#	BTL ID	SAMPLE AMOUNT GRAMS (g)	FINAL VOLUME (ml)	REMARKS	% TOTAL SOLIDS	DILUTION FACTOR
LCS -	-- --	50	**50**		——	1
LRB-	-- --	50	**50**		——	1

NOTES: *1) Spike values (unless otherwise stated):*
LCS = 0.05 ppm = 50 mls / 0.25 mls of 10 ppm WS1

2.1. Samples: Water = 0.05 ppm = 50 mls / 0.25 mls of 10 ppm WS1

Soil = 0.10 ppm = 50 mls / 0.50 mls of 10 ppm WS1
WS 1 - Lot # Y-MEB194014 + Z-CICP18146

2) Spile values for minerals (Ca-Mg-K-Na)
LCS = 1.0 ppm = 50 mls / 0.50 mls HP Stock Solution
Samples (Water or Soil) = 2.0 ppm = 50 mls / 1.0 mls HP Stock Solution
High Purity Stock Solution - Lot # 620719

3) HNO_3 Lot # 068109

SOP #078082: ANALYSIS OF POLYCHLORINATED BIPHENYLS BY GC

Revision: 10
Date: 04/29/08

Location: PCB Laboratory (Sample analysis)
Extraction Laboratory (sample extraction and clean-up procedures)

This method is restricted to use by, or under the supervision of trained analysts experienced in the use of gas chromatographs (GC) and skilled in the interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method as well as a working knowledge of Chrom Perfect and the PCB calculator software.

1.0 SCOPE AND APPLICATION

1.1 This method is used to determine the concentrations of polychlorinated biphenyls (PCBs) as Aroclors in extracts from solid and aqueous matrices. Open-tubular, capillary columns are employed with electron capture detectors (ECD). The target compounds listed below may be determined by a dual-column analysis system.

Parameter	*CAS #:*
Aroclor 1016	12674-11-2
Aroclor 1221	11104-28-2
Aroclor 1232	11141-16-5
Aroclor 1242	53469-21-9
Aroclor 1248	12672-29-6
Aroclor 1254	11097-69-1
Aroclor 1260	11096-82-5

1.2 Aroclors are multi-component mixtures. When samples contain more than one Aroclor, a higher level of analyst expertise is required to attain acceptable levels of qualitative and quantitative analysis. The same is true of Aroclors that have been subjected to environmental degradation ("weathering") or degradation by treatment technologies. Such weathered multi-component mixtures may have significant differences in peak patterns than those of Aroclor standards. Quantitation of PCBs as Aroclors is appropriate for many regulatory compliance determinations, but is particularly difficult when the Aroclors have been weathered by long exposure in the environment.

1.3 This method also includes different clean-up procedures used to assist in removing some of the more common found interferences.

1.4 This method describes a dual-column GC set up for the determination of total PCB Aroclor concentrations. A hardware configuration of two analytical columns joined to a single injection port is utilized.

1.5 The MDLs for Aroclors are determined annually on all instruments analyzing PCBs. Estimated quantitation limits are determined using the referenced SW 846 Method 8082, Table 1, specifically Table 4 for the data generated by this laboratory.

2.0 SUMMARY OF METHOD

2.1 A measured volume or weight of sample (approximately 1 L for liquids, 20 g for soil, and 0.3 g for oil samples) is extracted using the appropriate matrix-specific sample extraction technique[1].

Note: Unusually contaminated samples may be extracted with lower sample amounts. The reporting limits are corrected accordingly. Sample specific notes are added and samples flagged.

2.2 Aqueous samples are extracted at neutral pH with methylene chloride using 3510pcb SOP (separatory funnel)

2.3 Solid samples are extracted with hexane using Method 3550pcb SOP (ultrasonic)

2.4 Extracts for PCB analysis are subjected to a sulfuric acid/potassium permanganate cleanup (Method 3665) designed specifically for PCBs. This cleanup technique will remove (destroy) many single component

[1] Reference for this procedure is SW-846, Revision 3, December 1996 Method 3510C, Liquid Liquid Separatory Funnel Extraction, and, Method 3550C, Ultrasonic Extraction.

organochlorine or organophosphorus pesticides. Therefore, the analysis of pesticides is not converted by this SOP.

2.5 After the acid clean-up, a sulfur clean-up (§ 7.2) is performed. The activated copper reacts with the sulfur interference to form a precipitate (ex. $2RSH + Cu^{++} \rightarrow Cu(SR)^2 + 2H^+$, where R is the organic radical and SH is the mercaptan radical).

2.6 After the clean-up procedures, the extract is analyzed by injecting a 1-2 uL aliquot into a gas chromatograph with narrow-bore fused silica capillary column and electron capture detector (GC/ECD).

2.7 The chromatographic data may be used to determine the seven Aroclors in § 1.1

3.0 INTERFERENCES

3.1 Interferences co-extracted from the samples will vary considerably from matrix to matrix. While general cleanup techniques are provided, unique samples may require additional cleanup approaches to achieve desired degrees of discrimination and quantitation. Sources of interference in this method can be grouped into three broad categories.

3.1.1 Contaminated solvents, reagents, or sample processing hardware.

3.1.2 Contaminated GC carrier gas, parts, column surfaces, or detector surfaces.

3.1.3 Compounds extracted from the sample matrix to which the detector will respond.

3.2 Interferences by phthalate esters introduced during sample preparation can pose a major problem in PCB determinations.

3.2.1 Common flexible plastics contain varying amounts of phthalate esters that are easily extracted or leached from such materials during laboratory operations. Interferences from phthalate esters are minimized by avoiding contact with any plastic materials and checking all solvents and reagents for interferences.

3.2.2 Exhaustive cleanup of solvents, reagents, and glassware may be required to eliminate background phthalate ester contamination. These materials can be removed through the use of procedure described in §7.2 (sulfuric acid/permanganate cleanup), which is required for all PCB analysis.

3.2.3 Cross-contamination of clean glassware is avoided by scrupulously cleaning and then baking glassware in a 550ºC oven for 4 – 12 hours.

3.2.3.1 Clean all glassware as soon as possible after use by rinsing with the last solvent used. This is followed by detergent washing with hot water, and rinses with tap water and DI water. Drain the glassware, and let dry for several hours, or rinse with methanol and drain. Store dry glassware in a clean environment.

3.2.3.2 Elemental sulfur (S_8) is readily extracted from soil samples and may cause chromatographic interferences in the determination of PCBs. Sulfur is removed using procedure described in § 7.2).

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph - An analytical system complete with a gas chromatograph suitable for on-column and split-splitless injection and all required accessories including syringes, analytical columns, gases, electron capture detectors (ECD), and a data system.

4.2 GC columns - The dual-column arrangement used by this method involves a single injection that is split between two columns mounted in a single gas chromatograph. Each column is connected to a separate ECD detector.

4.2.1 Narrow-bore columns are installed in split/splitless (Grob-type) injectors.

4.2.2 30m x 0.25mm ID fused silica capillary column chemically bonded with SE-54 (DB-5, 0.25um film thickness).

4.2.3 30m x 0.25mm ID fused silica capillary column chemically bonded with 35 percent phenyl methylpolysiloxane (DB-608, 0.25um film thickness)

4.2.4 Column pair is mounted in a press-fit Y-shaped glass 3-way fused-silica connector (Supelco)

4.2.5 Column rinsing kit - Bonded-phase column rinse kit

4.2.6 Glass vials for both sample storage, cleaning, and standard preparation.

4.2.7 Hamilton Syringes (1ul to 1000 ul)

4.2.8 Sample Vials: 1.8 ml screw cap with PTFE liner and 4.0 ml calibrated screw cap

5.0 REAGENTS

5.1 Reagent grade or pesticide grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.

Note: Store the standard solutions (stock, composite, calibration, internal, and surrogate standards) at 4ºC in polytetrafluoroethylene (PTFE)-sealed amber containers, or in a dark area. When a lot of standards is prepared, the aliquots of that lot are stored in individual small vials. All stock standard solutions are replaced every 12 months or sooner depending if the QC indicates a problem. All working standard solutions are replaced after six months or sooner if routine QC indicates a problem.

5.2 Sample extracts are prepared by liquid - liquid extraction (3510pcb SOP) for waster samples or ultrasonic extraction (3550pcb SOP) for solid and oil samples. Both procedures undergo a solvent exchange step prior to analysis. The following solvents are necessary for dilution of sample extracts. All solvent lots should be pesticide quality or equivalent.

5.2.1 n-Hexane, C_6H_{14}

5.2.2 Methanol, CH_3OH

5.2.3 Acetone, CH_3COCH_3

5.3 DI Water

5.4 Stock standard solutions (1000 mg/L) Commercially prepared stock standard solutions are used. All standards that are purchased must be certified by the manufacturer or by an independent source.

5.5 Calibration standards for Aroclors

5.5.1 A standard containing a mixture of Aroclor 1016 and Aroclor 1260 includes many of the peaks represented in the other five Aroclor mixtures. A multi-point initial calibration employing a mixture of Aroclors 1016 and 1260 at five concentrations demonstrates the linearity of the detector response without the necessity of performing initial calibrations for each of the seven Aroclors.

5.5.2 The 1016/1260 mixture is used as a standard to demonstrate that a sample does <u>not</u> contain peaks that represent any one of the Aroclors. This standard can also be used to determine the concentrations of either Aroclor 1016 or Aroclor 1260, should they be present in a sample. Prepare a minimum of five calibration standards containing equal concentrations of both Aroclor 1016 and Aroclor 1260 by dilution of the stock standard with hexane. The curve concentrations bracket the linear range of the detector. (0.1 to 1.0 ppm, see Table 7; Also see Table 8 for standard preparation).

5.5.3 Method 8082 states that: "*Single standards of each of the other five Aroclors are required to aid the analyst in pattern recognition. Assuming that the Aroclor 1016/1260 standards have been used to demonstrate the linearity of the detector, these single standards of the remaining five Aroclors are also used to determine the calibration factor for each Aroclor…The concentrations should correspond to the mid-point of the linear range of the*

detector." At this time, a 5-point calibration curve for each Aroclor is employed. During a sample batch, if an Aroclor is identified in a sample, a standard of that Aroclor is analyzed. If the standard concentration falls within the control limits for that Aroclor, the sample is quantitated using the 5-point curve for that Aroclor.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples are sampled using 1L Amber glass jars or 4 –8 oz. glass jars for solids. Oil and wipe samples must only be collected in glass jars. (No plastic containers should be used, see §3.2)

6.2 Extracts are stored under refrigeration at 4ºC and are analyzed within 40 days of extraction.

7.0 PROCEDURE

7.1 Samples are extracted using the 3510PCB SOP and 3550PCB SOP.

7.1.1 Water samples are extracted at a neutral pH with methylene chloride using a separatory funnel

7.1.2 Solid samples are extracted with ultrasonic extraction.

7.1.3 Spiked samples are used to verify the applicability of the selected extraction technique for each new sample type (*i.e.* water, soil, oil, *etc.*). These samples are spiked with Aroclor 1016/1260 mixture at 0.500 mg/l concentration.

7.2 Extract clean-ups (MANDATORY FOR ANALYSIS AND QC SAMPLES)

7.2.1 **Sulfuric Acid Clean-up**[2]: This method is suitable for the rigorous cleanup of sample extracts prior to analysis for polychlorinated biphenyls. This method is used to reduce elevated baselines in overly complex chromatograms that prevent accurate quantitation of PCBs. This method cannot be used to cleanup extracts for other target analytes, as it will destroy most organic chemicals including the pesticides Aldrin, Dieldrin, Endrin, Endosulfan (I and II), and Endosulfan sulfate.

7.2.1.1 Place up to 3 ml of concentrated sulfuric acid into the final hexane extract 4 ml vial. Make sure this is done only in the hood area. Safety glasses should be worn at all times.

7.2.1.2 Place the cap on the vial and shake the extract with the acid. The acid will dissolve and carbonize the interferences commonly found in PCB samples.

7.2.1.3 Blanks and replicate analysis samples must be subjected to the same cleanup as the samples associated with them.

7.2.1.4 If the acid is "carbonized" or turns a dark brown color, new fresh acid can be added. Potassium Permanganate ($KMnO_4$) can be used when the sulfuric acid capacity is exceeded as an oxidizing reagent

7.2.2 **Sulfur Clean-up**[3]: This clean-up is performed at the GC laboratory station. Elemental sulfur is encountered in many liquid and sediment samples (commonly found in industrial wastes). The solubility of sulfur in various solvents is very similar to the organochlorine compounds of interest. Therefore, the sulfur interference follows along with the target compounds through the normal extraction and Florisil cleanup techniques. Sulfur will be quite evident in gas chromatograms obtained from electron capture detectors.

[2] Reference for Sulfuric Acid clean-up is SW-846, Revision 3, December 1996 Method 3665A: Sulfuric Acid
[3] Reference for Sulfur clean-up is SW-846, Revision 3, December 1996 Method 3660B: Sulfur Clean-up using copper.

7.2.2.1 Add approximately 1g of high grade, activated copper shots or copper powder to the final hexane sample extract. The activated copper is prepared by rinsing the copper with diluted nitric acid, rinsed with acetone and dried before use.

7.2.2.2 Vortex for 1 minute. Allow the copper to settle to the bottom. If a high precipitate occurs, the sample can be centrifuged. If the copper seems to be saturated, more can be added.

7.2.2.3 If copper powder is used, follow steps 7.2.2.1 – 7.2.2.2 and then carefully transfer the "cleaned" extract into another vial to prevent the "powder" from plugging up the auto syringe.

7.3 **Alumina Clean-up** is an adsorption technique used when the chromatogram base line is still elevated after the two clean-up procedures listed above were performed. Alumina clean-up[4] is used to separate the high molecular weight petroleum wastes from PCBs using liquid chromatography.

7.3.1 Alumina Column Clean-up: the column is packed with the required amount of adsorbent, topped with a water adsorbent (Na_2SO_4), and then loaded with the sample to be analyzed. Elution of the analytes is effected with a suitable solvent(s), leaving the interfering compounds on the column. The elute is then concentrated (if necessary).

7.3.2 Place a clean glass wool plug in the bottom of a 50 ml disposable chromatographic column.

7.3.2.1 On top of this plug, add 2 cm of anhydrous Na_2SO_4 and tap it down.

7.3.3 Pour about 10 g of activated (130°C for 12 hours) Alumina (150 mesh) into the column.

7.3.4 Tap it down and place 2 cm of anhydrous (130°C for 12 hours) Na_2SO_4 on top of the Alumina.

7.3.5 Rinse the column with 40 ml hexane and place the eluted hexane in a bottle labeled "Clean Used Hexane".

Note *The column should not be allowed to become dry throughout the rest of the analysis. The disposable column will stop flowing naturally when the solvent level is at the top of the Na_2SO_4.*

7.3.6 Weigh 0.3 g of oil (3%-5% of Alumina weight) and dissolve it in 2 ml hexane. *Note: This oil solution can be treated with concentrated H_2SO_4 before advancing to the next step.*

7.3.7 Using a long pasture pipette, place it on the column followed by rinse of the sample vial and the column with 2 ml hexane.

7.3.8 Place Azulene (400 mg/L in hexane) on the column. Azulene is a blue color indicator to help visually to follow the sample through the column. To make the Azulene solution, weigh 50 mg of high purity Azulene powder to 125 ml hexane.

7.3.9 Wash the column with 10 ml hexane and place the eluted hexane in a bottle labeled "Dirty Used Hexane". This washes the aliphatic interferences out of the sample.

7.3.10 Place surrogate standard mixture (in hexane – not methanol) on the column and rinse with 1 ml hexane.

7.3.11 Elute 80 ml 6% ethyl ether in hexane through the column and collect it for the analysis of PCBs and/or Pesticides.

7.3.12 Concentrate the eluted hexane from step 7.3.11 to 0.5 ml inside the Zymark Evaporation Station.

[4] Reference for Alumina clean-up is SW-846, Revision 3, December 1996 Method 3611B: Alumina Column Clean-up & Separation of Petroleum Products.

7.3.13 Transfer it quantitatively to a graduated 4 ml vial rinsing the evaporating tube with 0.5 ml hexane, bringing the volume of cleaned sample in the vial to 1 ml.

7.3.14 Add 3 – 4 ml H2SO4 (concentrated) to the vial cap and shake. *Note: this carbonizes and dissolves much of the remaining interfering compounds*.

7.4 GC conditions

7.4.1 **Dual-column analysis:** The dual-column/dual-detector has two 30m x 0.25mm ID fused-silica open-tubular columns of different polarities, and thus has different selectivities towards the target compounds. The columns are connected to an injection tee and ECD detectors. For types of columns see Table 1.

7.4.2 GC temperature programs and flow rates are listed in Table 1.

7.5 Calibration

7.5.1 Prepare calibration standards as described in the standard preparation logbook for PCBs/Pesticides (See Table 7). Both initial calibration and calibration verification standards are prepared using two different vendors to insure the quality and correctness of the standards.

Note: Prior to calibration, GC operating conditions should be established which optimize both peak resolution and sensitivity. The total run time should be long enough permit the elution of the second surrogate standard (DCBP). Once established, the same operating conditions must be used for both calibrations and sample analyses.

Note: Because of the sensitivity of the electron capture detector, the injection port and column should always be cleaned prior to performing the initial calibration.

7.5.2 PCBs are quantitatively determined as Aroclors. The initial calibration consists of the following protocols:

7.5.2.1 A standard containing a mixture of Aroclor 1016 and Aroclor 1260 will include many of the peaks represented in the other five Aroclor mixtures. Therefore, this mixture of 1016/1260 is used to demonstrate the linearity of the detector (RPD value of the curve) and that a sample does *not* contain peaks that represent any one of the Aroclors. This standard is also used to determine the concentrations of either Aroclor 1016 or Aroclor 1260, if they are present in a sample. Therefore, an initial five-point calibration is performed using the mixture of Aroclors 1016 and 1260.

7.5.2.2 Standards of the other five Aroclors are necessary for pattern recognition. SW 846 states: "*These standards are also used to determine a single-point calibration factor for each Aroclor… The Aroclor 1016/1260 mixture is used to determine correct detector response. The standards for the remaining five Aroclors are analyzed before the analysis of any samples, and may be analyzed before or after the analysis of the five 1016/1260"*.

7.5.2.3 A 5-point initial calibration for each of the 5 Aroclors is established. As long as a calibration verification standard at a midpoint concentration passes within the required control limits, samples are analyzed after the standard and computed based upon a 5-point calibration. In situations where only a few Aroclors are of interest for a specific project, the analyst can use a five-point initial calibration of each of the Aroclors of interest (*e.g*., five standards of Aroclor 1254 if this Aroclor is of concern) and not use the 1016/1260 mixture.

7.5.3 An auto sampler is used to inject 1-2uL volumes of each calibration standard. Depending on the volume of sample injected (*i.e.* 1 or 2 uL), the initial calibration, the QC samples, and samples must be analyzed with the same injection volume.

7.5.4 Record the peak area for each characteristic Aroclor peak to be used for quantitation using the Chrom Perfect Software.

7.5.5 A minimum of 3 peaks is chosen for each Aroclor, and preferably 5 peaks (See Table 2 for Quantification Peaks). The peaks are characteristic of the Aroclor in question. If possible, choose peaks in the Aroclor standards that are at least 25% of the height of the largest Aroclor peak. For each Aroclor, the set of 3 to 5 peaks should include at least one peak that is unique to that Aroclor. Use at least five peaks for the Aroclor 1016/1260 mixture, none of which should be found in both of these Aroclors.

7.5.6 Tables 2a and 2b list recommended diagnostic peaks in each Aroclor, along with their retention times on two GC columns suitable for dual-column analysis.

7.5.7 Calculate the calibration factor (CF) for each characteristic Aroclor peak in each of the initial calibration standards using the equation below.

$$CF = \frac{\text{Peak Area (or Height) in the Standard}}{\text{Total Mass of the Standard Injected (in nanograms)}}$$

7.5.8 Calibration factors from the initial calibration are used to evaluate the linearity of the initial calibration. The PCB calculator initial calibration report is generated which involves the calculation of the mean calibration factor, the standard deviation, and the relative standard deviation (RSD) for each Aroclor. The RSD for a given calibration range must be $\leq$ 20% in order to employ the calibration method described in § 7.5.7 [5]

7.5.9 A better representation of the calibration data may be obtained by narrowing the calibration range (by lowering the upper level standard) or by using a least-squares regression in accordance with SW-846, Method 8000. A linear regression may be used with a 5-point calibration curve, and the C.O.D. must be > 0.99. Additional standards must be analyzed in order to utilize a non-linear calibration (*see* Method 8000). All least-squares regressions used for OHIO VAP analysis will use a calculated intercept and quadratic fits will only be used for compounds exhibiting nonlinear behavior.

7.6 Retention Time Windows

~~7.6.1~~1.1.1 Retention time windows are crucial to the identification of target compounds. Absolute retention times are used for the identification of PCBs as Aroclors. Retention time windows are established to compensate for minor shifts in absolute retention times as a result of sample loading and normal chromatographic variability. The width of the retention time window is established by analyzing successive calibration standards of the same Aroclor mixture. The standard deviation (σ) of these repeated measurements is used to determine this window. The window is defined as the mean retention time $\pm$ 3σ. The results of this analysis are contained in Table 3. Given that the maximum window for an individual PCB is approximately 0.08 min., a nominal identification window of 0.1 minutes is utilized for all PCBs.

~~7.7~~1.7 Gas chromatographic analysis of sample extracts

~~7.7.1~~1.7.1 The same GC operating conditions used for the initial calibration are used for sample analyses and calibration verification.

[5] Reference for RSD values is SW-846, Revision 3, December 1996 Method 8000B Determinative Chromatographic Separations

~~7.7.2~~1.7.2 An analytical sequence of laboratory samples and QC samples should be templated after the following:

- Calibration verification mixture (1016/1260)
- Laboratory control sample
- Blank
- Reagent Blank
- Up to 20 samples
- Duplicate sample
- Matrix spike and/or matrix spike duplicate sample
- Batch-terminating standard

~~7.7.3~~1.7.3 Verify the calibration each 12-hour shift by injecting a calibration verification standard prior to conducting any sample analyses. A calibration standard must also be injected at intervals of not less than once every twenty samples. The calibration verification standard is a mixture of Aroclor 1016 and Aroclor 1260 from a different source then the initial calibration standards.

~~7.7.4~~1.7.4 The calibration factor for each analyte calculated from the calibration verification standard (CF_v) must not exceed a difference of more than ± 15 % when compared to the mean calibration factor from the initial calibration curve:

$$\% \text{ Difference} = \frac{\overline{CF} - CF_v}{\overline{CF}} \times 100$$

~~7.7.5~~1.7.5 Corrective action: if this criterion is exceeded for any calibration factor, inspect the gas chromatographic system to determine the cause and perform whatever maintenance is necessary before verifying calibration and proceeding with sample analysis. If routine maintenance does not return the instrument performance to meet the QC requirements based on the last initial calibration, then a new initial calibration must be performed. Please refer to Table 9 Quality Control Items, Frequency and Corrective Action

~~7.7.6~~1.7.6 Inject a 1-2 uL (See §7.5.3) aliquot of the concentrated sample extract.

~~7.7.7~~1.7.7 Qualitative identifications of target analytes are made by examination of the sample chromatograms, as described in §7.8.

~~7.7.8~~1.7.8 Quantitative results are determined for each identified Aroclor, using the procedures described in §7.9. If the responses in the sample chromatogram exceed the calibration range of the system, dilute the extract and reanalyze.

~~7.7.9~~1.7.9 Each sample analysis must be bracketed with an acceptable initial calibration, calibration verification standard(s) (each 12-hour shift), or calibration standards interspersed within the samples. When a calibration verification standard fails to meet the QC criteria, all samples that were injected after the last standard that last met the QC criteria must be re-injected.

~~7.7.10~~1.7.10 A batch of 20 sample injections (including QC samples, see above) may continue as long as the calibration verification standards and standards interspersed with the samples meet instrument QC requirements. A smaller batch than 20 samples can be analyzed in order to minimize the number of samples that must be re-injected if the standards fail the QC limits. The sequence ends when the set of samples has been injected or when quantitative QC criteria are exceeded.

~~7.7.11~~1.7.11 If the peak response is less than 2.5 times the baseline noise level, the validity of the quantitative result may be questionable. The analyst should consult with the source of the sample to determine whether further concentration of the sample or additional clean-ups are warranted.

~~7.7.12~~1.7.12 Use the calibration standards analyzed during the sequence to evaluate retention time stability. If any of the standards fall outside their daily retention time windows, the system is out of control. Determine the cause of the problem and correct it.

~~7.8~~1.8 Qualitative Identification (The equations governing the quantification, recovery and precision are referenced in the glossary section of the QA/QC manual)

~~7.8.1~~1.8.1 The identification of PCBs as Aroclors using this method with an electron capture detector is based on agreement between the retention times of peaks in the sample chromatogram with the retention times and windows established through the analysis of standards of the target analytes (*see* Tables 2a, 2b, and 3).

~~7.8.2~~1.8.2 Tentative identification of an analyte occurs when a peak from a sample extract falls within the established retention time window for a specific target analyte. Each tentative identification is confirmed using a second GC column of dissimilar stationary phase (as in the dual-column analysis), based on a clearly identifiable Aroclor pattern. The second column is calibrated and utilized for purposes of qualitative identification only.

~~7.8.3~~1.8.3 Tentative identification of an Aroclor pattern is based upon an approximate match of the relative characteristic peak heights between the sample and reference standard. Use the individual Aroclor standards (not the 1016/1260 mix) to determine the pattern of peaks on Aroclors 1221, 1232, 1242, 1248, and 1254. The patterns for Aroclors 1016 and 1260 are evident in the mixed calibration standards (See Figure 1).

~~7.8.4~~1.8.4 Positive identifications require a second column confirmation. Both QC samples and calibrations are verified with the second (confirmation) column.

~~7.9~~1.9 Quantitation of PCBs

~~7.9.1~~1.9.1 The quantitation of PCB residues as Aroclors is accomplished by comparison of the sample chromatogram to that of the most similar Aroclor standard. A choice must be made as to which Aroclor is most similar to that of the residue and whether that standard is truly representative of the PCBs in the sample.

~~7.9.2~~1.9.2 The characteristic quantitative peaks for each Aroclor are listed in Tables 2a and 2b and illustrated in Figure 1. The amount of Aroclor is calculated using the 5-point calibration curve for each of the 3 to 5 characteristic peaks chosen. The concentration is determined using the average concentration for each of the characteristic peaks.

~~*7.9.3*~~*1.9.3* In the event that the data system is unable to properly integrate the peaks of interest (typically due to peak co-elution or matrix interference), a manual integration procedure is performed. The applicability, procedure, and documentation of the manual integration are addressed in the SOP *Manual Integration of Chromatographic Data*.

~~*7.9.4*~~*1.9.4* Compound identifications are supported by at least one additional qualitative technique (i.e., second column confirmation).

~~*7.9.4.1*~~*1.9.4.1* For Ohio VAP samples, both columns must meet the calibration and QC criteria.

~~*7.9.5*~~*1.9.5* The second column quantitation can be applied upon request to any project. In this case, all QC requirements listed above are applied to each set of chromatographic data. PCB concentrations from each column are reported.

Note: Weathering of PCBs in the environment and changes resulting from waste treatment processes may alter the PCBs to the point that the pattern of a specific Aroclor is no longer recognizable. Samples containing more than one Aroclor present similar problems.

~~7.10~~1.10 Chromatographic System Maintenance as Corrective Action

~~7.10.1~~1.10.1 When system performance does not meet the established QC requirements, corrective action is required, and may include one or more of the following.

~~7.10.1.1~~1.10.1.1 Splitter connections for dual columns which are connected using a press-fit a Y-shaped fused-silica connector, clean and deactivate the splitter port insert or replace with a cleaned and deactivated splitter. Break off the first few inches (up to one foot) of the injection port side of the column. Remove the columns and solvent back-flush according to the manufacturer's instructions. If these procedures fail to eliminate the degradation problem, it may be necessary to deactivate the metal injector body and/or replace the columns.

~~7.10.2~~1.10.2 Metal injector body

~~7.10.2.1~~1.10.2.1 Turn off the oven and remove the analytical columns when the oven has cooled. Remove the glass injection port insert (instruments with on-column injection). Lower the injection port temperature to room temperature. Inspect the injection port and remove any noticeable foreign material.

~~7.10.2.2~~1.10.2.2 Place a beaker beneath the injector port inside the oven. Using a wash bottle, rinse the entire inside of the injector port with acetone and then rinse it with toluene, catching the rinsate in the beaker.

~~7.10.2.3~~1.10.2.3 Consult the manufacturer's instructions regarding deactivating the injector port body. Glass injection port liners may require deactivation with a silanizing solution containing dimethyldichlorosilane.

~~7.10.3~~1.10.3 Column rinsing

~~7.10.3.1~~1.10.3.1 The column should be rinsed with several column volumes of an appropriate solvent. Both polar and non polar solvents are recommended. Depending on the nature of the sample residues expected, the first rinse might be water, followed by methanol and acetone. Methylene chloride is a good final rinse and in some cases may be the only solvent required. The column should then be filled with methylene chloride and allowed to stand flooded overnight to allow materials within the stationary phase to migrate into the solvent. The column is then flushed with fresh methylene chloride, drained, and dried at room temperature with a stream of ultra-pure nitrogen.

8.0 QUALITY CONTROL AND METHOD PERFORMANCE

8.1 Quality control procedures necessary to evaluate the GC system operation include evaluation of retention time windows, calibration verification and chromatographic analysis of samples.

8.2 The QC Reference Sample is a sample that is analyzed prior to any analysis to demonstrate the initial proficiency of the analyst or the instrument. In cases when a new instrument is introduced or a new analyst, this sample when analyzed within the control limits of ±20% demonstrates the initial proficiency of the method. The QC reference sample should be spiked with in the linear calibration range. If Aroclors are not expected in samples from a particular source, then prepare the QC reference samples with a mixture of Aroclors 1016 and 1260.

8.3 Method Detection Limit (MDL). The MDL is determined for each of the PCB Aroclors as specified in the QA/QC manual. The results of this study for the past three years are given in Table 4. A new MDL study is performed annually for each Aroclor.

~~8.4~~1.4 Accuracy & Precision - Accuracy & Precision are determined for sample matrices of interest by computing the mean recovery and relative standard deviation of the LCS analysis. The upper and lower control limits for matrix spike recovery are determined as the mean $\pm 3\sigma$. The results for the water and solid matrices are given in Table 5.

~~8.5~~1.5 The Continuing Calibration Verification (CCV) concentrate should contain PCBs as Aroclors at mid point of the curve. If Aroclors are not expected in samples from a particular source, then prepare the QC reference samples with a mixture of Aroclors 1016 and 1260. However, when specific Aroclors are known to be present or expected in samples, the specific Aroclors should be used for the CCV.

~~8.5.1~~1.1.1 The frequency of analysis of the CCV analysis is equivalent to a minimum of 1 per 12 hours not to exceed 20 samples between CCVs. A closing calibration verification is required at the end of the run.

~~8.5.2~~1.1.2 If the averaged recovery of compounds found in the CCV is less than 85% or greater than 115% of the true value, the laboratory performance is judged to be out of control, and the problem must be corrected. Please refer to Table 9 Quality Control Items, Frequency and Corrective Action

~~8.5.3~~1.1.3 [A new set of calibration standards should be prepared and analyzed.

~~8.5.4~~1.1.4 Include a calibration standard after each group of 20 samples. The response factors for the calibration should be within 15 percent of the initial calibration. When this continuing calibration is out of this acceptance window, the laboratory should halt the analysis and take corrective action. Please refer to Table 9 Quality Control Items, Frequency and Corrective Action

~~8.6~~1.6 Sample Quality Control for Preparation and Analysis – A batch includes the analysis of QC samples including a method blank, a matrix spike, matrix spike duplicate and/or a duplicate (per client request), and a laboratory control sample (LCS). Surrogates are added to each field and QC sample.

~~8.6.1~~1.6.1 Documenting the effect of the matrix should include the analysis of at least one matrix spike and one duplicate unspiked sample or one matrix spike/matrix spike duplicate pair. The decision on whether to prepare and analyze duplicate samples or a matrix spike/matrix spike duplicate must be based on a knowledge of the samples in the sample batch. If samples are not expected to contain target analytes, laboratories should use a matrix spike and matrix spike duplicate pair, spiked with the Aroclor 1016/1260 mixture. However, when specific Aroclors are known to be present or expected in samples, the specific Aroclors should be used for spiking. If samples are expected to contain target analytes, then laboratories may use one matrix spike and a duplicate analysis of an unspiked field sample.

~~8.6.2~~1.6.2 If a sample is qualitatively identified as having an Aroclor which was *not* analyzed as part of the QC samples, the sample is subsequently re-analyzed along with a calibration check standard of the appropriate type.

~~8.6.3~~1.6.3 A Laboratory Control Sample (LCS) is included with each analytical batch. The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. The LCS is spiked with the same analytes at the same concentrations as the matrix spike. When the results of the matrix spike analysis indicate a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix.

~~8.7~~1.7 Surrogate recoveries - Surrogate recovery data is analyzed from individual samples in order to determine matrix-specific control limits. The surrogate standard must contain the following compounds TCX (tetrachloro-m-xylene) and DCBP (decachlorobiphenyl). The surrogate standard is prepared by the GC analyst at a concentration of 0.03mg/l. and utilized by the extraction analyst. Table 6 contains surrogate recovery data and laboratory-established control limits, and is inclusive of the effect of copper and sulfuric acid clean-up procedures. The surrogate standards are calibrated using a 5-point curve.

~~8.8~~1.8 The MS/MSD and LCS spikes contain a mixture of Aroclor 1016/1260. This spike should be prepared at a concentration at or below the medium level of the PCB curve. The MS/MSD and LCS standard is prepared by the GC analyst at a concentration of 0.5mg/l.

9.0 APPENDICES

Table 1. GC Operating Conditions For PCBs As Aroclors (Dual Column)

Property	*Setting*
Column #1	DB-5, 30m x 0.25mm ID, 0.25µm film thickness
Column #2	DB-608, 20 m x 0.25 mm ID, 0.25 µm film thickness
Carrier gas flow (He)	6ml/min
Makeup gas flow (N_2)	20ml/min
Temperature program	T_o = 180ºC, hold 1.0min 180ºC to 250ºC, ramp at 6.0ºC/min T_f = 250ºC, hold 2.34min
Injector temperature	250ºC
Detector temperature	320ºC
Injection volume	1-2 µl, no air plug
Solvent	Hexane
Injector	On-column
Detector	Dual ECD
Range attenuation	10/8
Splitter	Supelco press-fit Y-shaped inlet splitter

Table 2a. Summary of Characteristic PCB Peak Retention Times (DB-5 Column) †

Peak	*1016*	*1221*	*1232*	*1242*	*1248*	*1254*	*1260*
1	1.85	‡1.73	1.71	1.84	2.30	3.45	5.08
2	‡2.30	‡1.82	‡1.86	‡2.30	‡2.90	4.63	6.46
3	‡2.53	‡1.88	2.32	‡2.53	3.06	‡5.11	‡7.07
4	‡2.89	2.93	2.55	‡2.89	3.44	5.69	7.37
5	‡3.05		‡2.91	‡3.04	‡3.80	‡5.92	‡7.75
6	3.16		‡3.06	3.16	‡4.02	‡6.53	8.18
7	‡4.01		‡3.18	‡4.00	‡4.61	7.14	8.77
8			4.02	4.94	‡4.96	‡7.78	‡9.54
9			4.96		5.91	8.47	‡10.30
10							12.07

Table 2b. Summary of Characteristic PCB Peak Retention Times (DB-608 Column) †

Peak	*1016*	*1221*	*1232*	*1242*	*1248*	*1254*	*1260*
1	2.58	2.32	2.30	2.58	4.00	6.64	7.93
2	3.26	2.52	2.60	3.25	4.69	7.61	8.37
3	4.29	2.61	3.27	3.99	5.35	7.90	8.76
4	4.55		4.02	4.28	6.08	8.36	9.26
5	5.34		4.31	4.53	6.20	8.79	9.86
6			4.56	6.06	6.84	9.44	10.05
7			6.08	6.82	7.89	9.90	10.98
8			6.84		8.34		11.53
9							12.75
10							

†: Based upon data from 09/99 to 10/99 (*see* \PCB*.CAL); retention times given in minutes.
‡: Quantitation peak.

Table 3. Retention Time Extraction Windows†

Aroclor	*n*	*σ (min)*	*Window (min)*
PCB-1016	204	0.0196	±0.0558
PCB-1221	n/a		
PCB-1232	n/a		
PCB-1242	238	0.0275	±0.0825
PCB-1248	48	0.0244	±0.0732
PCB-1254	120	0.0220	±0.0660
PCB-1260	120	0.0140	±0.0420
Cumulative Window – All PCBs	730	0.0219	±0.0657

†: Based upon data from 06/99 to 09/99 (*see* PCB_STD.XLS).

Table 4. PCB Method Detection Limit Studies (all units in ppb)†

Aroclor	*Year*	*IDL*	*MDL – water*	*MDL – soil*	*PQL – water*	*PQL – soil*
PCB-1016	1998	0.02			0.1	330
	1999	0.05			0.1	330
	2000	0.008			0.1	330
	2001	0.02			0.1	330
	2003	0.008			0.1	330
	2004		0.1	3	0.1	330
PCB-1221	1998	0.04			0.1	330
	1999	0.03			0.1	330
	2000				0.1	330
	2001	0.008			0.1	330
	2003	0.01			0.1	330
	2004		0.05	2	0.1	330
PCB-1232	1998	0.02			0.1	330
	1999	0.06			0.1	330
	2000				0.1	330
	2001	0.02			0.1	330
	2003	0.007			0.1	330
	2004		0.06	4	0.1	330
PCB-1242	1998	0.04			0.1	330
	1999	0.09			0.1	330
	2000	0.03			0.1	330
	2001	0.009			0.1	330
	2003	0.006			0.1	330
	2004		0.1	3	0.1	330
PCB-1248	1998	0.06			0.1	330
	1999	0.04			0.1	330
	2000	0.02			0.1	330
	2001	0.02			0.1	330
	2003	0.006			0.1	330
	2004		0.1	4	0.1	330
PCB-1254	1998	0.03			0.1	330
	1999	0.06			0.1	330
	2000	0.01			0.1	330
	2001	0.02			0.1	330
	2003	0.01			0.1	330
	2004		0.08	3	0.1	330
PCB-1260	1998	0.04			0.1	330
	1999	0.04			0.1	330
	2000	0.02			0.1	330
	2001	0.01			0.1	330
	2003	0.02			0.1	330
	2004		0.1	4	0.1	330

†: Based upon data from 1998 to 2004 (*see* PCB_STAT.XLS).

Table 5. Matrix Spike Accuracy and Precision Data†

Aroclor	*Matrix*	*Spike*	*n*	*%Rec.*	*%RSD*	*LCL(%)*	*UCL(%)*
PCB-1016/1260	Water	0.5 µg/l	457	91.4	10.8	59.1	123.7
PCB-1016/1260	Soil	25.0 µg/kg	567	88.2	11.8	52.9	123.4

†: Based upon data from 01/02 to 12/03 (*see* PCB_STAT.XLS).

Table 6. Surrogate Standard Recovery Ranges†

Compound	*Matrix*	*Spike*	*n*	*%Rec.*	*%RSD*	*LCL(%)*	*UCL(%)*
TCX (Tetrachloro-m-xylene)	Water	0.01 µg/l	845	85.7	16.8	35.4	136.0
	Soil	0.50 µg/kg	445	82.6	16.8	32.2	133.1
DCBP (Decachlorobiphenyl)	Water	0.01 µg/l	810	81.9	18.8	25.5	138.4
	Soil	0.50 µg/kg	393	81.8	18.8	25.4	138.2

†: Based upon sample data results from 01/02 to 12/03 (*see* PCB_STAT.XLS). These data include the effect of copper and sulfuric acid clean-up procedures, which are performed on all samples.

Table 7. Calibration Concentration Mixtures

Aroclor	C_1 *(ppm)*	C_2 *(ppm)*	C_3 *(ppm)*	C_4*(ppm)*	C_5*(ppm)*
PCB-1016	0.1	0.3	0.5	0.8	1.0
PCB-1221	0.1	0.3	0.5	0.8	1.0
PCB-1232	0.1	0.3	0.5	0.8	1.0
PCB-1242	0.1	0.3	0.5	0.8	1.0
PCB-1248	0.1	0.3	0.5	0.8	1.0
PCB-1254	0.1	0.3	0.5	0.8	1.0
PCB-1260	0.1	0.3	0.5	0.8	1.0
PCB-1016/1260†	0.1	0.3	0.5	0.8	1.0

†: The concentration for the 1016/1260 mixture is the concentration of each Aroclor.

Table 8. Standard Preparation for Calibration Mixtures

Revised: 9/18/01

Mixture Volume: 1000 ul
Mixture Concentration: 100 mg/l
Mixture Name: ***PCB 1016/1260***

Compound/Mix	*C(stock) mg/l*	*C(final) mg/l*	*V(stock) ul*
PCB 1016	1000	100	100.00
PCB 1260	1000	100	100.00
Solvent - Hexane			800.00

Mixture Volume: 1000 ul
Mixture Concentration: **0.5** mg/l

Compound/Mix	*C(stock) mg/l*	*C(final) mg/l*	*V(stock) ul*
PCB 1016/1260	100	0.5	5.00
TCX/DCBP	1.0	0.006	6.00
Solvent - Hexane			989.00

Mixture Volume: 1000 ul
Mixture Concentration: **0.1** mg/l

Compound/Mix	*C(stock) mg/l*	*C(final) mg/l*	*V(stock) ul*
PCB 1016/1260	100	0.1	1.00
TCX/DCBP	1.0	0.002	2.00
Solvent - Hexane			997.00

Mixture Volume: 1000 ul
Mixture Concentration: **0.8** mg/l

Compound/Mix	*C(stock) mg/l*	*C(final) mg/l*	*V(stock) ul*
PCB 1016/1260	100	0.8	8.00
TCX/DCBP	1.0	0.008	8.00
Solvent - Hexane			984.00

Mixture Volume: 1000 ul
Mixture Concentration: **0.3** mg/l

Compound/Mix	*C(stock) mg/l*	*C(final) mg/l*	*V(stock) ul*
PCB 1016/1260	100	0.3	3.00
TCX/DCBP	1.0	0.004	4.00
Solvent - Hexane			993.00

Mixture Volume: 1000 ul
Mixture Concentration: **1.0** mg/l

Compound/Mix	*C(stock) mg/l*	*C(final) mg/l*	*V(stock) ul*
PCB 1016/1260	100	1	10.00
TCX/DCBP	1.0	0.010	10.00
Solvent - Hexane			980.00

Table 9. Quality Control Items, Frequency and Corrective Action

QC Item	Frequency	Acceptance Criteria	Corrective Action
Initial Calibration (IC)	Prior to all analytical runs	Method-based	Examine the entire analytical system; some or all of the following: clip/replace column, heat detector, change injection septum, replace calibration standards, re-calibrate.
Continuing Calibration (CCV)	20 Samples / 12 hours	Method Based	Examine the entire analytical system; some or all of the following: clip/replace column, heat detector, change injection septum, replace calibration standards, re-calibrate; failure requires the re-analysis of all associated analytical runs.
LCS and MS	20 samples	Lab-based	A failed LCS should be re-extracted and re-analyzed. A failed MS requires no action provided that the LCS is acceptable. If additional sample exists, the samples associated with a failed LCS should be re-extracted and re-analyzed.
Duplicate or MSD	20 samples	n/a	Relative Percent Differences (RPDs) are computed and included in the QC report
Method Blank	20 samples	n/a	Method blank contamination is flagged on the analytical report for any identified target compound. Blanks indicative of contaminated extraction glassware should result in a thorough re-cleaning of the affected glassware. If the method blank contamination for a batch is atypical, the blank should be re-extracted and re-analyzed. If additional sample exists, the samples associated with a failed, re-extracted blank should also be re-extracted and re-analyzed.
Surrogate Standard	All samples	Lab-based	Adverse matrix effects on areas/recoveries are demonstrated either by screening the extract of re-analyzing the extract within a 12-hour QC batch. The resulting analytical report is flagged appropriately. If additional sample exists, the sample should be re-extracted prior to re-analysis if a matrix effect cannot be demonstrated.
Target Compound	All samples	Method-based	Target compounds beyond the calibration range are diluted and re-analyzed and/or flagged as estimated on the analytical report.

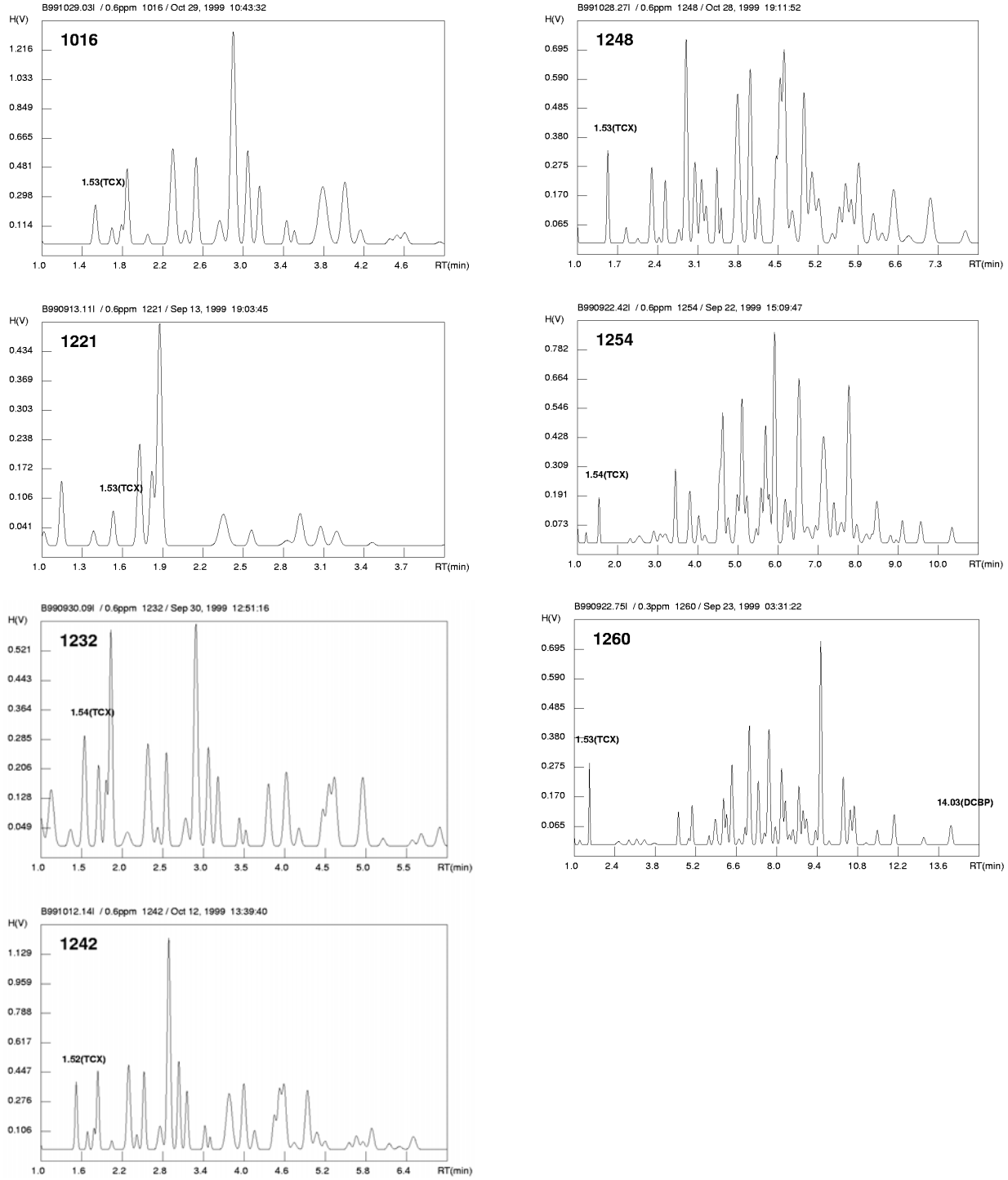

Figure 1. Example Aroclor chromatographic patterns from midpoint calibration standards for PCB 1016, 1221, 1232, 1242, 1248, 1254, and 1260 (column DB-5); based upon data from 09/99 to 10/99; see Table 2a for an enumeration of the retention times of the characteristic peaks.

10.0 APPROVAL AND ISSUE:

_____

Analyst Date

_____

Andy Ball, QA Officer Date

_____

Maya V. Murshak, Technical Director Date

METHOD 3550B PCBS/PESTICIDES

Location: Extraction Laboratory; GC/ECD Laboratory

These procedures are restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with these techniques and methods.

1.0 SCOPE AND APPLICATION

1.1 This method is used for extracting nonvolatile and semivolatile organic compounds from solids such as soils, sludges, and wastes. The ultrasonic process ensures intimate contact of the sample matrix with the extraction solvent. The extracts are cleaned up prior to analysis.

2.0 SUMMARY OF METHOD

2.1 For most samples, 1g - 30g of sample (depending on the matrix; typically 1g for oils and 30g for soils) is mixed with anhydrous sodium sulfate to form a free-flowing solid. Add hexane and extract three times using ultrasonic extraction. The extract is separated from the sample by centrifugation or through a filter paper. The extract is ready for cleanup and analysis.

3.0 INTERFERENCES

3.1 The decomposition of some analytes has been demonstrated under basic extraction conditions. Organochlorine pesticides may de-chlorinate.

3.2 Degradation of PCBs, as well as more complex matrix (i.e. oil, tar, sulfur, etc.) can interfere with the "clarity" of the chromatograms.

4.0 APPARATUS AND MATERIALS

4.1 Apparatus for grinding dry waste samples

4.2 Ultrasonic device – Branson Sonifier, Model 450

4.3 Ultrasonic Disrupter - power wattage of 300 watts, with pulsing.

- 4.3.1 3/4" horn
- 4.3.2 Sonabox – (Ultrasonics #432B)

4.4 Apparatus for percent dry weight

- 4.4.1 Drying oven (105ºC - 120ºC)
- 4.4.2 Desiccator
- 4.4.3 Crucibles – disposable aluminum
- 4.4.4 Glass pipettes - 1ml, disposable
- 4.4.5 Beakers – 250ml
- 4.4.6 Filter paper - Whittman No. 41

4.5 Zymark Evaporation Station

4.6 Evaporation tubes

4.7 Water bath - Heated, capable of temperature control (± 5ºC).

4.8 Balance - Top-loading, capable of accurately weighing to the nearest 0.01 g.

4.9 Vials – 4 ml, with polytetrafluoroethylene (PTFE)-lined screw caps.

4.10 Glass scintillation vials - 20-mL, with PTFE-lined screw caps.

4.11 Tongue depressors, disposable

4.12 Drying column - 50ml Pyrex chromatographic column with Pyrex glass wool at bottom.

4.13 Syringe - 5-mL.

5.0 REAGENTS

Note: Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. Reagents should be stored in glass to prevent the leaching of contaminants from plastic containers.

5.1 Reagent water

5.2 Sodium sulfate (granular, anhydrous), Na_2SO_4.

5.3 Extraction - All solvents must be pesticide quality or equivalent

5.3.1 Hexane, C_6H_{14}, boiling point 68.7°C

5.3.2 Nonchromix

6.0 SAMPLE CONTAINERS AND STORAGE

6.1 All samples for the analysis of Pesticides and PCBs should be stored in 4 oz. non-preserved glass containers only.

6.2 Approximately 2g to 30g (depending on the matrix) of sample is needed for extraction.

6.3 Refrigerate at 4ºC.

6.4 Holding Time for solid samples is 14 days to extraction and 40 days after extraction

7.0 GLASSWARE CLEANING

7.1 Immediately after use rinse glassware with the last solvent used in it. Drain it into a bottle labeled "Wash Solvent"

7.2 Wash well with hot water and laboratory detergent by hand.

7.3 Rinse three times with hot tap water followed by three times with DI water.

7.4 Place in dishwasher.

7.5 Rinse with acetone.

7.6 Rinse with hexane.

7.7 All PCB glassware is placed in a furnace oven at 550°C for 12 hours prior to use. (This is done to avoid any cross contamination).

7.8 Separatory Funnels are washed with 40 ml hexane and evaporated to 1 ml final volume to analyze for cross contamination.

Note: All glassware must be immaculate. Glassware should be cleaned as soon as possible after the extraction. A quick reference guide is posted in the extraction laboratory. If the glassware is extremely dirty or has not been treated in more than a week, coat and soak it with concentrated H_2SO_4 preferably with Nonchromix added. Then rinse with tap water and follow the cleaning procedure above.

8.0 PROCEDURE[1]

8.1 The extraction device has a minimum of 300 watts of power and is equipped with ¾" size disrupter horns.

8.1.1 The horn is maintained, by inspection of the horn tip for excessive wear that would be seen as "cavities" on the bottom of the instrument.

8.1.2 Samples are prepared by thorough mixing with sodium sulfate so that it forms a free-flowing solid prior to the addition of the solvent.

8.1.3 Three extractions are performed with hexane solvent.

8.1.4 Extraction is performed in the specified pulse mode, and the horn tip is positioned just below the surface of the solvent yet above the sample.

[1] Reference for this procedure is SW-846, Revision 3, December 1996 Method 3550B, Ultrasonic Extraction

8.1.5 Very active mixing of the sample and the solvent must occur when the ultrasonic pulse is activated. Observe such mixing at some point during the extraction process to insure that the placement of the horn is correct.

8.2 Sample handling

8.2.1 Sediment/soil samples - Decant and discard any water layer on a sediment sample. Mix sample thoroughly, especially composited samples. Discard any foreign objects such as sticks, leaves, and rocks.

8.2.2 Waste samples - Samples consisting of multiple phases are separated into two phases. Per client request one or the other phase is extracted. If both phases need to be extracted, two separate extractions are performed.

8.2.3 Dry waste samples amenable to grinding - Grind or drill the waste so that it either passes through a 1-mm sieve or can be extruded through a 1-mm hole. Minimum of 10g of sample should pass through the sieve.

8.2.4 Gummy, fibrous, or oily materials not amenable to grinding are cut, shredded, or otherwise reduced in size to allow mixing and maximum exposure of the sample surfaces for the extraction.

8.3 Extraction method:

8.3.1 Weigh approximately 1-30 g of sample (depending on the matrix) into a 250-ml beaker. Typically, on a standard soil, 30 grams of sample is used. Record the weight to the nearest 0.1 g.

8.3.2 Nonporous or wet samples (gummy or clay type) that do not have a free-flowing sandy texture must be mixed with 60 g of anhydrous sodium sulfate, using disposable tongue depressors. If required, more sodium sulfate may be added. After addition of sodium sulfate, the sample should be free flowing.

8.3.3 Add 1.0 ml of the surrogate standard solution to all samples, spiked samples, QC samples, and blanks.

8.3.4 For the sample in each batch selected for spiking (*i.e.* LCS, MS, MSD), add 1.0 ml of the matrix spiking solution.

8.3.5 Add 60 ml of Hexane to the beaker.

8.3.6 Place the bottom surface of the tip of the 3/4 inch disrupter horn about 1/2 inch below the surface of the solvent, but above the sediment layer.

8.3.7 Extract ultrasonically for 3 minutes, with output control knob set at 6 and with mode switch on Pulse (pulsing energy rather than continuous energy) and percent-duty cycle knob set at 50% (energy on 50% of time and off 50% of time).

8.3.8 Decant through a conical gravity filter (Whatman No. 41 filter paper) and sodium sulfate to catch any excess water.

8.3.9 Repeat the extraction two or more times with an additional 60 ml portion of hexane. Pour off the solvent after each ultrasonic extraction. On the final ultrasonic extraction, pour the entire sample onto the filter with extraction solvent.

8.4 Evaporation method

8.4.1 Place the concentrator tube in the TurboVap Evaporation Station, that has the water bath @ 42ºC (+/- 2°C), 21 psi, until 1 ml final volume.

8.4.2 Transfer the sample extract to a 4 ml vial. Adjust up to 1 ml final volume.

8.4.3 Final 1 ml adjustment: if the transfer is greater then 1 ml, use the clean nitrogen gas to evaporate to the meniscus on the vial marked with a 1 ml mark and compare to the calibrated vial. If the transferred extract is less then 1 ml, add final extract solvent to the meniscus.

8.4.3.1 The vials are calibrated per Lot # of vials with a NIST traceable syringe. One vial is filled with exactly 1 ml for comparison.

8.4.4 Follow with clean –up procedures as appropriate for the analysis.

9.0 PCB CLEAN-UPS (SEE PCB ANALYSIS SOP FOR DETAILS)

9.1 Sulfuric Acid Clean-up[2]

9.2 Sulfur Clean-up[3]

9.3 Alumina Column Clean-up

9.4 Quality Control

9.5 Samples are extracted in batches of 20 samples or less. For every batch there should be an LCS, MS, and MSD/DUP depending on the clients request. All the reagent blanks, matrix spikes, or replicate samples should be subjected to exactly the same analytical procedures as those used on actual samples. In case of the client not providing the necessary sample amount to perform the required QC samples, equivalent laboratory matrix samples can be analyzed.

9.6 The surrogate standard must contain the following compounds TCX (tetrachloro-m-xylene) and DCBP (decachlorobiphenyl). The surrogate standard is prepared by the GC analyst at a concentration of 0.01mg/l.

9.7 The MS/MSD and LCS spikes will contain a mixture of Aroclor 1016/1260. MS/MSD spike should be prepared at a concentration at or below the medium level of the PCB curve. The MS/MSD and LCS standard is prepared by the GC analyst at a concentration of 0.05mg/l.

9.8 New lot blanks are analyzed to insure the purity of the materials and reagents.

Note: The working standards are prepared every six to 12 months or when evidence of bias or trends are observed to show that the standards need to be replaced.

10.0 DOCUMENTATION

All pertinent information is entered into an extraction logbook (See Table 1). The extraction log sheet has to contain the following information on the header/table:

- Date
- ANALYSTS INITIALS
- Method
- Surrogate/MS/MSD/LCS standard unique traceability ID
- Hexane Lot #
- Sample I.D. #
- Matrix
- Sample weight
- Solvent ID & Volume (ml)
- Final extract volume
- Surrogate standard spike volume
- MS spike volume
- Additional clean-ups (i.e. alumina) are marked in the notes section as "C"

11.0 REFERENCES

11.1 Method 3550 SW

[2] Reference for Sulfuric Acid clean-up is SW-846, Revision 3, December 1996 Method 3665A: Sulfuric Acid
[3] Reference for Sulfur clean-up is SW-846, Revision 3, December 1996 Method 3660B: Sulfur Clean-up using copper.

12.0 APPROVAL & ISSUE:

Analyst	Date
Andy Ball, QC Officer	Date
Maya V. Murshak, QA Director	Date

SOP #043510: SEPARATORY FUNNEL LIQUID-LIQUID EXTRACTION BY METHOD 3510C

Revision: 9
Date: 12/12/06

Location: Extraction Laboratory
GC/ECD Laboratory

These procedures are restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with these techniques and methods.

1.0 SCOPE AND APPLICATION

This SOP is a procedure for isolating organic compounds from aqueous samples. This method is applicable to the isolation and concentration of water-insoluble and slightly water-soluble organics in preparation for a variety of chromatographic procedures, specifically PCBs and Pesticides.

2.0 SUMMARY OF METHOD

2.1 A measured volume of sample, usually 1 liter, at a pH 5-9, is extracted with methylene chloride using a separatory funnel.

2.2 The extract is concentrated, and, exchanged into hexane solvent which is also compatible with the cleanup procedures utilized for PCBs.

2.3 Clean glassware and matrix cleanup procedures are used to obtain the optimum analytical chromatograms.

3.0 INTERFERENCES

3.1 The decomposition of some analytes has been demonstrated under basic extraction conditions. Organochlorine pesticides may de-chlorinate.

3.2 Degradation of PCBs, as well as more complex matrices (i.e. oil, tar, sulfur, etc.) can interfere with the "clarity" of the chromatograms.

4.0 APPARATUS AND MATERIALS

4.1 Separatory funnel - 2-liter, with polytetrafluoroethylene (PTFE) stopcock.

4.2 Evaporation tubes, 250-ml volume, Zymark with end point of 0.5 ml.

4.3 Zymark Turbo Vap II Concentration Station with temperature control water bath.

4.4 Vials – 4 ml, glass with PTFE-lined screw caps or crimp tops.

4.5 pH indicator paper - pH range including the desired extraction pH.

4.6 Glass beakers, 250 ml.

4.7 Glass funnel and ring stand

4.8 Filter paper, coarse grade

4.9 Adhesive labels

4.10 Syringe - 5-mL NIST certified

4.11 Graduated cylinder - 1-liter

5.0 REAGENTS

Note: Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. Reagents should be stored in glass to prevent the leaching of contaminants from plastic containers.

5.1 Reagent water

5.2 Sodium sulfate (granular, anhydrous), Na_2SO_4..

5.3 Sulfuric acid, concentrated, as well as solution (1:1 v/v), H_2SO_4. Slowly add 50 mL of H_2SO_4 to 50 ml of DI water.

5.4 Extraction/exchange solvents - All solvents must be pesticide quality or equivalent

5.4.1 Methylene chloride, CH_2Cl_2 , boiling point 49°C

5.4.2 Hexane, C_6H_{14}, boiling point 68.7°C

5.4.3 Nonchromix

6.0 SAMPLE CONTAINERS AND STORAGE

6.1 All samples for the analysis of Pesticides and PCBs should be stored in Amber glass containers only.

6.2 Approximately 1L volume of sample is needed for extraction.

6.3 Refrigerate at 4ºC.

6.4 The holding time for samples is 7 days until extraction and 40 days thereafter.

Note: If samples contain significantly less volume then 1L, QA & client need to be notified. Higher detection limits will be applied to low volume extracts.

7.0 GLASSWARE CLEANING

7.1 Immediately after use rinse glassware with the last solvent used in it. Drain it into a bottle labeled "Wash Solvent"

7.2 Wash well with hot water and laboratory detergent by hand.

7.3 Rinse three times with hot tap water followed by three times with DI water.

7.4 Place in dishwasher.

7.5 Rinse with acetone.

7.6 Rinse with hexane.

7.7 All PCB glassware is placed in a furnace oven at 550°C for 12 hours prior to use. (This is done to avoid any cross contamination).

7.8 Separatory Funnels are washed with 40-ml hexane and evaporated to 1-ml final volume to analyze for cross contamination.

Note: All glassware must be immaculate. Glassware should be cleaned as soon as possible after the extraction. A quick reference guide is posted in the extraction laboratory. If the glassware is extremely dirty or has not been treated in more than a week, coat and soak it with concentrated H_2SO_4 preferably with Nonchromix added. Then rinse with tap water and follow the cleaning procedure above.

8.0 PROCEDURE[1]

8.1 Mark the level of sample on the outside of the bottle. Sample volume needed for extraction should be close to 1L. Pour the sample into the 2-liter separatory funnel.

8.2 Pipette 1.0 ml of the surrogate spiking solution into the funnel and swirl the sample.

8.2.1 For matrix spike samples and LCS, add 1ml surrogate and 1 ml matrix spike standard.

8.2.2 Check the pH of the sample with wide-range pH paper and adjust the pH, if necessary, to a pH between 6 – 9.

8.3 Add 60 ml of methylene chloride into the sample bottle to rinse it and transfer this rinse solvent to the separatory funnel.

8.4 Shake the separatory funnel vigorously for 1 minute on a vertical placement with full ventilation at motor speed 68. Seal the separatory funnel and shake vigorously for 2 minutes on a horizontal placement at motor speed 70 in accordance with Table 1 shake program. Initial venting should be done immediately after the separatory funnel has been sealed and shaken once. The separatory funnel should be vented into a hood to avoid exposure of the analyst to solvent vapors. Allow the organic layer to separate from the water phase for 1 to 10 minutes, depending on the matrix of the sample.

[1] Reference for this procedure is SW-846, Revision 3, December 1996 Method 3510C, Liquid Liquid Separatory Funnel Extraction

Note: 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.

8.5 Drain the extract through a filter filled with approximately 10g of Na_2SO_4 into a 250-ml glass Zymark evaporation tube.

8.6 Add 60ml methylene chloride to the separatory funnel. Seal and shake the separatory funnel vigorously for 1 minute on a horizontal placement at motor speed 74. Vent the funnel and continue for 2 minutes in accordance with Table 1 shake program. Initial venting should be done immediately after the separatory funnel has been sealed and shaken once. The separatory funnel should be vented into a hood to avoid exposure of the analyst to solvent vapors. Allow the organic layer to separate from the water phase for 1 to 10 minutes, depending on the matrix of the sample.

8.7 Repeat step 8.6 once more with 60ml methylene chloride each in accordance with Table 1 shake program.

8.8 After all of the extract solvent has been collected, place the evaporation tube into the Turbo Vap II evaporation station, with the bath water at 42°C +/- 2°C and 21 psi. Allow the sample to evaporate down to 1ml methylene chloride or until the evaporation station signals completion. Use nitrogen to blow down the sample to make sure that it does not spill out.

8.9 Add 30 ml hexane and evaporate down to 1ml final volume under the same conditions as above.

8.10 Transfer the final volume into a pre-calibrated 4-ml glass vial, rinse the evaporation tube with clean Hexane and bring to 1-ml. If the final volume is over 1ml, use nitrogen gas or a special airline to evaporate to the 1-ml mark.

8.11 Final 1 ml adjustment: if the transfer is greater then 1 ml, use the clean nitrogen gas to evaporate to the meniscus on the vial marked with a 1 ml mark and compare to the calibrated vial. If the transferred extract is less then 1 ml, add final extract solvent to the meniscus.

8.11.1 The vials are calibrated per Lot # of vials with a NIST traceable syringe. One vial is filled with exactly 1 ml for comparison.

8.12 Find the original volume of the sample by pouring tap water into the sample container to the mark. Pour the water into a 1000 ml graduated cylinder, and record the volume in the extraction logbook and label.

9.0 PCB CLEAN-UPS (SEE PCB ANALYSIS SOP FOR DETAILS)

9.1 Sulfuric Acid Clean-up[2]

9.2 Sulfur Clean-up[3]

9.3 Alumina Column Clean-up

10.0 QUALITY CONTROL

10.1 Samples are extracted in batches of 20 samples or less. For every batch there should be an LCS, MS, and MSD/DUP depending on the client's request. All the reagent blanks, matrix spikes, or replicate samples should be subjected to exactly the same analytical procedures as those used on actual samples. In case of the client not providing the necessary sample volume to perform the required QC samples, equivalent laboratory matrix samples can be analyzed.

10.2 The surrogate standard must contain the following compounds TCX (tetrachloro-m-xylene) and DCBP (decachlorobiphenyl). The surrogate standard is prepared by the GC analyst at a concentration of 0.01mg/l.

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[2] Reference for Sulfuric Acid clean-up is SW-846, Revision 3, December 1996 Method 3665A: Sulfuric Acid

[3] Reference for Sulfur clean-up is SW-846, Revision 3, December 1996 Method 3660B: Sulfur Clean-up using copper.

10.3 The MS/MSD and LCS spikes will contain a mixture of Aroclor 1016/1260. MS/MSD spike should be prepared at a concentration at or below the medium level of the PCB curve. The MS/MSD and LCS standard is prepared by the GC analyst at a concentration of 0.05mg/l.

10.4 New lot blanks are analyzed to insure the purity of the materials and reagents.

Note: The working standards are prepared every six to 12 months or when evidence of bias or trends are observed to show that the standards need to be replaced.

11.0 DOCUMENTATION

All pertinent information is entered into an extraction logbook (See Table 1). The extraction log sheet has to contain the following information on the header/table:

- Date
- ANALYSTS INITIALS
- Method
- Surrogate/MS/MSD/LCS standard unique traceability ID
- Hexane & Methylene Chloride Lot #
- Sample I.D. #
- Matrix
- Sample volume
- Solvent ID & Volume (ml)
- Final extract volume
- Surrogate standard spike volume
- MS spike volume
- Additional clean-ups (i.e. alumina) are marked in the notes section as “C”

12.0 REFERENCES

12.1 Method 3510 SW

13.0 APPROVAL & ISSUE:

13.1 The following personnel have read, accepted and approved this standard operating practice.

_____

Analyst Date

_____

Andy Ball, QC Officer Date

_____

Maya V. Murshak, Technical Director Date

13.0 TABLES

Table 1. Extraction Funnel Shake Program

Stage	Solvent Volume	pH	Funnel Position	Shaker Time	Shaker Intensity
1	60 ml	5-9	horizontal/closed	3 min	70
2	60 ml	5-9	horizontal/closed	3 min	70
3	60 ml	5-9	horizontal/closed	3 min	70

MICROWAVE ASSISTED ACID DIGESTION OF LIQUID SAMPLES AND EXTRACTS

1.0 SCOPE AND APPLICATION

1.1 This digestion procedure is used for the preparation of aqueous samples, mobility-procedure extracts, and wastes that contain suspended solids for analysis, by inductively coupled plasma mass spectrometry (ICP-MS). The procedure is a hot acid leach for determining available metals. The method referenced with in this SOP is SW-846 Method 3015A. This SOP is for use on all samples that do not require Ohio VAP certification.

1.2 Samples prepared by using nitric acid digestion are analyzed by ICP-MS for the following metals:

Metal (Symbol)	CAS#:
Aluminum (Al)	7429-90-5
Antimony (Sb)	7440-36-0
Arsenic (As)	7440-38-2
Barium (Ba)	7440-39-3
Boron (B)	7440-42-8
Beryllium (Be)	7440-41-7
Cadmium (Cd)	7440-43-9
Calcium (Ca)	7440-70-2
Chromium (Cr)	7440-47-3
Cobalt (Co)	7440-48-4
Copper (Cu)	7440-50-8
Iron (Fe)	7439-89-6
Lead (Pb)	7439-92-1
Lithium (Li)	7439-93-2
Magnesium (Mg)	7439-95-4
Manganese (Mn)	7439-96-5
Molybdenum (Mo)	7439-95-4
Nickel (Ni)	7440-02-0
Potassium (K)	7440-09-7
Selenium (Se)	7782-49-2
Silver (Ag)	7440-22-4
Sodium (Na)	7440-23-5
Strontium (Sr)	7440-24-6
Thallium (Th)	7440-28-0
Titanium (Ti)	7440-32-6
Vanadium (V)	7440-62-2
Zinc (Zn)	7440-66-6

2.0 SUMMARY OF METHOD

2.1 A representative 0.5 to 25 g/ml aqueous sample is digested in 1 ml of concentrated nitric acid in a polypropylene digestion vessel brought to a final volume of 50 ml and heated using microwave heating. After the digestion process, the sample is cooled, and then filtered, centrifuged, or allowed to settle prior to analysis.

3.0 INTERFERENCES

3.1 Addition of nitric acid to samples that contain organics, such as TCLP extracts, could result in a violent reaction and splattering (loss) of the sample, leading to loss of analytes and/or sample, which must be avoided. A smaller sample size can be used but the final water volume must be adjusted to approximately 10 ml prior to the heating stage.

4.0 APPARATUS AND MATERIALS

4.1 Microwave Digestion System CEM–Model MDS – 81D and MARSX-Model # 907600

4.1.1 The MDS-81D consists of a microwave drying system with an operator selectable power output of 0-600 watts in 1% increments, a microwave cavity with a variable speed exhaust fan, a programmable microprocessor based digital computer, Teflon® coated cavity, exhaust tubing and standard screen rotating turntable, rotated at 6 rpm to insure uniform microwave heating.

4.1.2 The MARSX consists of a microwave drying system with an operator selectable power output of 0-1200 watts in, a microwave cavity with a variable speed exhaust fan, a programmable microprocessor based digital computer, Teflon® coated cavity, exhaust tubing and standard rotating turntable, and self calibration features.

4.1.3 Microwave Digestion System Specifications:

MDS-81D		MARSX	
Power	600 Watts	Power	1200 Watts
Pressure	0 - 200 psi	Pressure	0 - 200 psi
Temperature	0 - 200°C	Temperature	0 - 200°C
Capacity	26 samples	Capacity	50 samples

4.2 Analytical balances, 510g capacity, minimum accuracy ± 0.001g and 250g capacity, minimum accuracy ±0.0001g.
4.3 Filter funnel, glass or disposable polypropylene.
4.4 Glass-fiber filter paper, 0.45 µm.
4.5 Membrane filters, 0.45 µm.
4.6 Digital bottle top dispenser capable of dispensing volumes of 0-5 ml in 0.02 ml increments.
4.7 Disposable polypropylene vessels, 50 ml, compatible with centrifuge.
4.8 Plastic containers to support minimum of 200 ml.
4.9 Disposable Pasteur pipettes.
4.10 Eppendorf automatic pipette with disposable combitips ranging from 2.50 ml to 50 ml capable of pipetting volumes ranging from 50 µl to 5,000 µl.
4.11 Centrifuge (IEC Centra GP8)

5.0 REAGENTS

5.1 Trace metal grade chemicals are used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, if applicable.

5.2 Deionized (DI) Water (Type I) is used which meets the specifications of the ASTM [1] standard criteria.

5.3 Concentrated nitric acid, HNO_3, Trace Metal Grade. Acid purity is monitored by analysis of the laboratory reagent blank.

5.4 Standards added to digestion:

5.4.1 Spiking Solutions

[1] 1985 Annual Book of ASTM Standards, Vol.11.01; "Standard Specification for Reagent Water"

5.4.1.1 Spiking solutions are prepared according to the Standard Prep Log. The formula, date source solutions, lot numbers, expiration date of stock standards, expiration date standard made, expiration and unique ID of any working standards used.

5.4.1.2 All standards are NIST traceable.

5.4.1.3 Multi-element standard solution **WS1** (see standard prep book), containing Al, Sb, As, Ba, Be, B, Cd, Cr, Co, Cu, Fe, Pb, Li, Mo, Mn, Ni, Se, Ag, Tl, Ti, V, Zn. This solution is made from stock NIST traceable standard and prepared according to the standard prep book.

5.4.1.3.1 WS1 is used to make the QC Spiking Solution. The QC Spiking Solution is used to spike the LCS, MS, and MSD samples prior to digestion.

5.4.1.4 Multi-element standard solution **HM** (see standard prep book), containing 100 µg/ml each of Ca, K, Mg, Na. From this solution, 1.0 ml is added to the QC samples (*i.e.* MS/MSD samples), and 0.50 ml to the laboratory control sample (LCS), by weighing the amounts (1.0 g, 0.50 g) on the scale).

5.4.2 Internal Standards (After digestion):

5.4.2.1 Lithium 6, 1000 µg/ml stock solution.

5.4.2.2 Scandium, 1000 µg/ml stock solution.

5.4.2.3 Yttrium, 1000 µg/ml stock solution.

5.4.2.4 Rhodium, 1000 µg/ml stock solution.

5.4.2.5 Rhenium, 1000 µg/ml stock solution.

5.4.2.6 Internal Standard working solution (**IS-WS**): From the above stock solutions, 2.5 g of each is transferred to a 1000 ml plastic bottle, along with 10 ml of concentrated HNO_3 and brought to a final volume of 1000 ml (by weight). The concentration in the flask will be 2.5 µg/ml. This represents the internal standards working solution from which 1 ml will be added to all samples (*i.e.* standards, samples, QC samples, blanks, etc.) prior to the analysis by the ICP/MS.

NOTE: The stock solutions are NIST traceable and provided with a certificate of analyses and MSDS sheets by the manufacturer.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples are collected in appropriate containers. The samples are collected in HNO_3 pre-preserved plastic container and are acidified to pH of <2. (Approximately 125 ml volume).

6.2 Holding times for metals are 6 months from the date of sampling, with the exception of Mercury, which is not covered by this SOP.

7.0 PROCEDURE

7.1 Calibration of Microwave Equipment

7.1.1 Microwaves are calibrated once a year according to the manufactures instructions.

7.2 All digestion vessels are disposable and are used only once, which allows for better sample control and prevents cross contamination.

CAUTION: -Toxic nitrogen oxide fumes may evolve, therefore all work must be performed in a properly operating ventilation system.
- Loss of sample through splattering inside the microwave system must be avoided. Physical observation is sufficient to determine if this is the case, therefore the batch of samples needs to be inspected at the end of the digestion cycle. If splattering has occurred, the samples are to be discarded, and a new batch is to be prepared.

7.3 Digestion using industrial Microwave.

7.3.1 A 0.5 to 25 ml/grams aliquot of a well shaken sample is transferred into the digestion vessel, sample volume is determined by sample matrix and sample history. The vessel is labeled with the sample number, which is also recorded on the preparation sheet.

7.3.2 With every batch of 20 analytical samples measure a volume of reagent water equal to the sample volume as described at 7.3.1 into a vessel labeled LRB. This represents the Laboratory Reagent Blank (LRB), which is carried through the entire digestion procedure, the same as an analytical sample.

7.3.3 With every batch of samples measure a volume of reagent water equal to the sample volume as described at 7.3.1 into a vessel labeled LCS. This represents the Laboratory Control Sample (LCS), which is carried through the entire digestion procedure, the same as an analytical sample.

7.3.4 For every 10 samples measure, in a similar manner, an amount equal to the parent sample of the sample designated for Matrix Spike (MS) and Matrix Spike duplicate (MSD) or duplicate (Dp).

7.3.4.1 Spiking for liquid samples is done by adding 0.5 ml of 5 ppm QC Spiking Solution.

7.3.5 Add 1 ml of concentrated nitric acid to each vessel, by using the bottle top dispenser in the hood.

7.3.6 For analysis of all metals except Ca, Mg, K and Na, add 0.5 ml of the QC Spiking Solution to the QC samples (LCS, MS/MSD). For Ca, Mg, K and Na, add 1.0 ml of the **HM** solution to the LCS, and 1.0 ml of the **HM** solution to the MS/MSD samples. The spike concentration and the Lot # of the stock solution used is recorded in the preparation log.

CAUTION: Addition of nitric acid to the non-aqueous (solvents) samples needs to be performed slowly, dropwise if possible in order to control the potential reaction. When the reaction has subsided, swirl the vessel lightly, dilute the sample to approximately 10 mL, and go to the next step.

7.3.7 Samples are slowly ramped in the microwave to 95±4 degrees Celsius over the course of a few minutes and maintained at this temperature for 30 minutes.

7.3.8 After the temperature program is completed, leave the vessels 5-10 minutes in the microwave, to cool down, and then move them into the hood. Add 1 ml of the Internal Standard working solution, using an Eppendorf automatic pipettor, and dilute to the 50 ml mark with DI Water into a calibrated digestion vessel (per lot).

7.3.9 If the digested sample contains particulate matter, which has the potential to clog the nebulizer, the sample needs to be centrifuged, allowed to settle, or filtered.

7.3.10 Settling: Allow the sample to stand until the supernatant is clear. Allowing a sample to stand overnight will usually accomplish this, however this can frequently be accomplished in a few hours. If it does not, centrifuge or filter the sample.

7.3.11 Centrifugation: Centrifugation at 4500 rpm for 3 minutes is usually sufficient to clear the supernatant.

7.3.11.1 Filtering: The filtering apparatus (flask and funnel) must be thoroughly rinsed with a 10% v/v nitric acid solution and copious amounts of DI Water. Filter the sample through a 0.45 µm filter paper and transfer the liquid to a new vessel. Glass fiber

filters are acceptable for all metals except Zn and Ba, for which membrane filters are required, due to the presence of these elements in the glass fiber filters.

7.3.12 Calculate the dilution factor (DF) by the formula:

$$DF = \frac{Final\ Volume\ (50)}{Sample\ amount}$$

7.3.13 This dilution factor is recorded in the sample preparation log, and is to be used in the determination of the final result by the ICP/MS.

8.0 QUALITY CONTROL

8.1 For each analytical batch of 20 samples processed, one laboratory reagent blank (LRB) must be carried throughout the entire sample preparation and analytical process. The LRB will be used for determining if the samples are being contaminated during preparation or from reagents.

8.2 For each analytical batch of 20 samples processed, one laboratory control sample (LCS) must be carried throughout the entire sample preparation and analytical process. The LCS will be used for determining the performance of the method for that particular batch.

8.3 Spiked samples (MS) must be employed to determine accuracy. A spiked sample must be included with each group of 10 samples processed.

8.4 Duplicate (Dp) samples or Matrix Spike Duplicate (MSD) must be processed for every ten samples. A duplicate sample is a real sample brought through the whole sample preparation and analytical process.

8.5 For each analytical batch of 20 sample processed the laboratory must perform a dilution test. The dilution test is performed by taking 10 ml of a parent sample after digestion and adding 0.8 ml of acid and 0.8 ml of internal standard and bring to a final volume of 50 ml. The dilution test is used to identify matrix interference and is not applicable if the measured concentration is less than 100 time the MDL for each measured analyte.

9.0 WASTE DISPOSAL

9.1 Samples

9.1.1 All digested samples are neutralized with baking soda and diluted before being disposed of with the normal laboratory waste water.

9.1.2 As a “small generator” of metals, Merit laboratories has been approved for this type of disposal from the local government.

9.2 Acid bottles

9.2.1 Acid bottles are rinsed out and neutralized with baking soda before being disposed of with the normal laboratory waste.

10.0 DOCUMENTATION

10.1 All pertinent information is entered into a digestion logbook. The digestion log sheet has to contain the following information on the header/table:

- Date.
- Analyst initials.
- Method reference.
- Sample #.
- Sample weight or volume.
- MS/MSD/LCS spike concentration.
- Total solids (if applicable)

- Acid Lot #
- Spike Lot #
- Dilution Factor
- Prep batch
- Final volume of sample
- Remarks
-

11.0 METHOD PERFORMANCE

11.1 The precision and accuracy of the method will depend upon the overall performance of the sample preparation and analysis.

12.0 REFERENCES

12.1 Horlick, G., et al., Spectrochim. Acta 40B, 1555 (1985).
12.2 Gray, A.L., Spectrochim. Acta 40B, 1525 (1985); 41B, 151 (1986).
12.3 Tan, S.H., and Horlick, G., Appl. Spectrosc. 40, 445 (1986).
12.4 Vaughan, M.A., and Horlick, G., Appl. Spectrosc. 40, 434 (1986).
12.5 Holden, N.E., "Table of the Isotopes," in Lide, D.R., Ed., CRC Handbook of Chemistry and Physics, 74th Ed., CRC press, Boca Raton, FL, 1993.
12.6 Hinners, T.A., Heithmar, E., Rissmann, E., and Smith, D., Winter Conference on Plasma Spectrochemistry, Abstract THP18; p. 237, San Diego, CA (1994).
12.7 Lichte, F.E., et al., Anal. Chem. 59, 1150 (1987).
12.8 Evans E.H., and Ebdon, L., J. Anal. At. Spectrom. 4, 299 (1989).
12.9 Beauchemin, D., et al., Spectrochim. Acta 42B, 467 (1987).
12.10 Houk, R.S., Anal. Chem. 58, 97A (1986).
12.11 Thompson, J.J., and Houk, R.S., Appl. Spectrosc. 41, 801 (1987).
12.12 SW-846, Method 6020 Revision 0, 1994.
12.13 Method 200.8, Revision 5.4, 1998.
12.14 SW-846, Method 6020A Revision 1, 2007
12.15 SW-846, Method 8000C Revision 3, 2003
12.16 SW-846, Method 3015

13.0 SAFETY

13.1 Every Laboratory area has eyewash, emergency shower, and fire extinguisher. The metals lab also has dust masks available for use with dust samples.

13.2 The air system through out the laboratory area is on a 100% fresh air exchange system, this system exchanges 100% the air in the laboratory area with air from outside 4 times per hour and 6 times per hour when the emergency purge button is hit.

13.3 A reference file of material safety data sheets (MSDSs) is available to all personnel.

13.4 Specific attention be paid (but not limited) to

13.4.1 Nitric acid is a corrosive, not combustible, but substance is a strong oxidizer and its heat of reaction with reducing agents or combustibles may cause ignition, and can react with metals to release flammable hydrogen gas.

13.4.2 Hydrochloric acid is corrosive, extreme heat or contact with metals can release flammable hydrogen gas, stable under ordinary conditions of use and storage, and incompatible with many substances and highly reactive with strong bases, metals, metal oxides, hydroxides, amines, carbonates, cyanides, sulfides, sulfites, and formaldehyde.

13.4.3 Many metal salts are extremely toxic if inhaled or swallowed. Extreme care must be taken to ensure that samples and standards are handled properly and that all exhaust gases are properly vented. Wash hands thoroughly after handling.

13.4.4 The acidification of samples containing reactive materials may result in the release of toxic gases, such as cyanides or sulfides. For this reason, the acidification and digestion of samples should be performed in an approved fume hood.

14.0 APPROVAL & ISSUE:

14.1 This section indicates which personnel have read, accepted and approved the SOP. All analysts involved with the SOP must acknowledge their comprehension of the SOP with a signature and a date.

_____

Analyst Date

_____

Andy Ball, QA/QC Officer Date

_____

Maya V. Murshak, Technical Director Date

Location: QA Officer's Office
pH laboratory
SOP Files

1.0 SCOPE

1.1 To measure pH in water samples.

2.0 SUMMARY OF METHOD

2.1 This SOP is designed to measure the pH of water samples. The procedure in this method is written for the Hach SensION3 Laboratory pH Meter (P/N 51750-18). This SOP follows EPA method 4500 H^+ B.

3.0 INTERFERENCES

3.1 Temperature can be an interference. Temperature can change the acid-base equilibrium constant.
3.2 Carbon Dioxide absorption from the atmosphere. This can form carbonic acid in water, which can cause interferences.
3.3 A pH above 10 can have sodium interference.

4.0 APPARATUS AND MATERIALS

4.1 Hach SensION3 Laboratory pH Meter (P/N 51750-18).
4.2 Platinum Series Combination pH Electrode with Temperature (Cat. #: 51910-00)
4.3 Potassium Chloride Electrolyte Cartridge (Cat.#: 25469-02)
4.4 Stir Plate
4.5 Magnetic Stir Bar
4.6 Plastic Cup
4.7 Paper Towel
4.8 50 mL Centrifuge Tubes

5.0 REAGENTS

5.1 pH, 4.00, color-coded red
5.2 pH, 7.00, color-coded yellow
5.3 pH, 10.00, color coded blue
5.4 pH, 5.00, color coded clear (Laboratory Control Sample), Micro Essential Lab Hydrion Products prepared by adding 1 pill per 100mL of DI Water
5.5 pH, 2.00, color coded clear, , Micro Essential Lab Hydrion Products prepared by adding 1 pill per 100mL of DI Water

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 pH analyses must be run as soon as possible after sample collection. The samples must be stored in an unpreserved plastic container.

7.0 PROCEDURE

7.1 Turn on the meter.
7.2 Inspect the Potassium Chloride Electrolyte Gel Cartridge to ensure that it is not empty. If it is empty replace it.
7.3 Prime the electrode by pushing the dispenser until gel comes out of the reference junction. Rinse excess gel from the tip and the outlet with deionized (DI) water.
7.4 Press the <CAL> button on the meter. The display will prompt for Standard 1 (pH= 7.00).
7.5 Place the electrode into fresh pH=7 buffer. Then press <Read/Enter> and stir until the display reads "pH STD 2. "Fresh" is defined as prepared within 7 days of calibration.
7.6 Remove the electrode from the pH=7 buffer and rinse it well with DI water, dry with a paper towel.

7.7 Place the electrode into pH=4 buffer. Stir and press <Enter>. Wait until the display prompts for STD 3, then press exit. This is a two point calibration.

7.8 The Slope and "Store?" will appear. If the slope is –58 +/- 3mV/ph Unit record it along with the pH readings of the two buffers on the bench sheet. If the slope is out of this range press <Exit> and recalibrate. Then press <Read/Enter> to save the calibration.

7.9 Remove the electrode from the buffer, rinse well with DI water and dry with a paper towel. The display will now automatically switch to the pH reading mode (i.e. "4.00 pH").

7.10 Place the electrode into pH=10 buffer, stir and wait until the reading is stable. The display must show 10.00 ± 0.05 pH units. Record this value on the bench sheet. If it is out of this range recalibrate until it reads in this range. Calibration is now complete. Recalibrate every 10 samples or every day whichever comes first.

7.11 Remove the electrode, rinse well with DI water, pat dry with paper towel, and place it into the Laboratory Control Sample (LCS).

7.12 Stir and wait for a stable pH reading on the display. Ensure that the pH reading for the LCS is with in the certified acceptance range.

7.13 Remove the electrode, rinse well with DI water. Place the electrode into the sample and stir. Wait until the display shows a stable pH reading and the sample has a temperature near (± 5^{o}C) the temperature of the buffers (room temperature).

7.14 Record all buffer readings, LCS, sample and sample duplicate readings as well as the temperature displayed on the small monitor in the pH bench book along with the Merit Sample Number, the date and your initials.

7.15 Replace the sample with a new aliquot and repeat the test (duplicate analysis).

7.16 Note that the samples and the pH buffers used for calibrating the instrument must be close to the sample temperature (+/- 5 ^{o}C).

7.17 After samples are tested. Read the LCS buffer at the end to ensure that the meter remained in calibration. If it reads beyond the range pH=5± 0.05 recalibrate and reread the samples.

7.18 To increase accuracy perform a calibration check at least every 10 samples. Recalibrate as needed.

7.19 Remove the electrode, rinse well with DI water, pat dry with a paper towel and place it in the overnight beaker containing East Lansing, MI tap water.

8.0 QUALITY CONTROL

8.1 All QA/QC information that needs to be analyzed are listed in the "Quality Control Requirements" table below.

8.2 This table also includes acceptable upper and lower limits, any corrective actions not specified in the procedures.

Quality Control Requirements

QC Work Task	Frequency	Acceptance Range	Corrective action
Calibration with two Std buffers (pH=7 & 4) plus third Std buffer (pH=10) verification	1/day and when calibration check is outside acceptance range	± 0.05 of pH Slope = -58=±3mV/pH unit	1. Clean electrode and reference junction. Then recalibrate. 2. Prepare new buffers and recalibrate. 3. Call for service.
Laboratory Control Sample	1/day or every 10 samples	Within certified range	Same as for calibration above.
Temperature of samples and Buffers	Record with each pH reading	Within ± 5°C of the buffers (room temperature	Hold at room temperature until within acceptable range.
Calibration check buffer pH 2.00 and pH 5.00	1/set or every 10 samples	± 0.05 pH units	Recalibrate and rerun samples read since the last acceptable calibration check.
End calibration check Read one standard	1/set or 1/day	± 0.05 pH units	Recalibrate and rerun samples read since the last acceptable calibration check

9.0 DOCUMENTATION

9.1 pH Bench book that records the following information:

- 9.1.1 Date of Standards Made, Expiration, and Calibration Value
- 9.1.2 Calibration information (buffer used, value read)
- 9.1.3 LCS values
- 9.1.4 Calibration Check
- 9.1.5 Lot #'s for Buffer Solutions
- 9.1.6 Calibration Slope Value
- 9.1.7 Merit ID Number
- 9.1.8 Date
- 9.1.9 pH Measured
- 9.1.10 Temperature at which the pH is measured
- 9.1.11 Matrix
- 9.1.12 Analyst Initials

10.0 METHOD PERFORMANCE

10.1 This method is evaluated by the blinds performed every quarter. If the pH values are not within the acceptable criteria, a the matter is investigated and a corrective plan is determined.

11.0 REFERENCES

11.1 *Standard Methods*, twentieth edition, Method 4500-H^+ B.

12.0 SAFETY

12.1 Eye protection and gloves must be worn while performing pH analyses.

12.2 Every Laboratory area has eyewash, emergency shower, and fire extinguisher. The metals lab also has dust masks available for use with dust samples.

12.3 The air system through out the laboratory area is on a 100% fresh air exchange system, this system exchanges 100% the air in the laboratory area with air from outside 6 times per hour and 30 times per hour when the emergency purge button is hit.

12.4 A reference file of material safety data sheets (MSDSs) is available to all personnel.

13.0 WASTE DISPOSAL AND POLLUTION PREVENTION

13.1 All laboratory waste must be managed, stored, and disposed in accordance with all federal and state laws and regulations.

13.2 Additional information can be found in the Sample Disposal SOP and Merit's Waste Management Plan and Handbook.

14.0 APPROVAL & ISSUE

14.1 This section indicates which personnel have read, accepted and approved the SOP. All analysts involved with the SOP must acknowledge their comprehension of the SOP with a signature and a date.

_____

Analyst Date

_____

Andy Ball, QA Officer Date

_____

Maya V. Murshak, Technical Director Date

Location: QA Officer's Office
pH laboratory
SOP Files

1.0 SCOPE

1.1 To measure pH in water samples.

2.0 SUMMARY OF METHOD

2.1 This SOP is designed to measure the pH of water samples. The procedure in this method is written for the Hach SensION3 Laboratory pH Meter (P/N 51750-18). This SOP follows EPA method 4500 H^+ B.

3.0 INTERFERENCES

3.1 Temperature can be an interference. Temperature can change the acid-base equilibrium constant.
3.2 Carbon Dioxide absorption from the atmosphere. This can form carbonic acid in water, which can cause interferences.
3.3 A pH above 10 can have sodium interference.

4.0 APPARATUS AND MATERIALS

4.1 Hach SensION3 Laboratory pH Meter (P/N 51750-18).
4.2 Platinum Series Combination pH Electrode with Temperature (Cat. #: 51910-00)
4.3 Potassium Chloride Electrolyte Cartridge (Cat.#: 25469-02)
4.4 Stir Plate
4.5 Magnetic Stir Bar
4.6 Plastic Cup
4.7 Paper Towel
4.8 50 mL Centrifuge Tubes

5.0 REAGENTS

5.1 pH, 4.00, color-coded red
5.2 pH, 7.00, color-coded yellow
5.3 pH, 10.00, color coded blue
5.4 pH, 5.00, color coded clear (Laboratory Control Sample), Micro Essential Lab Hydrion Products prepared by adding 1 pill per 100mL of DI Water
5.5 pH, 2.00, color coded clear, , Micro Essential Lab Hydrion Products prepared by adding 1 pill per 100mL of DI Water

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 pH analyses must be run as soon as possible after sample collection. The samples must be stored in an unpreserved plastic container.

7.0 PROCEDURE

7.1 Turn on the meter.
7.2 Inspect the Potassium Chloride Electrolyte Gel Cartridge to ensure that it is not empty. If it is empty replace it.
7.3 Prime the electrode by pushing the dispenser until gel comes out of the reference junction. Rinse excess gel from the tip and the outlet with deionized (DI) water.
7.4 Press the <CAL> button on the meter. The display will prompt for Standard 1 (pH= 7.00).
7.5 Place the electrode into fresh pH=7 buffer. Then press <Read/Enter> and stir until the display reads "pH STD 2. "Fresh" is defined as prepared within 7 days of calibration.
7.6 Remove the electrode from the pH=7 buffer and rinse it well with DI water, dry with a paper towel.

7.7 Place the electrode into pH=4 buffer. Stir and press <Enter>. Wait until the display prompts for STD 3, then press exit. This is a two point calibration.

7.8 The Slope and "Store?" will appear. If the slope is –58 +/- 3mV/ph Unit record it along with the pH readings of the two buffers on the bench sheet. If the slope is out of this range press <Exit> and recalibrate. Then press <Read/Enter> to save the calibration.

7.9 Remove the electrode from the buffer, rinse well with DI water and dry with a paper towel. The display will now automatically switch to the pH reading mode (i.e. "4.00 pH").

7.10 Place the electrode into pH=10 buffer, stir and wait until the reading is stable. The display must show 10.00 ± 0.05 pH units. Record this value on the bench sheet. If it is out of this range recalibrate until it reads in this range. Calibration is now complete. Recalibrate every 10 samples or every day whichever comes first.

7.11 Remove the electrode, rinse well with DI water, pat dry with paper towel, and place it into the Laboratory Control Sample (LCS).

7.12 Stir and wait for a stable pH reading on the display. Ensure that the pH reading for the LCS is with in the certified acceptance range.

7.13 Remove the electrode, rinse well with DI water. Place the electrode into the sample and stir. Wait until the display shows a stable pH reading and the sample has a temperature near (± 5^{o}C) the temperature of the buffers (room temperature).

7.14 Record all buffer readings, LCS, sample and sample duplicate readings as well as the temperature displayed on the small monitor in the pH bench book along with the Merit Sample Number, the date and your initials.

7.15 Replace the sample with a new aliquot and repeat the test (duplicate analysis).

7.16 Note that the samples and the pH buffers used for calibrating the instrument must be close to the sample temperature (+/- 5 ^{o}C).

7.17 After samples are tested. Read the LCS buffer at the end to ensure that the meter remained in calibration. If it reads beyond the range pH=5± 0.05 recalibrate and reread the samples.

7.18 To increase accuracy perform a calibration check at least every 10 samples. Recalibrate as needed.

7.19 Remove the electrode, rinse well with DI water, pat dry with a paper towel and place it in the overnight beaker containing East Lansing, MI tap water.

8.0 QUALITY CONTROL

8.1 All QA/QC information that needs to be analyzed are listed in the "Quality Control Requirements" table below.

8.2 This table also includes acceptable upper and lower limits, any corrective actions not specified in the procedures.

Quality Control Requirements

QC Work Task	Frequency	Acceptance Range	Corrective action
Calibration with two Std buffers (pH=7 & 4) plus third Std buffer (pH=10) verification	1/day and when calibration check is outside acceptance range	± 0.05 of pH Slope = -58=±3mV/pH unit	1. Clean electrode and reference junction. Then recalibrate. 2. Prepare new buffers and recalibrate. 3. Call for service.
Laboratory Control Sample	1/day or every 10 samples	Within certified range	Same as for calibration above.
Temperature of samples and Buffers	Record with each pH reading	Within ± 5°C of the buffers (room temperature	Hold at room temperature until within acceptable range.
Calibration check buffer pH 2.00 and pH 5.00	1/set or every 10 samples	± 0.05 pH units	Recalibrate and rerun samples read since the last acceptable calibration check.
End calibration check Read one standard	1/set or 1/day	± 0.05 pH units	Recalibrate and rerun samples read since the last acceptable calibration check

9.0 DOCUMENTATION

9.1 pH Bench book that records the following information:

- 9.1.1 Date of Standards Made, Expiration, and Calibration Value
- 9.1.2 Calibration information (buffer used, value read)
- 9.1.3 LCS values
- 9.1.4 Calibration Check
- 9.1.5 Lot #'s for Buffer Solutions
- 9.1.6 Calibration Slope Value
- 9.1.7 Merit ID Number
- 9.1.8 Date
- 9.1.9 pH Measured
- 9.1.10 Temperature at which the pH is measured
- 9.1.11 Matrix
- 9.1.12 Analyst Initials

10.0 METHOD PERFORMANCE

10.1 This method is evaluated by the blinds performed every quarter. If the pH values are not within the acceptable criteria, a the matter is investigated and a corrective plan is determined.

11.0 REFERENCES

11.1 *Standard Methods*, twentieth edition, Method 4500-H^+ B.

12.0 SAFETY

12.1 Eye protection and gloves must be worn while performing pH analyses.

12.2 Every Laboratory area has eyewash, emergency shower, and fire extinguisher. The metals lab also has dust masks available for use with dust samples.

12.3 The air system through out the laboratory area is on a 100% fresh air exchange system, this system exchanges 100% the air in the laboratory area with air from outside 6 times per hour and 30 times per hour when the emergency purge button is hit.

12.4 A reference file of material safety data sheets (MSDSs) is available to all personnel.

13.0 WASTE DISPOSAL AND POLLUTION PREVENTION

13.1 All laboratory waste must be managed, stored, and disposed in accordance with all federal and state laws and regulations.

13.2 Additional information can be found in the Sample Disposal SOP and Merit's Waste Management Plan and Handbook.

14.0 APPROVAL & ISSUE

14.1 This section indicates which personnel have read, accepted and approved the SOP. All analysts involved with the SOP must acknowledge their comprehension of the SOP with a signature and a date.

_____

Analyst Date

_____

Andy Ball, QA Officer Date

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Maya V. Murshak, Technical Director Date

METHOD 8270C/8015M (DRO)

1.0 SCOPE AND APPLICATION

1.1 This method can be used to quantitate most basic, neutral and acidic organic compounds (BNAs) that are soluble in methylene chloride and capable of being eluted, without derivatization, as sharp peaks from a gas chromatographic fused-silica capillary column coated with a slightly polar silicone. Such compounds include polynuclear aromatic hydrocarbons (PNAs), chlorinated hydrocarbons and pesticides, phthalate esters, organophosphate esters, nitrosamines, haloethers, aldehydes, ethers, ketones, anilines, pyridines, quinolines, aromatic nitro compounds, and phenols, including nitrophenols. See Tables 1a and 1b for a list of compounds (along with their characteristic ions) that have been evaluated.

1.2 In most cases, this method is not appropriate for the quantitation of multicomponent analytes, e.g., Aroclors, Toxaphene, Chlordane, *etc*., because of limited sensitivity for those analytes. When these analytes have been identified by another technique, this method is appropriate for confirmation of the presence of these analytes when concentration in the extract permits. However, this method is used for the analysis of petroleum hydrocarbons, namely diesel range organics (DROs). DROs correspond to the range of alkanes from C_{10} to C_{28} and covering a boiling point range of approximately 170°C - 430°C. The identification of specific fuel types may be complicated by environmental processes such as evaporation, biodegradation, or when more than one fuel type is present.

1.3 The following compounds may require special treatment when being determined by this method:

- Benzidine may be subject to oxidative losses during solvent concentration and its chromatographic behavior is poor.
- Under the alkaline conditions of the extraction step from aqueous matrices, α-BHC, β-BHC, Endosulfan I and II, and Endrin are subject to decomposition. Neutral extraction should be performed if these compounds are expected.
- Hexachlorocyclopentadiene is subject to thermal decomposition in the inlet of the gas chromatograph, chemical reaction in acetone solution, and photochemical decomposition.
- N-nitrosodimethylamine is difficult to separate from the solvent under the chromatographic conditions described.
- N-nitrosodiphenylamine decomposes in the gas chromatographic inlet and cannot be separated from diphenylamine.
- Pentachlorophenol, 2,4-dinitrophenol, 4-nitrophenol, benzoic acid, 4,6-dinitro-2-methylphenol, 4-chloro-3-methylphenol, 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.
- Pyridine may perform poorly at the GC injection port temperatures listed in the method. Lowering the injection port temperature may reduce the amount of degradation. The analyst needs to use caution if modifying the injection port temperature as the performance of other analytes may be adversely affected.
- In addition, analytes in the list provided above are flagged when there are limitations caused by sample preparation and/or chromatographic problems.

1.4 The estimated quantitation limit (PQL) of Method 8270/8015 for determining an individual compound is approximately 330 µg/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 ground water samples (see Tables 2a and 2b). For DROs, the values are 4 mg/kg (soil/sediment, wet weight) and 0.1 mg/L for ground water (see Table 2c). PQLs will be proportionately higher for sample extracts that require dilution to avoid saturation of the detector.

1.5 This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatograph/mass spectrometers and skilled in the interpretation of mass spectra. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 The samples are prepared for analysis by gas chromatography/mass spectrometry (GC/MS) using the appropriate sample preparation (refer to Methods 3500, 3510, 3550).

2.2 The semivolatile compounds are introduced into the GC/MS by injecting the sample extract into a gas chromatograph (GC) with a narrow-bore fused-silica capillary column. The GC column is temperature-programmed to separate the analytes, which are then detected with a mass spectrometer (MS) connected to the gas chromatograph.

2.3 Analytes eluted from the capillary column are introduced into the mass spectrometer via a jet separator or a direct connection. Identification of target analytes is accomplished by comparing their mass spectra with the electron impact spectra of authentic standards. Quantitation is accomplished by comparing the response of a major (quantitation) ion relative to an internal standard using a five-point (or more) calibration curve.

2.4 The method includes specific calibration and quality control steps that supersede the general requirements provided in Method 8000.

3.0 INTERFERENCES

3.1 Raw GC/MS data from all blanks, samples, and spikes must be evaluated for interferences. Determine if the source of interference is in the preparation and/or cleanup of the samples and take corrective action to eliminate the problem.

3.2 Contamination by carryover can occur whenever high-concentration and low-concentration samples are sequentially analyzed. This is virtually never a problem for direct injection GC/MS analysis, provided that the sample syringe is rinsed with solvent between sample injections. If carryover is suspected, questionable samples should be re-injected after the system has been demonstrated to be free of contamination.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph/mass spectrometer system

4.1.1 Gas chromatograph - An analytical system complete with a temperature-programmable gas chromatograph suitable for splitless injection and all required accessories, including syringes, analytical columns, and gases. The capillary column should be directly coupled to the source.

4.1.2 Column - 30 m × 0.25 mm ID × 0.5 µm film thickness silicone-coated fused-silica capillary column (Hewlett Packard HP-5ms SV or equivalent).

4.1.3 Mass spectrometer capable of scanning from 35 to 500 amu every 1 sec 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 the criteria in Table 4 when 1 µL of the GC/MS tuning standard is injected through the GC (50 ng of DFTPP)

4.1.4 GC/MS interface - Any GC-to-MS interface may be used that gives acceptable calibration points at 50 ng per injection for each compound of interest and achieves acceptable tuning performance criteria. For a narrow-bore capillary column, the interface is usually capillary-direct into the mass spectrometer source.

4.1.5 Data system - A computer system is interfaced to the mass spectrometer. Hewlett-Packard Chemstation software (with environmental data analysis) is used to acquire and process GC/MS data.

4.2 Syringes - 1 to 1000 µL Hamilton syringes are used in the preparation of standards, spiking solutions, and standards.

4.3 Balance - Analytical, capable of weighing 0.0001 g.

4.4 Bottles - glass with polytetrafluoroethylene (PTFE)-lined screw caps or crimp tops.

5.0 REAGENTS

5.1 Reagent grade inorganic chemicals shall be used in all tests. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without introducing adverse interferences.

5.2 Organic-free reagent water - All references to water in this method refer to organic-free reagent water.

5.3 Stock standard solutions

5.3.1 Certified stock standard solutions are purchased when available for the bulk of desired analytes. They are typically available at concentrations of 1000 to 2000 mg/L.

5.3.2 Supplemental compounds added to calibration mixes are generally prepared gravimetrically from neat standard references (in order to create a stock solution of 1000 to 10000 mg/L).

5.3.3 Stock standard solutions are stored in bottles with PTFE-lined screw-caps. They are refrigerated and protected from light, as recommended by the standard manufacturer.

5.3.4 Neat standard references are used in order to create a stock solution ~10000 mg/L for DRO standards.

5.3.5 Stock standard solutions are replaced prior to expiration, or sooner if comparison with quality control check samples indicates a problem.

5.4 Internal standard solutions - The internal standards used are 1,4-Dichlorobenzene-d_4, Naphthalene-d_8, Acenaphthene-d_{10}, Phenanthrene-d_{10}, Chrysene-d_{12}, and Perylene-d_{12}. Internal standards are spiked into the sample extracts and calibration standards at a uniform concentration of 40 ng/µL (≡ 40 mg/L).

5.5 GC/MS tuning standard - A methylene chloride solution containing 50 ng/µL of decafluorotriphenylphosphine (DFTPP), pentachlorophenol, and benzidine is used to evaluate GC/MS tuning criteria, injection port inertness, and GC column performance.

5.6 Calibration standards - A minimum of five calibration standards should be prepared at five different concentrations. If possible, the lowest calibration standard corresponds to a sample concentration at or below the standard reporting limit. The remaining standards should correspond to the working range of the GC/MS system (10-100 ng/µL for BNAs, 2-100 ng/µL for PNAs, and 0.1-1.0 g/L for DROs). Each standard should contain each analyte for detection by this method. The preparation instructions for the creation of calibrations standards from stock solutions commonly used in BNA, PNA, and DRO analysis are found in the Calibration Recipes excel file.

5.7 Surrogate standards - The surrogates used are Phenol-d_6, 2-Fluorophenol, 2,4,6-Tribromophenol, Nitrobenzene-d_5, 2-Fluorobiphenyl, and p-Terphenyl-d_{14}. See Method 3500 for instructions on preparing the surrogate solutions. For BNA analysis, all six surrogate standards are used. For PNA analysis, only Nitrobenzene-d_5, 2-Fluorobiphenyl, and p-Terphenyl-d_{14} are used.

5.7.1 Surrogate spiking mixes are created at 100 mg/L and spiked into samples in 1 mL aliquots. The resulting ideal concentration in a 1 mL extract as 100ng/µL.

5.7.2 Surrogate Standard Check: inject a sample of the spiking solution (with internal standard added) into the GC/MS to determine recovery of surrogate standards. It is recommended that this check be done whenever a new surrogate spiking solution is prepared.

5.8 Matrix spike and laboratory control standards - See Method 3500 for instructions on preparing the matrix spike standard. The same standard is used as the laboratory control standard (LCS).

5.8.1 Matrix spiking mixes for single component analytes are generally created at 50 mg/L and spiked into samples in 1 mL aliquots. The resulting ideal concentration in a 1 mL extract is 50ng/µL.

5.8.2 The matrix spiking mix for DRO is created at 1000 mg/L and spiked into samples in 1 mL aliquots. The resulting ideal concentration in a 1 mL extract is 1000 ng/µL.

5.8.3 Matrix Spike Check: inject a sample of the spiking solution (with internal standard added) into the GC/MS to determine recovery of surrogate standards. It is recommended that this check be done whenever a new surrogate spiking solution is prepared.

5.9 Acetone, hexane, methylene chloride, isooctane, carbon disulfide, toluene, and other appropriate solvents - All solvents should be pesticide quality or equivalent.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Unanalyzed sample extracts are refrigerated and protected from light in sealed vials.

6.2 The holding time for samples is 7 days until extraction and 40 days thereafter.

6.3 Samples and target compound standards are stored separately.

7.0 PROCEDURE

7.1 Sample preparation

7.1.1 Soil and water are normally prepared via an extraction procedure (*cf.* Methods 3500, 3510, 3550; SOPs: 3510bna.doc and 3550bna.doc) prior to GC/MS analysis.

7.1.2 In cases where the sample is an oil or a solvent, the sample is simply diluted with methylene chloride and analyzed at a concentration appropriate for the level of analytes/interferences in the sample. In this situation, the sample is reported on a weight basis and analyzed in a batch of soil samples.

7.2 GC/MS operating conditions - see Table 3 for routine operating conditions for both BNA and PNA analysis.

7.3 Initial calibration

7.3.1 The GC/MS system must be hardware-tuned using a 50 ng injection of DFTPP prior to the analysis of calibration standards and samples.

7.3.1.1 In the absence of any other manipulations, evaluate the mass spectrum of the highest intensity level from the total ion chromatogram for the DFTPP peak. This is the default approach used.

7.3.1.2 If the above evaluation is adversely affected by ion peak asymmetry, average the three highest intensity scans of the peak or average the mass spectrum ranging from the 10% initial peak intensity to the tailing 10% peak intensity level from the total ion chromatogram for the DFTPP peak.

7.3.1.3 If the above evaluation is adversely affected by background contamination, perform a background subtraction with a spectrum within 20 scans of the DFTPP peak which does not represent a target compound. Use of this procedure may be indicative of failing MS performance. The MS source should be cleaned and re-tuned.

7.3.1.4 The DFTPP mass intensity criteria in Table 4 are used as tuning acceptance criteria.

7.3.1.5 All subsequent standards, samples, MS/MSDs, and blanks associated with a DFTPP analysis must use the identical mass spectrometer instrument conditions.

7.3.1.6 The GC/MS tuning standard solution should also be used to assess GC column performance and injection port inertness. Benzidine and pentachlorophenol should be present at their normal responses, and peak tailing should be minimal.

7.3.1.7 The injection port is replaced prior to any calibration sequence or 12-hour BNA analytical sequence. If chromatography is still poor, it may also be necessary to clip off the first 6-12 in. of the capillary column. Clipping the column may necessitate recalibration, as retention times and responses can shift considerably.

7.3.2 Analyze 1-2 µL of each calibration standard (containing internal standards) and tabulate the area of the primary characteristic ion against concentration for each target analyte (as indicated in Tables 1a and 1b). A set of at least five calibration standards is necessary. The injection volume must be the same for all standards and sample extracts. Figure 1 shows a chromatogram of a calibration standard containing base/neutral and acid analytes. Depending on the current state of the GC/MS system, a 2 µL injection may be required to achieve appropriate responses for the lower levels of the least sensitive compounds. When possible, however, a 1 µL can be used to yield a better dynamic range for the high sensitivity compounds.

7.3.3 Calculate response factors (*RF*s) for each target analyte relative to one of the internal standards as follows: $RF = A_s C_i / A_i C_s$. Here, A_s and A_i are the areas of the standard compound and corresponding internal standard, respectively. Likewise, C_s and C_i are the respective concentrations (in any consistent set of units) of the standard compound and corresponding internal standard.

7.3.4 System performance check compounds (SPCCs)

7.3.4.1 A system performance check must be performed to ensure that minimum *RF*s are met before the calibration curve is used. For semivolatiles, the System Performance Check Compounds (SPCCs) are: N-nitroso-di-n-propylamine; hexachlorocyclopentadiene; 2,4-dinitrophenol; and 4-nitrophenol.

7.3.4.2 The minimum acceptable average *RF* for these compounds is 0.050. These SPCCs typically have low *RF*s (0.1-0.2) and tend to decrease in response as the chromatographic system begins to deteriorate or the standard material begins to deteriorate. They are usually the first to show poor performance. Therefore, they must meet the minimum requirement when the system is calibrated.

7.3.4.3 If the minimum response factors are not met, the system must be evaluated, and corrective action must be taken before sample analysis begins. Possible problems include standard mixture degradation, contamination at the front end of the analytical column, and active sites in the column or chromatographic system. Replacing the calibration standards, and/or clipping/replacing the column will likely solve this problem.

7.3.5 Calibration check compounds (CCCs)

7.3.5.1 The purpose of the CCCs is to evaluate the calibration from the standpoint of the integrity of the system. High variability for these compounds may be indicative of system leaks or reactive sites on the column. Meeting the CCC criteria is in addition to the successful calibration of the target analytes using one of the approaches described in Section 7.0 of Method 8000.

7.3.5.2 Calculate the mean response factor and the relative standard deviation (RSD) of the response factors for each target analyte. The RSD should be less than or equal to 15%

for each target analyte. However, the RSD for each individual CCC (see Semi Volatile QC Reference) must be less than or equal to 30%.

7.3.5.3 If the RSD of any CCC is greater than 30%, then the chromatographic system is too reactive for analysis to begin. Clean or replace the injector liner and/or capillary column, then repeat the calibration procedure.

7.3.6 Evaluation of retention times - The relative retention time (RRT) of each target analyte in each calibration standard should agree within 0.06 RRT units. This is accomplished by setting the retention time extraction windows in the Chemstation software.

7.3.7 Linearity of target analytes - If the %RSD of any target analytes is 15% or less, then the relative response factor may be assumed to be constant over the calibration range, and the average relative response factor may be used for quantitation

7.3.7.1 Refer to Method 8000 if a least-squares regression is used to determine a linear or quadratic fit to the calibration data. Note that quadratic polynomials are generally fit through the origin in order to prevent the symptomatic aphysical prediction of high concentrations at very low responses. (All least-squares regressions used for OHIO VAP analysis will use a calculated intercept and quadratic fits will only be used for compounds exhibiting nonlinear behavior). In any event, the COD for any regression fit should be ≥0.99. In addition, 6 calibration data points are required for a calibration fit with 3 free parameters, while 5 are required for a calibration fit with 1 or 2 free parameters.

7.3.7.2 When the RSD exceeds 15%, the plotting and visual inspection of a calibration curve can be a useful diagnostic tool. The inspection may indicate analytical problems, including errors in standard preparation, the presence of active sites in the chromatographic system, analytes that exhibit poor chromatographic behavior, *etc*.

7.3.7.3 The quality of the calibration fit for any particular compound is communicated to the data user via the Quality Control report for a given batch of samples. The calibration summary report includes: the concentration and RF for each standard in the calibration curve, the type of calibration fit, the calibration fit parameters (*i.e*. average RF or regression coefficients), and the appropriate calibration quality metric (*i.e*. %RSD or COD).

7.4 GC/MS calibration verification - Calibration verification consists of three steps that are performed at the beginning of each 12-hour analytical shift.

7.4.1 Prior to the analysis of samples or calibration standards, inject 50 ng of the DFTPP standard into the GC/MS system. The resultant mass spectrum for DFTPP must meet the criteria given in Table 4 before sample analysis begins. These must be *injected* within 12 hours of the injection time for the DFTPP.

7.4.2 The initial calibration for each compound of interest should be verified once every 12 hours prior to sample analysis, using the introduction technique and conditions used for samples. This is accomplished by analyzing a calibration standard at a concentration near the midpoint concentration (50 ng/µL) for the calibration range of the GC/MS. The results from the calibration standard analysis must meet the verification acceptance criteria provided below for the SPCC and CCC compounds.

7.4.3 A method blank is run every 20 samples to ensure that the total system (preparation glassware, introduction device, transfer lines, and the GC/MS system itself) is free of contaminants.

7.4.4 System performance check compounds (SPCCs)

7.4.4.1 A system performance check must be made during every 12-hour analytical shift. Each SPCC in the calibration verification standard must meet a minimum response factor of 0.050. This is the same check that is applied during the initial calibration.

7.4.4.2 If the minimum response factors are not met, the system must be evaluated, and corrective action must be taken before sample analysis begins (see previous).

7.4.5 Calibration check compounds (CCCs)

7.4.5.1 After the system performance check is met, the CCCs listed in Semi Volatile Organic QC Reference are used to check the validity of the initial calibration. Percent drift is used to evaluate the CCC response and it must be ≤20%. Drift is defined as the normalized deviation of the measured from the spike value of a target component: $\%D = \left|C - C_{spike}\right| / C_{spike}$.

7.4.5.2 If the percent drift for each CCC is ≤20%, then the initial calibration is assumed to be valid. If the criterion is not met for any one CCC, then corrective action must be taken prior to the analysis of samples (see previous).

7.4.5.3 Problems similar to those listed under SPCCs could affect the CCCs. If the problem cannot be corrected by other measures, a new initial calibration must be generated. The CCC criteria must be met before sample analysis begins.

7.5 GC/MS analysis of samples

7.5.1 Samples are screened at a diluted state via GC/MS whenever possible prior to analysis within a 12-hour QC batch. This can identify potentially low surrogate recoveries, high target compound concentrations, non-target matrix interferences. This will minimize contamination of the GC/MS system from unexpectedly high concentrations of organic compounds.

7.5.2 Allow the sample extract to warm to room temperature. 3 µL of the internal standard solution is added to a 300 µL aliquot of sample in a crimp-top vial for subsequent autosampler analysis. If the sample extract is to be diluted prior to analysis, a smaller sample volume is used (even though the net volume of nominally 300 µL remains the same). The Dilution Reference has a list of commonly used dilutions as well as the required amount of sample, solvent, and internal standard for each dilution.

7.5.3 Inject a 1-2 µL aliquot of the sample extract into the GC/MS system, using the same operating conditions that were used for the calibration.

7.5.4 If the response for any quantitation ion exceeds the initial calibration range of the GC/MS system by more than 10%, the sample extract should be diluted and reanalyzed. In any event, a result based on an extrapolation of calibration curve beyond the working range is flagged on the analytical report.

7.5.5 The EICP area for all of the internal standards in all spikes, blanks, and samples is monitored relative to the most recent calibration verification standard. Changes by more than a factor of two (*i.e.* 50% to 200%) can indicate adverse matrix effects (in the case of an isolated sample) or degrading MS performance (in the case of a systematic low bias). A single-sample matrix effect is documented either via screening or re-analysis and is noted on the analytical report (see Semi Volatile QC Reference). Similarly, the retention times for all of the internal standards in all spikes, blanks, and samples is monitored relative to the most recent calibration verification standard. The change in retention time for any internal standard by more than 30 seconds of the most recent calibration verification standard is indicative of the same potential problems listed above and should be flagged/corrected as appropriate.

7.6 Qualitative analysis

7.6.1 The qualitative identification of compounds determined by this method is based on retention time and on comparison of the sample mass spectrum, after background correction, with characteristic ions in a reference mass spectrum. The reference mass spectrum must be generated by the laboratory using the conditions of this method. The characteristic ions from the reference mass spectrum are given in Tables 1a and 1b. Compounds are identified when the following criteria are met.

7.6.1.1 Initial selection of a target compound peak is performed by the Chemstation data system search routine. The search is based on the presence of a target chromatographic peak containing ions specific for the target compound at a compound-specific retention time.

7.6.1.2 The RRT of the sample component is within ± 0.06 RRT units of the RRT of the standard component. This is accomplished using retention time extraction windows within the Chemstation data system.

7.6.1.3 The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum. (Example: For an ion with an abundance of 50% in the reference spectrum, the corresponding abundance in a sample spectrum can range between 20% and 80%.)

7.6.1.4 Structural isomers that produce very similar mass spectra are identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

7.6.1.5 Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When gas chromatographic peaks obviously represent more than one sample component (*i.e.*, a broadened peak with shoulder(s) or a valley between two or more maxima), appropriate selection of analyte spectra and background spectra is important.

7.6.1.6 Examination of extracted ion current profiles of appropriate ions can aid in the selection of spectra and in qualitative identification of compounds. When analytes coelute (*i.e.*, only one chromatographic peak is apparent), the identification criteria may be met, but each analyte spectrum will contain extraneous ions contributed by the coeluting compound.

7.6.1.7 In the two previous cases, analyst expertise as well as knowledge of site history may be important in accepting/rejecting the identification of a compound. In the event of continued uncertainty, the analyst should preferentially make a conservative judgement and accept an identified hit, allowing the potential for a false positive.

7.6.2 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 purpose of the analyses being conducted. Only after visual comparison of sample spectra with the nearest library searches may the analyst assign a tentative identification. Guidelines for 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%.
- 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.

7.7 Quantitative analysis

7.7.1 Once a compound has been identified, the quantitation of that compound will be based on the integrated abundance of the primary characteristic ion from the EICP.

7.7.2 The curve fit applied in the initial calibration is the same as that used to compute the concentration of a target analyte in a sample. All curve fits are evaluated by the data system and are of the form: $A_s/A_i = k_0 + k_1[C_s/C_i] + k_2[C_s/C_i]^2$. Here A_s and A_i are the areas of the target and internal standard, C_s and C_i are the concentrations of the target and internal standard, and k_i is the i^{th}-order regression coefficient. Note that for a mean RF fit to the calibration data, $k_1 \equiv$ <RF>, while k_0, $k_2 \equiv 0$.

7.7.3 The concentration of any non-target analytes identified in the sample may be estimated by assuming a mean RF of 1 and by using the TIC areas for the nearest internal standard and target compound. The resulting concentration should be reported indicating: (1) that the value is an estimate, and (2) which internal standard was used to determine concentration. Use the nearest internal standard free of interferences.

7.7.4 Structural isomers that produce very similar mass spectra should be quantitated as individual isomers if they have sufficiently different GC retention times. Otherwise, structural isomers are quantitated as isomeric pairs (such as p- and m-cresol).

7.8 Special procedures for diesel range organics (DROs) - The following items detail the differences in the calibration procedures for multicomponent, diesel range organics from the general, single component procedures outlined above.

7.8.1 A set of at least five calibration standards per §7.2 and §7.3.2. The preparation instructions for the creation of the DRO calibration standards can be found in the Calibration Recipes excel file. Figure 2 represents a DRO chromatogram.

7.8.2 Instead of using the measured responses from the TIC to represent the DRO calibration, the total area of ions characteristic to the fuel in question is used in an internal standard calibration. Using characteristic ions to represent a fuel has the advantage of reducing biases from other components present in the chromatogram (namely surrogate and internal standards), and the use of an internal standard improves the stability of a calibration. Diesel range organics consist primarily of straight and branched alkanes (~C_{10} to C_{28}). For the alkanes, the characteristic mass used is m/z = 57 (corresponding to the ion $C_4H_9^+$). This single ion is used for quantitation.

7.8.3 Calculate response factors (*RF*s) for each target mass relative to one of the internal standards as follows: $RF = A_s C_i / A_i C_s$. Here, A_s and A_i are the areas of the characteristic mass over its respective time range and corresponding internal standard, respectively. Likewise, C_s and C_i are the respective concentrations (in any consistent set of units) of the *total fuel* and corresponding internal standard. The characteristic time ranges for each mass depend upon current chromatographic conditions. The time ranges used for the sample chromatograms in Figures 1 and 2 are listed in the respective figure.

7.8.4 The relative area response vs. relative concentration for each characteristic mass is calibrated in the same manner as described in §7.3.7 and §7.7.

7.8.5 The net result for a DRO analysis is based upon the single characteristic mass (57).

7.8.6 In addition the routine SPCC/CCC check standard, a DRO check standard is analyzed in order characterize the efficacy of the present DRO calibration in terms of recovery and retention times.

8.0 QUALITY CONTROL

8.1 All of the quality control items employed and evaluated are listed in Semi Volatile QC Reference. In addition, the Semi Volatile QC Reference indicates the frequency of each QC item along with appropriate courses of corrective action.

8.2 Quality control items are inspected by the analyst as the data becomes available. At the conclusion of the analytical batch, all of the samples, spikes, standards, *etc*. are processed and evaluated automatically and stored electronically for future reference/retrieval.

9.0 METHOD PERFORMANCE

9.1 Laboratory-specific performance data is provided in this document

9.2 Tables 2a, 2b, and 2c present the results for the most recent detection limit studies. The MDL, PQL and ratio of PQL/MDL are given for each analyte in the BNA and PNA target compound lists.

9.3 Lower and upper acceptance limits for all surrogate and matrix spiking compounds can be found in the Semi Volatile QC Reference.

10.0 REFERENCES

1. SW-846, 1996, Revision 3; Methods 3500, 3510, 3550, 8000, 8015, 8270.

11.0 APPROVAL AND ISSUE

Analyst	Date
Andy Ball, QA Officer	Date
Maya V. Murshak, Technical Director	Date

12.0 TABLES AND FIGURES

Table 1a. Summary of Retention Times† and Characteristic Ions for Base/Neutral/Acid Semi-Volatile Organics

#	**Compound**	t_R (*min*)	$t_R/t_{R,I}$ (-)	$t_R-t_{R,I}$ (*min*)	1^0 *m/z*	2^0 *m/z*	3^0 *m/z*	4^0 *m/z*
1)	1,4-DICHLOROBENZENE-D4	6.92	1.000	0.00	152	150	115	
2)	N-Nitrosodimethylamine	3.79	0.548	-3.13	74	42	43	
3)	2-Picoline	4.61	0.666	-2.31	93	92	66	
4)	Methyl methanesulfonate	5.16	0.746	-1.76	80	79	95	
5)	2-Fluorophenol	5.31	0.767	-1.61	112	92	64	
6)	Ethyl methanesulfonate	5.99	0.866	-0.93	79	109	97	
7)	Phenol-d5	6.45	0.932	-0.47	99	71	42	
8)	Phenol **	6.47	0.935	-0.45	94	66	65	
9)	Aniline	6.53	0.944	-0.39	93	65	66	
10)	2-Chlorophenol **	6.68	0.965	-0.24	128	130	92	
11)	Bis(2-chloroethyl)ether	6.59	0.952	-0.33	93	63	95	
12)	1,3-Dichlorobenzene	6.94	1.003	0.02	146	148	111	
13)	1,4-Dichlorobenzene **	6.94	1.003	0.02	146	148	111	
14)	1,2-Dichlorobenzene	7.18	1.038	0.26	146	148	111	
15)	Bis(2-chloroisopropyl)ethe	7.3	1.055	0.38	45	121	77	
16)	Benzyl Alcohol	7.09	1.025	0.17	108	107	79	77
17)	Acetophenone	7.46	1.078	0.54	105	77	120	
18)	o-Cresol	7.24	1.046	0.32	108	107	79	
19)	p,m-Cresol	7.42	1.072	0.50	107	108	79	
20)	Hexachloroethane	7.59	1.097	0.67	117	119	201	
21)	N-Nitrosodi-n-propylamine*	7.48	1.081	0.56	70	43	42	41
22)	NAPHTHALENE-D8	8.59	1.000	0.00	136	68	108	
23)	Nitrobenzene-d5	7.66	0.892	-0.93	82	128	98	
24)	Nitrobenzene	7.69	0.895	-0.90	123	123	65	
25)	N-Nitrosopiperidine	7.89	0.919	-0.70	114	55	56	
26)	Isophorone	7.98	0.929	-0.61	82	95	138	
27)	2-Nitrophenol	8.11	0.944	-0.48	139	109	65	
28)	2,4-Dimethylphenol	8.12	0.945	-0.47	107	122	121	
29)	Bis(2-chloroethoxy)methane	8.25	0.960	-0.34	93	63	95	
30)	2,4-Dichlorophenol	8.4	0.978	-0.19	162	164	98	
31)	1,2,4-Trichlorobenzene **	8.52	0.992	-0.07	180	182	145	
32)	Naphthalene	8.61	1.002	0.02	128	127	129	
33)	4-Chloroaniline	8.69	1.012	0.10	127	129	65	
34)	2,6-Dichlorophenol	8.71	1.014	0.12	162	164	127	
35)	Hexachlorobutadiene	8.83	1.028	0.24	225	223	227	
36)	N-Nitroso-di-n-butylamine	9.13	1.063	0.54	84	116	158	
37)	4-Chloro-3-methylphenol **	9.28	1.080	0.69	107	142	77	
38)	2-Methylnaphthalene	9.5	1.106	0.91	141	142	115	
40)	1,2,4,5-Tetrachlorobenzene	9.77	1.137	1.18	216	214	218	
41)	Hexachlorocyclopentadiene	9.79	1.140	1.20	237	235	239	
42)	2,4,6-Trichlorophenol	9.94	1.157	1.35	196	198	200	
43)	2,4,5-Trichlorophenol	9.94	1.157	1.35	196	198	132	
44)	2-Fluorobiphenyl	9.98	1.162	1.39	172	171	173	
45)	2-Chloronaphthalene	10.13	1.179	1.54	162	127	164	
46)	1-Chloronaphthalene	10.18	1.185	1.59	162	164	127	
47)	2-Nitroaniline	10.29	1.198	1.70	138	65	92	

#	**Compound**	t_R (*min*)	$t_R/t_{R,I}$ (-)	t_R-$t_{R,I}$ (*min*)	1^0 *m/z*	2^0 *m/z*	3^0 *m/z*	4^0 *m/z*
48)	Acenaphthylene	10.67	1.242	2.08	152	151	150	
49)	Dimethyl Phthalate	10.54	1.227	1.95	163	164	77	
50)	2,6-Dinitrotoluene	10.64	1.239	2.05	165	121	148	
51)	3-Nitroaniline	10.82	1.260	2.23	138	92	65	
52)	Acenaphthene **	10.91	1.270	2.32	154	153	152	
53)	2,4-Dinitrophenol	10.95	1.275	2.36	184	63	107	
54)	Dibenzofuran	11.12	1.295	2.53	168	169	139	
55)	4-Nitrophenol **	10.99	1.279	2.40	65	139	81	109
56)	2,4-Dinitrotoluene **	11.15	1.298	2.56	165	89	63	
57)	2,3,4,6-Tetrachlorophenol	11.32	1.318	2.73	232	230	234	131
58)	Fluorene	11.56	1.346	2.97	166	165	167	
59)	Diethyl phthalate	11.43	1.331	2.84	149	150	177	
60)	4-Chlorophenyl phenyl ethe	11.53	1.342	2.94	204	141	206	
61)	4-Nitroaniline	11.61	1.352	3.02	138	65	92	
62)	2,4,6-Tribromophenol	11.89	1.384	3.30	330	332	141	
63)	PHENANTHRENE-D10	12.8	1.000	0.00	188	80	94	
64)	4,6-Dinitro-2-methylphenol	11.67	0.912	-1.13	198	121	105	
65)	N-Nitrosodiphenylamine	11.69	0.913	-1.11	169	168	167	
66)	1,2-Diphenylhydrazine	11.74	0.917	-1.06	182	105	77	
67)	Azobenzene	11.74	0.917	-1.06	182	105	77	
68)	4-Bromophenyl phenyl ether	12.16	0.950	-0.64	248	250	77	
69)	1,3,5-Trinitrobenzene	12.08	0.944	-0.72	213	74	75	
70)	Phenacetin	12.11	0.946	-0.69	108	109	179	137
71)	Hexachlorobenzene	12.37	0.966	-0.43	249	282	286	
72)	4-Aminobiphenyl	12.51	0.977	-0.29	169	168	170	
73)	Pentachlorophenol **	12.6	0.984	-0.20	266	264	268	
75)	Pronamide	12.6	0.984	-0.20	173	174	145	
76)	Pentachloronitrobenzene	12.72	0.994	-0.08	237	249	295	
77)	Phenanthrene	12.83	1.002	0.03	178	176	179	
78)	Anthracene	12.83	1.002	0.03	178	176	179	
79)	di-N-butyl phthalate	13.62	1.064	0.82	149	150	104	
80)	Fluoranthene	14.65	1.145	1.85	202	200	203	
81)	Terphenyl-d14	15.28	1.194	2.48	244	122	212	
82)	CHRYSENE-D12	17.34	1.000	0.00	240	236	120	
83)	Benzidine	14.83	0.855	-2.51	184	185	92	
84)	Pyrene **	15.03	0.867	-2.31	202	200	203	
85)	p-Dimethylaminoazobenzene	15.57	0.898	-1.77	225	120	77	
86)	Butyl benzyl phthalate	16.23	0.936	-1.11	149	91	206	
88)	Benzo(a)anthracene	17.29	0.997	-0.05	228	226	229	
89)	3,3'-Dichlorobenzidine	17.25	0.995	-0.09	252	254	126	
90)	Chrysene	17.38	1.002	0.04	228	226	229	
92)	PERYLENE-D12	20.3	1.000	0.00	264	260	265	
91)	Bis(2-ethylhexyl)phthalate	17.42	0.858	-2.88	149	167	279	
93)	Di-n-octyl phthalate	18.66	0.919	-1.64	149	43	167	
95)	Benzo(b)fluoranthene	19.47	0.959	-0.83	252	253	126	
96)	7,12-Dimethylbenz(a)anthra	19.5	0.961	-0.80	256	241	239	
97)	Benzo(k)fluoranthene	19.47	0.959	-0.83	252	253	126	

#	**Compound**	t_R (*min*)	$t_R/t_{R,I}$ (-)	t_R-$t_{R,I}$ (*min*)	1^0 *m/z*	2^0 *m/z*	3^0 *m/z*	4^0 *m/z*
98)	Benzo(a)pyrene	20.16	0.993	-0.14	252	253	126	
99)	3-Methylcholanthrene	21.04	1.036	0.74	268	252	253	269
100)	Dibenz(a,j)acridine	22.54	1.110	2.24	279	280	139	278
101)	Indeno(1,2,3-cd)pyrene	23.1	1.138	2.80	276	138	277	
102)	Dibenzo(a,h)anthracene	23.14	1.140	2.84	278	139	279	
103)	Benzo(ghi)perylene	23.92	1.178	3.62	276	138	277	

†: Absolute retention times (t_R) listed are from calibration BU061002.M. Absolute and relative retention times ($t_R/t_{R,I}$) may shift with the present condition of the column (*i.e*. new, clipped, *etc*.), but the differential retention times (t_R - $t_{R,I}$) tend to remain constant given the same chromatographic temperature program.

Table 1b. Summary of Retention Times† and Characteristic Ions for Polynuclear Aromatic Semi-Volatile Organics

#	**Compound**	t_R (*min*)	$t_R/t_{R,I}$ (-)	t_R-$t_{R,I}$ (*min*)	1^0 *m/z*	2^0 *m/z*	3^0 *m/z*	4^0 *m/z*
1)	1,4-DICHLOROBENZENE-D4	3.96	1.000	0.00	152	152		
2)	NAPHTHALENE-D8	5.21	1.000	0.00	136	68	108	
3)	Nitrobenzene-d5	4.52	0.868	-0.69	82	54	128	
4)	Naphthalene	5.23	1.004	0.02	128	127	129	
5)	2-Methylnaphthalene	5.88	1.129	0.67	141	141	115	
6)	ACENAPHTHALENE-D10	6.94	1.000	0.00	164	162	160	
7)	2-Fluorobiphenyl	6.23	0.898	-0.71	172	171	173	
8)	Acenaphthylene	6.78	0.977	-0.16	152	151	150	
9)	Acenaphthene **	6.97	1.004	0.03	154	153	76	
10)	Fluorene	7.49	1.079	0.55	166	165	167	
11)	PHENANTHRENE-D10	8.52	1.000	0.00	188	80	94	
12)	Phenanthrene	8.54	1.002	0.02	178	176	179	
13)	Anthracene	8.6	1.009	0.08	178	176	179	
14)	Fluoranthene	10.09	1.184	1.57	202	200	203	
15)	Terphenyl-D14	10.62	1.246	2.10	244	122	212	
16)	CHRYSENE-D12	12.5	1.000	0.00	240	236	120	
17)	Pyrene **	10.44	0.835	-2.06	202	101	200	
18)	Benzo(a)anthracene	12.46	0.997	-0.04	228	226	229	
19)	Chrysene	12.54	1.003	0.04	228	226	229	
20)	PERYLENE-D12	15.22	1.000	0.00	264	260	132	
21)	Benzo(b)fluoranthene	14.51	0.953	-0.71	252	253	126	
22)	Benzo(k)fluoranthene	14.56	0.957	-0.66	252	253	125	
23)	Benzo(a)pyrene	15.12	0.993	-0.10	252	253	126	
24)	Indeno(1,2,3-cd)pyrene	17.38	1.142	2.16	276	138	277	
25)	Dibenzo(ah)anthracene	17.39	1.143	2.17	278	139	279	
26)	Benzo(ghi)perylene	17.99	1.182	2.77	276	138	277	

†: Absolute retention times (t_R) listed are from calibration PF060829.M. Absolute and relative retention times ($t_R/t_{R,I}$) may shift with the present condition of the column (*i.e*. new, clipped, *etc*.), but the differential retention times (t_R - $t_{R,I}$) tend to remain constant given the same chromatographic temperature program.

Table 2a. Summary of Practical Quantitation Limits for Base/Neutral/Acid Semi-Volatile Organics †

COMPOUND	PQL_S (µg/kg)	PQL_W (µg/L)	IDL_S (µg/kg)	IDL_W (µg/L)	MDL_S (µg/kg)	MDL_W (µg/L)	PQL_S/IDL_S	PQL_W/IDL_W
Pyridine	330	10.0	18.6	0.559	24.9	0.8	17.9	17.9
N-Nitrosodimethylamine	330	10.0	12.7	0.380	32.4	0.6	26.3	26.3
2-Picoline	330	10.0	25.3	0.759	94.0	6.8	13.2	13.2
Methyl methanesulfonate	330	10.0	17.8	0.534	162.6	2.3	18.7	18.7
Ethyl methanesulfonate	330	10.0	9.0	0.271	150.1	3.8	36.8	36.8
Phenol **	330	10.0	14.6	0.439	278.0	4.0	22.8	22.8
Aniline	330	10.0	27.0	0.809	250.9	15.7	12.4	12.4
2-Chlorophenol **	330	10.0	14.8	0.443	261.4	3.6	22.6	22.6
Bis(2-chloroethyl)ether	330	10.0	7.9	0.238	247.3	4.4	42.0	42.0
1,3-Dichlorobenzene	330	10.0	15.9	0.476	226.3	5.1	21.0	21.0
1,4-Dichlorobenzene **	330	10.0	8.4	0.253	242.6	5.8	39.5	39.5
1,2-Dichlorobenzene	330	10.0	8.1	0.242	231.5	5.9	41.4	41.4
Bis(2-chloroisopropyl)ether	330	10.0	7.8	0.234	265.3	4.2	42.7	42.7
Benzyl Alcohol	330	10.0	10.9	0.328	307.0	4.5	30.5	30.5
Acetophenone	330	10.0	9.6	0.287	248.5	4.9	34.9	34.9
o-Cresol	330	10.0	8.3	0.249	257.4	3.3	40.1	40.1
p,m-Cresol	330	10.0	9.6	0.287	280.2	3.9	34.8	34.8
Hexachloroethane	330	10.0	13.0	0.390	222.5	4.3	25.7	25.7
N-Nitrosodi-n-propylamine*	330	10.0	11.2	0.336	305.9	5.5	29.8	29.8
Nitrobenzene	330	10.0	12.0	0.361	223.7	3.3	27.7	27.7
N-Nitrosopiperidine	330	10.0	15.7	0.471	243.3	4.0	21.2	21.2
Isophorone	330	10.0	10.1	0.304	238.6	4.0	32.9	32.9
2-Nitrophenol	330	10.0	59.8	1.793	208.3	4.0	5.6	5.6
2,4-Dimethylphenol	330	10.0	18.9	0.568	234.7	3.3	17.6	17.6
Bis(2-chloroethoxy)methane	330	10.0	13.2	0.397	232.1	4.3	25.2	25.2
2,4-Dichlorophenol	330	10.0	13.3	0.399	220.8	4.5	25.0	25.0
1,2,4-Trichlorobenzene **	330	10.0	16.5	0.494	209.0	4.1	20.2	20.2
Benzoic Acid	330	10.0	7.4	0.222	N/A	7.3	45.0	45.0
Naphthalene	330	10.0	12.7	0.380	222.2	4.9	26.3	26.3
4-Chloroaniline	330	10.0	118.1	3.542	307.7	9.2	2.8	2.8
2,6-Dichlorophenol	330	10.0	20.2	0.607	224.3	4.2	16.5	16.5
Hexachlorobutadiene	330	10.0	17.8	0.534	188.0	2.7	18.7	18.7
N-Nitroso-di-n-butylamine	330	10.0	17.8	0.535	256.1	4.6	18.7	18.7
4-Chloro-3-methylphenol **	330	10.0	12.6	0.377	264.8	4.2	26.5	26.5
2-Methylnaphthalene	330	10.0	14.4	0.433	223.4	4.5	23.1	23.1
1,2,4,5-Tetrachlorobenzene	330	10.0	22.2	0.667	197.6	3.5	15.0	15.0
Hexachlorocyclopentadiene	330	10.0	49.8	1.493	204.3	4.8	6.7	6.7
2,4,6-Trichlorophenol	330	10.0	16.1	0.483	212.0	3.2	20.7	20.7
2,4,5-Trichlorophenol	330	10.0	54.6	1.637	178.8	3.1	6.1	6.1
1-Chloronaphthalene	330	10.0	11.5	0.344	224.6	3.7	29.1	29.1
2-Chloronaphthalene	330	10.0	33.2	0.997	199.4	3.3	10.0	10.0
2-Nitroaniline	330	10.0	24.2	0.725	263.4	3.8	13.8	13.8
Acenaphthylene	330	10.0	40.4	1.212	247.1	3.4	8.3	8.3
Dimethyl Phthalate	330	10.0	10.2	0.305	322.0	3.8	32.8	32.8
2,6-Dinitrotoluene	330	10.0	24.4	0.732	315.2	3.9	13.7	13.7
3-Nitroaniline	330	10.0	27.8	0.833	368.1	5.1	12.0	12.0

COMPOUND	PQL_S (µg/kg)	PQL_W (µg/L)	IDL_S (µg/kg)	IDL_W (µg/L)	MDL_S (µg/kg)	MDL_W (µg/L)	PQL_S/IDL_S	PQL_W/IDL_W
Acenaphthene **	330	10.0	17.0	0.509	398.5	3.1	19.6	19.6
2,4-Dinitrophenol	330	10.0	63.4	1.902	N/A	5.7	5.3	5.3
Dibenzofuran	330	10.0	17.4	0.522	385.9	3.5	19.1	19.1
4-Nitrophenol **	330	10.0	145.4	4.361	249.7	8.0	2.3	2.3
2,4-Dinitrotoluene **	330	10.0	20.9	0.628	276.9	3.5	15.9	15.9
1-Naphthylamine	330	10.0	54.0	1.619	460.8	24.9	6.2	6.2
2-Naphthylamine	330	10.0	130.3	3.908	442.8	30.8	2.6	2.6
2,3,4,6-Tetrachlorophenol	330	10.0	17.4	0.521	245.5	2.9	19.2	19.2
Fluorene	330	10.0	13.2	0.396	348.9	3.8	25.2	25.2
Diethyl phthalate	330	10.0	17.2	0.516	298.5	3.8	19.4	19.4
4-Chlorophenyl phenyl ether	330	10.0	12.5	0.376	365.0	4.2	26.6	26.6
4-Nitroaniline	330	10.0	210.8	6.323	340.7	5.7	1.6	1.6
4,6-Dinitro-2-methylphenol	330	10.0	20.6	0.619	142.9	3.5	16.2	16.2
N-Nitrosodiphenylamine	330	10.0	14.8	0.445	290.2	4.5	22.5	22.5
1,2-Diphenylhydrazine	330	10.0	10.9	0.326	333.3	4.3	30.7	30.7
Azobenzene	330	10.0	10.9	0.326	333.1	4.3	30.7	30.7
4-Bromophenyl phenyl ether	330	10.0	9.0	0.270	314.3	3.9	37.0	37.0
1,3,5-Trinitrobenzene	330	10.0	19.9	0.596	246.9	4.8	16.8	16.8
Phenacetin	330	10.0	17.2	0.517	185.5	4.2	19.3	19.3
Hexachlorobenzene	330	10.0	13.3	0.399	279.8	4.3	25.1	25.1
4-Aminobiphenyl	330	10.0	96.7	2.900	495.4	29.9	3.4	3.4
Pentachlorophenol **	330	10.0	15.8	0.474	176.0	2.9	21.1	21.1
Pronamide	330	10.0	14.0	0.419	273.4	5.1	23.9	23.9
Pentachloronitrobenzene	330	10.0	24.6	0.738	282.6	4.9	13.6	13.6
Phenanthrene	330	10.0	9.3	0.280	263.3	4.0	35.8	35.8
Anthracene	330	10.0	16.7	0.500	245.5	4.3	20.0	20.0
di-N-butyl phthalate	330	10.0	13.1	0.394	201.5	5.1	25.4	25.4
Fluoranthene	330	10.0	15.0	0.450	225.2	4.5	22.2	22.2
Benzidine	330	10.0	78.9	2.368	59.1	25.4	4.2	4.2
Pyrene **	330	10.0	7.3	0.219	260.1	5.0	45.7	45.7
p-Dimethylaminoazobenzene	330	10.0	14.0	0.421	229.7	4.3	23.8	23.8
Butyl benzyl phthalate	330	10.0	5.0	0.151	361.7	4.8	66.0	66.0
Benzo(a)anthracene	330	10.0	7.5	0.226	269.4	5.6	44.3	44.3
3,3'-Dichlorobenzidine	330	10.0	15.0	0.450	326.5	16.8	22.2	22.2
Chrysene	330	10.0	8.0	0.240	273.4	5.4	41.6	41.6
Bis(2-ethylhexyl)phthalate	330	10.0	12.8	0.384	481.3	5.5	26.0	26.0
Di-n-octyl phthalate	330	10.0	20.8	0.625	330.7	5.0	16.0	16.0
Benzo(b)fluoranthene	330	10.0	21.5	0.646	267.5	6.7	15.5	15.5
7,12-Dimethylbenz(a)anthracene	330	10.0	19.0	0.571	230.3	6.8	17.5	17.5
Benzo(k)fluoranthene	330	10.0	17.7	0.530	269.6	5.6	18.9	18.9
Benzo(a)pyrene	330	10.0	22.5	0.675	253.1	5.2	14.8	14.8
3-Methylcholanthrene	330	10.0	12.3	0.369	264.6	4.9	27.1	27.1
Dibenz(a,j)acridine	330	10.0	17.3	0.520	49.4	6.0	19.2	19.2
Indeno(1,2,3-cd)pyrene	330	10.0	15.5	0.465	262.2	6.0	21.5	21.5
Dibenzo(a,h)anthracene	330	10.0	19.1	0.574	254.9	6.5	17.4	17.4
Benzo(ghi)perylene	330	10.0	8.8	0.263	273.9	5.7	38.1	38.1

†: Data are from 08/08/2001 (IDL data) and 02/04/2002 (MDL data).

Table 2b. Summary of Practical Quantitation Limits for Polynuclear Aromatic Semi-Volatile Organics†

COMPOUND	PQL_W (µg/L)	PQL_S (µg/kg)	IDL_W (µg/L)	IDL_S (µg/kg)	PQL_W/IDL_W	PQL_S/IDL_S
Naphthalene	5.0	330	0.957	31.9	5.2	10.4
2-Methylnaphthalene	5.0	330	0.478	15.9	10.5	20.9
Acenaphthylene	5.0	330	0.312	10.4	16.0	32.0
Acenaphthene	5.0	330	0.680	22.7	7.3	14.7
Fluorene	5.0	330	0.322	10.7	15.5	31.0
Phenanthrene	5.0	330	0.489	16.3	10.2	20.4
Anthracene	5.0	330	0.414	13.8	12.1	24.1
Fluoranthene	5.0	330	0.404	13.5	12.4	24.7
Pyrene	5.0	330	0.123	4.1	40.8	81.6
Benzo(a)anthracene	5.0	330	0.273	9.1	18.3	36.6
Chrysene	5.0	330	0.330	11.0	15.2	30.3
Benzo(b)fluoranthene	5.0	330	1.297	43.2	3.9	7.7
Benzo(k)fluoranthene	5.0	330	0.854	28.5	5.9	11.7
Benzo(a)pyrene	5.0	330	0.368	12.3	13.6	27.2
Indeno(1,2,3-cd)pyrene	5.0	330	0.300	10.0	16.7	33.4
Dibenzo(ah)anthracene	5.0	330	0.438	14.6	11.4	22.8
Benzo(ghi)perylene	5.0	330	0.624	20.8	8.0	16.0

†: Data are from 05/26/2001.

Table 2c. Practical Quantitation Limits for Diesel Range Organics†

COMPOUND	PQL_W (mg/L)	PQL_S (mg/kg)	IDL_W (mg/L)	IDL_S (mg/kg)	PQL_W/IDL_W	PQL_S/IDL_S
Diesel Range Organics	0.1	4	0.0078	0.26	15.5	12.9

†: Data are from 05/26/2001.

Table 3. GC/MS Operating Conditions - Base/Neutral/Acid (BNA) and Polynuclear Aromatic (PNA) Semi-Volatile Organics Analysis†

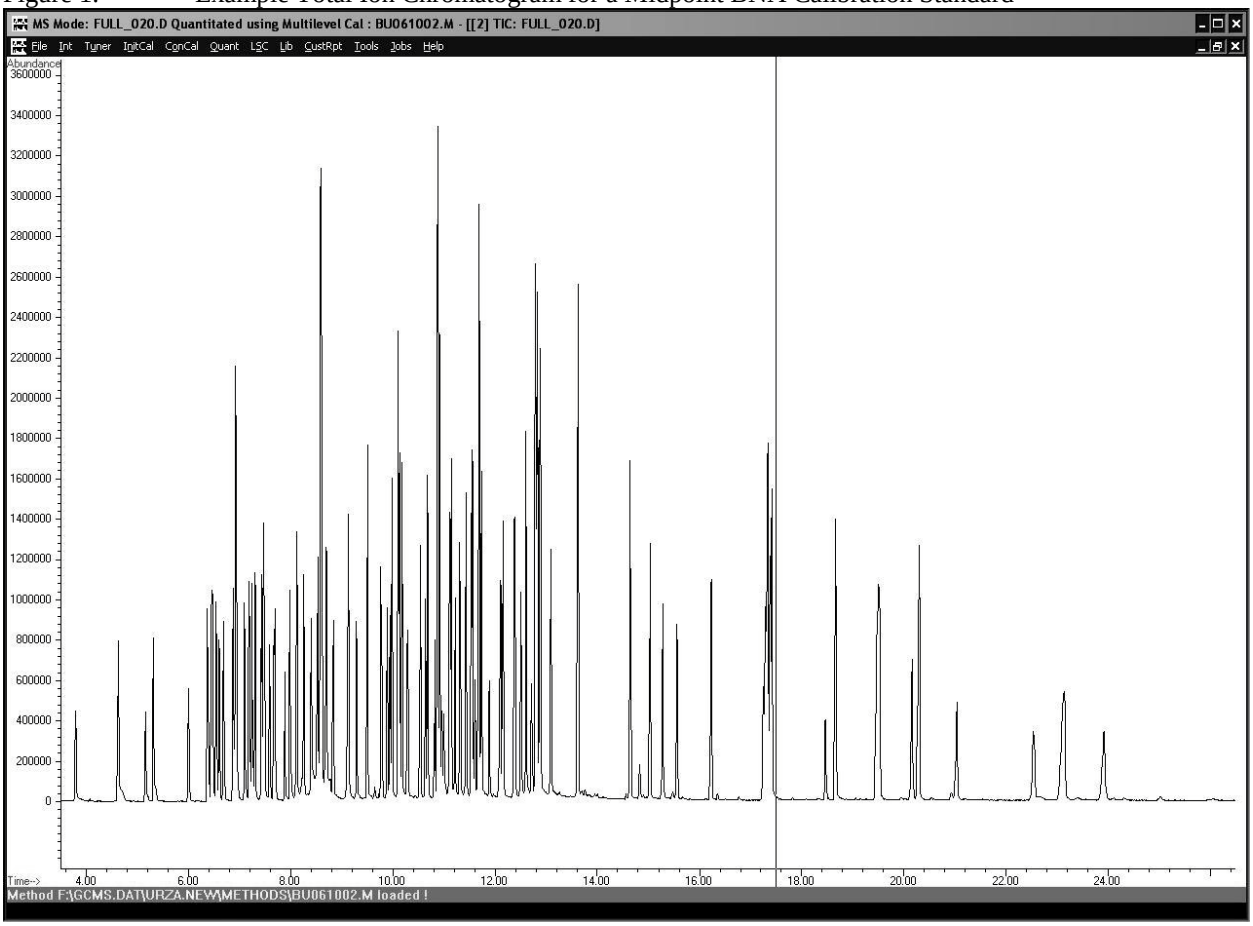
Operating Parameter	**BNA Analysis**	**PNA Analysis**
Chromatographic Column	HP-5MS SV, *L* = 30 *m*, *ID* = 0.25 *mm*	HP-5MS SV, *L* = 30 *m*, *ID* = 0.25 *mm*
Carrier Gas	Helium (He) at 2 *ml*/*min*	Helium (He) at 2 *ml*/*min*
Temperature Program	*Variable-Instrument dependent*	*Variable-Instrument dependent*
Injector Temperature	250°C	250°C
Detector Temperature	280°C	280°C
Injection Volume	1-2µ*l*	1µ*l*
Mass Scanning Range	40 *m*/*z* - 450 *m*/*z*	35 *m*/*z* - 550 *m*/*z*
Mass Scanning Rate	1.8 *Hz*	1.4 *Hz*

†: Note that DROs may be analyzed by either of the two sets of operating conditions.

Table 4. DFTPP Tune Evaluation Criteria

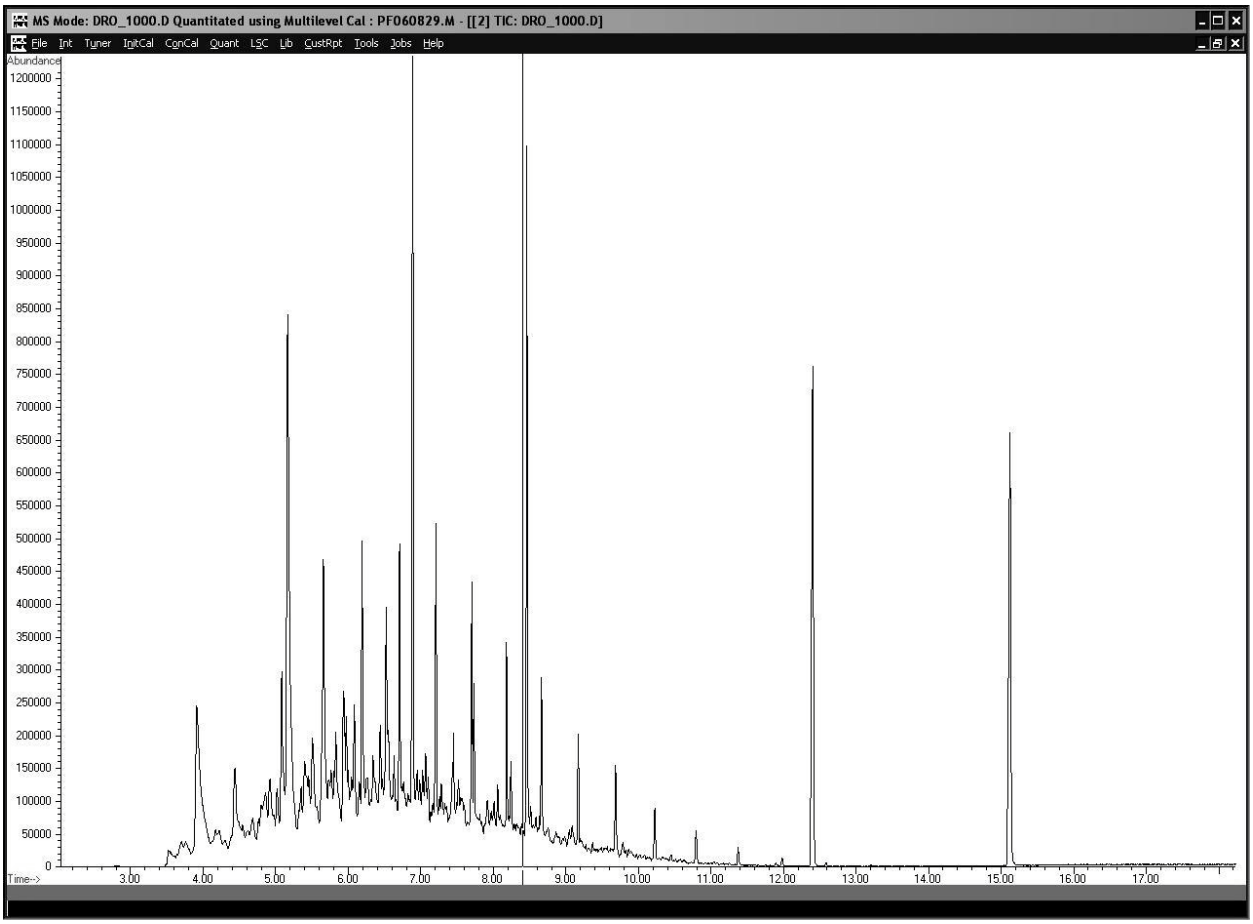
Target *m/z*	**Relative *m/z***	**LCL (%)**	**UCL (%)**
51	198	30.0	80.0
68	69	0.0	2.0
69	198	0.0	NA
70	69	0.0	2.0
127	198	25.0	75.0
197	198	0.0	1.0
198	198	100.0	100.0
199	198	5.0	9.0
275	198	10.0	30.0
365	198	1.0	NA
441	443	0.0	100.0
442	198	40.0	110.0
443	442	15.0	24.0

Figure 1. Example Total Ion Chromatogram for a Midpoint BNA Calibration Standard[†]



[†]: Data file FULL_020.D from calibration BU061002.M (20 ng/µL). GC/MS acquisition parameters are given by Table 4 for BNA Analysis.

Figure 2. Example Total Ion Chromatogram for a Diesel Range Organics Calibration Standard†



†: Data file DRO_1000.D from calibration PD061007.M (1.0 g/L). GC/MS acquisition parameters are given by Table 4.

SOP #043550B: ULTRASONIC EXTRACTION FOR BNAS/PNAS/HERBICIDES USING METHOD 3550B

Revision: 5
Date: 03/03/06

Location: Extraction Laboratory
Semi-volatiles GC/MS Laboratory
QA Officer's Files

These procedures are restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with these techniques and methods.

1.0 SCOPE AND APPLICATION

1.1 This method is used for extracting nonvolatile and semivolatile base/neutral/acid (BNA), polynuclear aromatic hydrocarbon (PNA) and herbicides organic compounds from solids such as soils, sludges, and wastes. The ultrasonic process ensures intimate contact of the sample matrix with the extraction solvent.

2.0 SUMMARY OF METHOD

2.1 For most of samples, 2g - 30g sample (depending on the matrix; 30g is typical for a soil) is mixed with anhydrous sodium sulfate to form a free-flowing solid. Extract with methylene chloride using ultrasound. For herbicides samples, acidified sodium sulfate is used instead.
2.2 The extract is separated from the sample and concentrated.
2.3 Clean glassware and matrix cleanup procedures are used to obtain the optimum analytical chromatograms.

3.0 INTERFERENCES

3.1 The decomposition of some analytes has been demonstrated under basic extraction conditions. Organochlorine pesticides may de-chlorinate.
3.2 Degradation of PCBs, as well as more complex matrix (i.e. oil, tar, sulfur, etc.) can interfere with the "clarity" of the chromatograms.

4.0 APPARATUS AND MATERIALS

4.1 Apparatus for grinding dry waste samples
4.2 Ultrasonic device - Branson Sonifier, Model 450
4.3 Ultrasonic Disrupter - power wattage of 300 watts, with pulsing.
  4.3.1 3/4" horn
  4.3.2 Sonabox - (Ultrasonics #432B)
4.4 Apparatus for percent dry weight
  4.4.1 Drying oven (105ºC - 120ºC)
  4.4.2 Dessicator
  4.4.3 Crucibles - disposable aluminum
  4.4.4 Glass pipettes - 1ml, disposable
  4.4.5 Beakers - 250ml
  4.4.6 Filter paper - Whittman No. 41
4.5 Zymark Evaporation Station
4.6 Evaporation tubes
4.7 Water bath - Heated, capable of temperature control (± 5ºC).
4.8 Balance - Top-loading, capable of accurately weighing to the nearest 0.01 g.
4.9 Vials - 4 ml, with polytetrafluoroethylene (PTFE)-lined screw caps.
4.10 Glass scintillation vials - 20-mL, with PTFE-lined screw caps.
4.11 Tongue depressors, disposable
4.12 Beakers - 250ml
4.13 Glass funnel
4.14 Filter paper, coarse grade
4.15 Adhesive labels
4.16 Syringe - 5-mL NIST certified
4.17 250mL Erlenmeyer flasks

5.0 REAGENTS

Note: Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. Reagents should be stored in glass to prevent the leaching of contaminants from plastic containers.

5.1 Sodium sulfate (granular, anhydrous), Na_2SO_4.
5.2 Extraction - All solvents must be pesticide quality or equivalent
  5.2.1 Methylene Chloride, CH_2Cl_2.
  5.2.2 Hexane, C_6H_{14}.
  5.2.3 Acetone, C_3H_6O.
5.3 Surrogate and matrix spiking solutions are prepared as listed in Table 1. The detailed list of compounds for each stock mixture is given in §9.
5.4 High purity Ether

6.0 SAMPLE CONTAINERS AND STORAGE

6.1 All samples for the analysis of BNAs/PNAs/Herbicides are stored in small glass containers only.
6.2 Approximately 2 to 30 g (depending on the matrix) of sample is needed for extraction.
6.3 Refrigerate at 4ºC.
6.4 Holding Time for solid samples is 14 days to extraction and 40 days after extraction.

7.0 GLASSWARE CLEANING

Note: All glassware must be immaculate. Glassware should be cleaned as soon as possible after the extraction. A quick reference guide is posted in the extraction laboratory.

7.1 Immediately after use rinse glassware with the last solvent used in it. Drain it into a bottle labeled "Wash Solvent."
7.2 Wash well with hot water and laboratory detergent by hand.
7.3 Rinse three times with hot tap water followed by three times with DI water.
7.4 Place in dishwasher.
7.5 Rinse with acetone.
7.6 Rinse with hexane.

8.0 PROCEDURE[1]

8.1 The extraction device has a minimum of 300 watts of power and is equipped with ¾" size disrupter horns.
  8.1.1 The horn is maintained, by inspection of the horn tip for excessive wear that would be seen as "cavities" on the bottom of the instrument.
  8.1.2 Samples are prepared by thorough mixing with sodium sulfate so that it forms a free-flowing solid prior to the addition of the solvent.
  8.1.3 Three extractions are performed with 60ml of Methylene Chloride solvent for 3 minutes each. For herbicides, use ether instead of methylene chloride.
  8.1.4 Extraction is performed in the specified pulse mode, and the horn tip is positioned just below the surface of the solvent yet above the sample.
  8.1.5 Very active mixing of the sample and the solvent must occur when the ultrasonic pulse is activated. Observe such mixing at some point during the extraction process to insure that the placement of the horn is correct.
8.2 Sample handling
  8.2.1 Sediment/soil samples - Decant and discard any water layer on a sediment sample. Mix sample thoroughly, especially composited samples. Discard any foreign objects such as sticks, leaves, and rocks.
  8.2.2 Waste samples - Samples consisting of multiple phases are separated into two phases. Per client request one or the other phase is extracted. If both phases need to be extracted, two separate extractions are performed.

[1] Reference for this procedure is SW-846, Revision 3, December 1996 Method 3550B, Ultrasonic Extraction

8.2.3 Dry waste samples amenable to grinding - Grind or drill the waste so that it either passes through a 1-mm sieve or can be extruded through a 1-mm hole. Minimum of 10g of sample should pass through the sieve.

8.2.4 Gummy, fibrous, or oily materials not amenable to grinding are cut, shredded, or otherwise reduced in size to allow mixing and maximum exposure of the sample surfaces for the extraction.

8.3 Extraction method

8.3.1 Weigh approximately 2-30 g of sample (depending on the matrix) into a 250-ml beaker. Record the weight to the nearest 0.1 g.

8.3.1.1 The default weight used is 30g for a soil sample.

8.3.1.2 If the sample is a solvent or an oil matrix, approximately 2g of the neat sample is put into a 4ml screw cap vial and given to the GC/MS analyst. No extraction is performed due to the exceptionally high chromatographic response of these sample types. These samples are diluted by a factor of 400:1 and analyzed directly (see Table 8, SOP: 8270B.901.doc). The relative response of this base dilution may result in a final analysis of the sample at a higher or lower net dilution.

8.3.2 Nonporous or wet samples (gummy or clay type) that do not have a free-flowing sandy texture must be mixed with 60 g of anhydrous sodium sulfate, using disposable tongue depressors. If required, more sodium sulfate may be added. After addition of sodium sulfate, the sample should be free flowing.

8.3.3 a) For BNA extraction: Add 1.0 ml of the BNA surrogate standard solution to all samples, spiked samples, QC samples, and blanks (see Table 1).

b) For PNA extraction: Add 1.0 ml of the PNA surrogate standard solution to all samples. Spiked samples, QC samples, and blanks (see Table 1).

c) For DRO extraction: Add 1.0 ml of the DRO surrogate standard solution to all samples. Spiked samples, QC samples, and blanks (see Table 1).

d) For herbicides extraction: Add 1.0 ml of the HERB surrogate standard solution to all samples. Spiked samples, QC samples, and blanks (see Table 1).

8.3.4 For the sample in each batch selected for spiking (*i.e.* LCS, MS, MSD), add 1.0 ml of the matrix spiking solution (BNA, PNA, DRO, or HERB as appropriate, see Table 1).

8.3.5 Place the bottom surface of the tip of the 3/4 inch disrupter horn about 1/2 inch below the surface of the solvent, but above the sediment layer.

8.3.6 Extract ultrasonically for 3 minutes, with output control knob set at 6 and with mode switch on Pulse (pulsing energy rather than continuous energy) and percent-duty cycle knob set at 50% (energy on 50% of time and off 50% of time).

8.3.7 Decant through a conical gravity filter (Whatman No. 41 filter paper) and sodium sulfate to catch any excess water into an evaporation tube. For herbicides, decant into a 250mL Erlenmeyer flask with 10-15g acidified sodium sulfate.

8.3.8 Repeat the extraction with two additional 60 ml portions of methylene chloride. Pour off the solvent after the ultrasonic extraction. On the final ultrasonic extraction, pour the entire sample onto the filter with extraction solvent.

8.3.9 For herbicides, let the 250 mL Erlenmeyer flask stand with occasional swirling for two hours. Transfer the extract to an evaporation tube.

8.4 Evaporation method

8.4.1 Place the concentrator tube in the TurboVap Evaporation Station, that has the water bath at 42+/2°C, 21 psi, until the extract reaches a 1 ml final volume.

8.4.2 Transfer the sample extract to a 4 ml pre-calibrated vial. Adjust to 1 ml final volume.

8.4.3 For herbicides follow the diazomethane methylation procedure outlined in the diazomethane generation SOP.

9.0 QUALITY CONTROL

9.1 Samples are extracted in batches of 20 samples or less. For every batch there should be a Blank, LCS, MS, and MSD/DUP depending on the clients request. All the reagent blanks, matrix spikes, or replicate samples should be subjected to exactly the same analytical procedures as those used on actual samples. In

case of the client not providing the necessary sample volume to perform the required QC samples, equivalent laboratory matrix samples can be analyzed.

9.2 The B/N surrogate standard must contain the following compounds: Nitrobenzene-d5, 5,000 ug/ml (CAS 4165-60-0), 2-flourobiphenyl, 5,000 ug/ml (CAS 321-60-8), p-terphenyl-d14, 5,000 ug/ml (CAS 1718-51-0). Cat. No. 31086, RESTEK (800-356-1688). The Acid surrogate standard must contain the following compounds: 2-flourophenol, 10,000 ug/ml (CAS 367-12-4), Phenol-d6, 10,000 ug/ml (CAS 13127-88-3), 2,4,6-tribromophenol, 10,000 ug/ml (CAS 118-79-6). Cat. No. 31087, RESTEK (800-356-1688). The concentrations listed are those in the stock spiking solutions. [the Acid surrogate standard is N/A for the PNA method.] The surrogate standard is prepared according to Table 1.

9.3 The B/N MS/MSD and LCS spikes will contain the following compounds; Acenaphthene, 5,000 ug/ml (CAS 83-32-9), 1,4-dichlorobenzene, 5,000 ug/ml (CAS 106-46-7), 2,4-dinitrotoluene, 5,000 ug/ml (CAS 121-14-2), n-nitroso-di-n-propylamine, 5,000 ug/ml (CAS 621-64-7), Pyrene, 5,000 ug/ml (CAS 129-00-0), 1,2,4-trichlorobenzene, 5,000 ug/ml (CAS 120-82-1). Cat. No. 31074, RESTEK (800-356-1688). The Acid MS/MSD and LCS spikes will contain the following compounds: 4-chloro-3-methylphenol, 10,000 ug/ml (CAS 59-50-7), 2-chlorophenol, 10,000 ug/ml (CAS 95-57-8), 4-nitrophenol, 10,000 ug/ml (CAS 100-02-7), pentachlorophenol, 10,000 ug/ml (CAS 87-86-5), phenol, 10,000 ug/ml (CAS 108-95-2). Cat. No. 31061/31071, RESTEK (800-356-1688). The concentrations listed are those in the stock spiking solutions. MS/MSD spike should be prepared at a concentration at or below the medium level of the BNA curve. The MS/MSD and LCS standards are prepared according to Table 1.

9.4 The PNA MS/MSD and LCS spikes will contain the following compounds; Naphthalene, 2,000 ug/ml, 2-Methylnaphthalene, 2,250 ug/ml, Acenaphthylene, 2,000 ug/ml, Acenaphthene, 2,000 ug/ml, Flourene, 2,000 ug.ml, Phenanthrene, 2,000 ug.ml, Anthracene, 2,000 ug/ml, Flouranthene, 2,000 ug/ml, Pyrene, 2,000 ug/ml, Benzo (a) anthracene, 2,000 ug/ml, Chrysene, 2,000 ug/ml, Benzo (b) flouranthene, 2,000 ug/ml, Benzo (k) flouranthene, 2,000 ug/ml, Benzo (a) pyrene, 2,000 ug/ml, Indeno (1,2,3-cd) pyrene, 2,000 ug/ml, Dibenzo (ah) anthracene, 2,000 ug/ml, Benzo(ghi) perylene, 2,000 ug/ml. The concentrations listed are those in the stock spiking solutions. MS/MSD spike should be prepared at a concentration at or below the medium level of the PNA curve. The MS/MSD and LCS standards are prepared according to Table 1.

9.5 The DRO MS/MSD and LCS spikes contains neat diesel fuel diluted to a concentration appropriate for the sensitivity of the GC/MS (1000 mg/L). The MS/MSD and LCS standards are prepared according to Table 1.

9.6 New lot blanks are analyzed to insure the purity of the materials and reagents.

Note: The working standards are prepared every six to 12 months or when evidence of bias or trends are observed to show that the standards need to be replaced.

10.0 DOCUMENTATION

10.1 All pertinent information is entered into an extraction logbook (See Table 1). The extraction log sheet has to contain the following information on the header/table:

- Date
- ANALYSTS INITIALS
- Method
- Surrogate/MS/MSD/LCS standard unique traceability ID
- Methylene Chloride #
- Sample #
- Matrix
- Sample weight
- Solvent ID & Volume (ml)
- Final extract volume

- Surrogate standard spike volume
- MS spike volume

11.0 REFERENCES

11.1 Method 3550A SW

12.0 APPROVAL & ISSUE

12.1 The following personnel have read, accepted and approved this standard operating practice:

_____

Analyst Date

_____

Andy Ball, QA Officer Date

_____

Maya V. Murshak, Technical Director Date

13.0Tables

Table 1. Surrogate and Spike Preparation for use in Extraction

BNA Surrogate:

For 100 ml total solution at 100 mg/L:
- 97 ml of Acetone
- 1 ml of 10,000 mg/L Acids surrogate
- 2 ml of 5,000 mg/L B/N surrogate

BNA MS Spike:

For 20 ml total solution at 50 mg/L:
- 19.7 ml of Acetone
- 100 ul of 10,000 mg/L Acids spike
- 200 ul of 5,000 mg/L B/N spike

PNA/DRO Surrogate:

For 100 ml total solution at 100 mg/L:
- 98 ml of Acetone
- 2 ml of 5,000 mg/L B/N surrogate

PNA MS Spike:

For 20 ml total solution at 50 mg/L:
- 19.1 ml of Acetone
- 500 ul of 2,000 mg/L PNA stock
- 444 ul of 2250 mg/L 2-Methylnapthalene stock

DRO MS Spike:

For 20 ml total solution at 1000 mg/L;
- 20.0 ml of Acetone
- 20.0 mg of neat Diesel Fuel (gravimetric preparation)

SOP #043510C: SEPARATORY FUNNEL EXTRACTION FOR BNAS/PNAS/TCLP/HERBICIDES BY METHOD 3510C

Revision: 6
Date: 03/03/06

Location: Extraction Laboratory
GC/ECD
GC/MS Laboratory
QA Director's Office Files

These procedures are restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with these techniques and methods.

1.0 SCOPE AND APPLICATION

1.1 This method is used for extracting nonvolatile and semivolatile base/neutral/acid (BNA) and polynuclear aromatic hydrocarbon (PNA) organic compounds from aqueous samples. This method is applicable to the isolation and concentration of water-insoluble and slightly water-soluble organics in preparation for a variety of chromatographic procedures. The BNA following method is congruent with TCLP and TTO procedures in their entirety and may also be used with PNA and Herbicide methods (with the omission or addition of appropriate steps).

2.0 SUMMARY OF METHOD

2.1 A measured volume of sample, usually 1 liter, is extracted with methylene chloride using a separatory funnel.
2.2 The extract is concentrated.
2.3 Clean glassware is used to obtain the optimum analytical chromatograms.

3.0 INTERFERENCES

3.1 The decomposition of some analytes has been demonstrated under basic extraction conditions. Organochlorine pesticides may de-chlorinate, phthalate esters may exchange, and phenols may react to form tannates.

4.0 APPARATUS AND MATERIALS

4.1 Separatory funnel - 2-liter, with polytetrafluoroethylene (PTFE) stopcock.
4.2 Evaporation tubes, 250-ml volume, Zymark with end point of 0.5-ml.
4.3 Zymark Turbo Vap II Concentration Station with temperature control water bath.
4.4 Vials – 4-ml, glass with PTFE-lined screw caps or crimp tops.
4.5 pH indicator paper - pH range including the desired extraction pH.
4.6 Glass beakers, 250-ml.
4.7 Glass funnel
4.8 Filter paper, coarse grade
4.9 Adhesive labels
4.10 Syringe - 5-mL NIST certified
4.11 Graduated cylinder - 1-liter
4.12 250 mL Erlenmeyer flasks

5.0 REAGENTS

Note: Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. Reagents should be stored in glass to prevent the leaching of contaminants from plastic containers.

5.1 Reagent water
5.2 Sodium sulfate (granular, anhydrous), Na_2SO_4.
5.3 Sulfuric acid, concentrated, as well as solution (1:1 v/v), H_2SO_4. Slowly add 50-ml of H_2SO_4 to 50-ml of DI water.
5.4 Sodium Hydroxide solution (1:1 v/v), NaOH. Slowly add 46 ml of DI water to 2-g of NaOH crystals.
5.5 Extraction/exchange solvents

5.5.1 Methylene chloride, CH_2Cl_2, boiling point 49°C.
5.5.2 Hexane, C_6H_{14}.
5.5.3 Acetone, C_3H_6O.

5.6 Surrogate and matrix spiking solutions are prepared as listed in Table 1. The detailed list of compounds for each stock mixture is given in §9.

5.7 High purity Ether

6.0 SAMPLE CONTAINERS AND STORAGE

6.1 All samples for the analysis of BNAs should be stored in Amber glass containers only.
6.2 Approximately 1-L volume of sample is needed for extraction.
6.3 Refrigerate at 4ºC.
6.4 The holding time for samples is 7 days until extraction and 40 days thereafter.

Note: If samples contain significantly less volume then 1L, QA & client need to be notified. Higher detection limits will be applied to low volume extracts.

7.0 GLASSWARE CLEANING

7.1 Immediately after use, rinse glassware with the last solvent used in it. Drain it into a bottle labeled "Wash Solvent"
7.2 Wash well with hot water and laboratory detergent by hand.
7.3 Rinse three times with hot tap water followed by three times with DI water.
7.4 Place in dishwasher.
7.5 Rinse with acetone.
7.6 Rinse with hexane.

Note: All glassware must be immaculate. Glassware should be cleaned as soon as possible after the extraction. A quick reference guide is posted in the extraction laboratory. If the glassware is extremely dirty or has not been treated in more than a week, coat and soak it with concentrated H_2SO_4 preferably with Nonchromix added. Then rinse with tap water and follow the cleaning procedure above.

8.0 PROCEDURE[1]

8.1 Mark the level of sample on the outside of the bottle. Pour the sample into the 2-liter separatory funnel.
8.2 For all samples, spikes, and blanks, pipette 1.0-ml of the appropriate surrogate spiking solution (see Table 1 and §9.2) into the funnel and swirl.
8.2.1 For matrix spike samples (including the LCS), add 1ml surrogate and 1-ml matrix spike standard (see Table 1 and §9.3). These volumes are appropriate for BNA, PNA, herbicide and DRO samples.
8.2.2 Check the pH of the sample with wide-range pH paper and adjust the pH, if necessary, to a pH < 2 using H_2SO_4.
8.3 Add 10-ml of Acetone into the separatory funnel and swirl the sample (N/A for herbicides and PNAs).
8.4 Add 35-ml (for PNA's and phenols), or 30 ml (forBNA/TCLP) of methylene chloride into the sample bottle to rinse it and transfer this rinse solvent to the separatory funnel (for herbicides, use ether instead of methylene chloride).
8.5 Seal the separatory funnel and shake vigorously for 3 minutes on a horizontal placement at motor speed 70 in accordance with Table 2 shake program. Initial venting should be done immediately after the separatory funnel has been sealed and shaken once. The separatory funnel should be vented into a hood to avoid exposure of the analyst to solvent vapors. Allow the organic layer to separate from the water phase for 1 to 10 minutes, depending on the matrix of the sample.

[1] Reference for this procedure is SW-846, Revision 3, December 1996 Method 3510C, Separatory Funnel Extraction.

8.5.1 Note: 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.

8.6 Drain the extract through a filter filled with approximately 10g of Na_2SO_4 into a 250-ml glass Zymark evaporation tube. (For herbicides, drain the extract into a 250-mL Erlenmeyer flask with approximately 10-15g acidified sulfate in the bottom.)

8.7 Add 35ml (for PNA/phenols), or 35 ml (for BNA/TCLP) methylene chloride to the separatory funnel. Seal and shake the separatory funnel vigorously for 1 minute on a horizontal placement at motor speed 74. Vent the funnel and continue for 2 minutes in accordance with Table 2 shake program. Initial venting should be done immediately after the separatory funnel has been sealed and shaken once. The separatory funnel should be vented into a hood to avoid exposure of the analyst to solvent vapors. Allow the organic layer to separate from the water phase for 1 to 10 minutes, depending on the matrix of the sample. (For herbicides, use ether in place of methylene chloride.)

8.8 Repeat step 9.7 twice more with 35ml, or appropriate volume, methylene chloride each in accordance with Table 2 shake program [Repeat only once with PNA or DRO methods]. (For herbicides, use ether in place of methylene chloride and skip to step 8.12.)

8.8.1 *Note: Samples requiring PNA and/or DRO analysis may be extracted in an analytical batch for BNAs, using the additional procedural steps and surrogate compounds, without loss of generality.*

8.9 Check the pH of the sample with wide-range pH paper and adjust the pH, if necessary, to a pH > 12 using NaOH [N/A for PNAs or DROs].

8.10 Repeat step 9.7 two times at two minutes each in accordance with Table 2 shake program [N/A for PNAs].

8.11 Rinse the funnel and Na_2SO_4 with 20-ml Methylene chloride into the collected sample.

8.12 For herbicides only, let the extract stand in the Erlenmeyer flask with occasional swirling for two hours. Transfer to evaporation tube.

8.1 After all of the extract solvent has been collected, place the evaporation tube into the Turbo Vap II evaporation station, with the bath water at 42°C +/- 2°C and 21 psi. Allow the sample to evaporate down to 1ml methylene chloride or until the evaporation station signals completion. Use nitrogen to blow down the sample to make sure that it does not spill out.

8.14 Transfer the final volume into a pre-calibrated 4-ml glass vial, rinse the evaporation tube with clean methylene chloride and bring to 1-ml. If the final volume is over 1ml, use nitrogen gas or a special airline to evaporate to the 1-ml mark

8.15 Find the original volume of the sample by pouring tap water into the sample container to the mark. Pour the water into a 1000 ml graduated cylinder, and record the volume in the extraction logbook and label.

8.16 For final herbicide extracts, follow diazomethane methylation procedures as explained in the SOP for its method.

9.0 QUALITY CONTROL

9.1 Samples are extracted in batches of 20 samples or less. For every batch there should be a Blank, LCS, MS, and MSD/DUP depending on the client's request. All the reagent blanks, matrix spikes, or replicate samples should be subjected to exactly the same analytical procedures as those used on actual samples. In case of the client not providing the necessary sample volume to perform the required QC samples, equivalent laboratory matrix samples can be analyzed.

9.2 The B/N surrogate standard must contain the following compounds: Nitrobenzene-d5, 5,000 ug/ml (CAS 4165-60-0), 2-flourobiphenyl, 5,000 ug/ml (CAS 321-60-8), p-terphenyl-d14, 5,000 ug/ml (CAS 1718-51-0). Cat. No. 31086, RESTEK (800-356-1688). The Acid surrogate standard must contain the following compounds: 2-flourophenol, 10,000 ug/ml (CAS 367-12-4), Phenol-d6, 10,000 ug/ml (CAS 13127-88-3), 2,4,6-tribromophenol, 10,000 ug/ml (CAS 118-79-6). Cat. No. 31087, RESTEK (800-356-1688). The concentrations listed are those in the stock spiking solutions. The Acid surrogate standard is N/A for the PNA and DRO methods. The surrogate standard is prepared according to Table 1.

9.3 The B/N MS/MSD and LCS spikes will contain the following compounds; Acenaphthene, 5,000 ug/ml (CAS 83-32-9), 1,4-dichlorobenzene, 5,000 ug/ml (CAS 106-46-7), 2,4-dinitrotoluene, 5,000 ug/ml (CAS 121-14-2), n-nitroso-di-n-propylamine, 5,000 ug/ml (CAS 621-64-7), Pyrene, 5,000 ug/ml (CAS 129-00-0), 1,2,4-trichlorobenzene, 5,000 ug/ml (CAS 120-82-1). Cat. No. 31074, RESTEK (800-356-1688). The Acid MS/MSD and LCS spikes will contain the following compounds: 4-chloro-3-methylphenol, 10,000 ug/ml (CAS 59-50-7), 2-chlorophenol, 10,000 ug/ml (CAS 95-57-8), 4-nitrophenol, 10,000 ug/ml (CAS 100-02-7), pentachlorophenol, 10,000 ug/ml (CAS 87-86-5), phenol, 10,000 ug/ml (CAS 108-95-2). Cat. No. 31061/31071, RESTEK (800-356-1688). The concentrations listed are those in the stock spiking solutions. MS/MSD spike should be prepared at a concentration at or below the medium level of the BNA curve. The MS/MSD and LCS standards are prepared according to Table 1.

9.4 The PNA MS/MSD and LCS spikes will contain the following compounds; Naphthalene, 2,000 ug/ml, 2-Methylnaphthalene, 2,250 ug/ml, Acenaphthylene, 2,000 ug/ml, Acenaphthene, 2,000 ug/ml, Flourene, 2,000 ug.ml, Phenanthrene, 2,000 ug.ml, Anthracene, 2,000 ug/ml, Flouranthene, 2,000 ug/ml, Pyrene, 2,000 ug/ml, Benzo (a) anthracene, 2,000 ug/ml, Chrysene, 2,000 ug/ml, Benzo (b) flouranthene, 2,000 ug/ml, Benzo (k) flouranthene, 2,000 ug/ml, Benzo (a) pyrene, 2,000 ug/ml, Indeno (1,2,3-cd) pyrene, 2,000 ug/ml, Dibenzo (ah) anthracene, 2,000 ug/ml, Benzo(ghi) perylene, 2,000 ug/ml. The concentrations listed are those in the stock spiking solutions. MS/MSD spike should be prepared at a concentration at or below the medium level of the PNA curve. The MS/MSD and LCS standards are prepared according to Table 1.

9.5 The DRO MS/MSD and LCS spikes contains neat diesel fuel diluted to a concentration appropriate for the sensitivity of the GC/MS (1000 mg/L). The MS/MSD and LCS standards are prepared according to Table 1.

9.6 New lot blanks are analyzed to insure the purity of the materials and reagents.

9.6.1 Note: The working standards are prepared every six to 12 months or when evidence of bias or trends are observed to show that the standards need to be replaced.

10.0 DOCUMENTATION

10.1 All pertinent information is entered into an extraction logbook. The extraction log sheet has to contain the following information on the header/table:

- Date
- ANALYSTS INITIALS
- Method
- Surrogate/MS/MSD/LCS standard unique traceability ID
- Methylene Chloride Lot #
- Sample I.D. #
- Matrix
- Sample volume
- Solvent ID & Volume (ml)
- Final extract volume
- Surrogate standard spike volume
- MS spike volume

11.0 REFERENCES

11.1 Method 3510C SW

12.0 APPROVAL & ISSUE:

12.1 The following personnel have read, accepted and approved this standard operating practice.

Analyst Date

Andrew Ball, QA Officer Date

Maya V. Murshak, Technical Director Date

12.0TABLES

Table 1. Surrogate and Spike Preparation for use in Extraction

BNA Surrogate:

For 100 ml total solution at 100 mg/L;
- 97 ml of Acetone
- 1 ml of 10,000 mg/L Acids surrogate
- 2 ml of 5,000 mg/L B/N surrogate

BNA MS Spike:

For 20 ml total solution at 50 mg/L;
- 19.7 ml of Acetone
- 100 ul of 10,000 mg/L Acids spike
- 200 ul of 5,000 mg/L B/N spike

PNA/DRO Surrogate:

For 100 ml total solution at 100 mg/L;
- 98 ml of Acetone
- 2 ml of 5,000 mg/L B/N surrogate

PNA MS Spike:

For 20 ml total solution at 50 mg/L;
- 19.1 ml of Acetone
- 500 ul of 2,000 mg/L PNA stock
- 444 ul of 2,250 mg/L 2-Methylnapthalene stock

DRO MS Spike:

For 20 ml total solution at 1000 mg/L;
- 20.0 ml of Acetone
- 20.0 mg of neat Diesel Fuel (gravimetric preparation)

Table 2. Automated Extraction Funnel Shaking Procedure.

Stage	Solvent Volume	pH	Funnel Position	Shaker Time	Shaker Intensity	BNA Extraction	PNA/DRO Extraction
1a	30 ml	<2	vertical/open	1 min.	68	☑	☑
1b			horizontal/closed	2 min.	70		
2a	30 ml	<2	horizontal/closed	1 min.	74	☑	☑
2b			horizontal/closed	2 min.	74		
3	30 ml	<2	horizontal/closed	3 min.	74	☑	☑
4	30 ml	<2	horizontal/closed	3 min.	74	☑	☐
5	30 ml	>12	horizontal/closed	3 min.	74	☑	☐
6	30 ml	>12	horizontal/closed	3 min.	74	☑	☐

Notes: (1) *Funnel Position* indicates whether the funnel is horizontally or vertically situated in the automatic shaker and whether the stopcock is open or closed.

(2) *Shaker Time* is the timer setting on the shaker unit. The funnel is vented at the end of every time interval (*i.e*. 1, 2, or 3 minutes).

(3) *Shaker Intensity* is the dial setting on the automatic shaker unit. A higher number indicates a more vigorous shake.

(4) *BNA/PNA/DRO Extraction* indicates whether the extraction stage is appropriate for the given class of analytes.

SOP #031601: TOTAL DISSOLVED SOLIDS
(Also called: Total Filterable Residue)
METHOD #: 2540C

Revision: 5
Date: 05/25/10

Location: QA Officer's Office
SOP Files
TCLP Laboratory
Solids Laboratory

1.0 Scope

1.1 To describe the method for measuring Total Dissolved Solids (TDS).

2.0 Summary of Method

2.1 An aliquot of sample is taken from a stirring sample and filtered through a filter (pre-weighed filter if TSS is also needed) into a clean side arm flask. After rinsing the solids retained on the filter, the filtrate is quantitatively transferred to a weighed evaporating dish. The sample is then evaporated at 103°C in the oven. Then the dish + solids is moved to a 180°C oven (usually a muffle oven) and dried to a constant weight (usually at least one hour). The weight of solids in the dish represents the TDS.

3.0 Interferences

3.1 Poor shaking or stirring can lead to wrong results.
3.2 Improper drying of the solids (not to constant weight) will give higher results than the true value.

4.0 Apparatus and Materials

4.1 If only TDS is needed use un-weighed glass fiber filters. If TSS is also needed, use Proweigh filters Catalogue number: F934447MM from Environmental Express (phone: 800-343-5319) or www.envexp.com or. Note: if TVSS are to be analyzed TVSS pre-primed (yellow) filters must be used (catalogue number: F93447VOL from Environmental Express). Or the TSS filter can be primed at 550 °C.
4.2 Vacuum filtering apparatus compatible with 47 mm glass fiber filters.
4.3 25 mL large mouth Pipets
4.4 Graduated cylinders: 50 mL, 100 mL.
4.5 150 mL aluminum or ceramic evaporating dishes
4.6 Oven
4.7 Muffle Furnace
4.8 Thermometer
4.9 Dessicator
4.10 Analytical Balance
4.11 Vacuum pump
4.12 Tweezers

5.0 Reagents

5.1 DI Water
5.2 LCS from ERA.

6.0 Sample Collection, Preservation and Handling

6.1 The sample is usually a composite sample collected in a plastic or glass liter bottle with no preservation other than refrigeration at 4±2°C. The holding time is 7 days from sample collection.

7.0 Procedure

7.1 Record the date, and time of analysis as well as your initials as the analyst on the bench sheet and in the appropriate batch for TDS. A batch is defined as 10 samples of the same or similar matrix.
7.2 If TSS is also needed, record the tin number and the filter weight of a preweighed 47 mm glass fiber filter on the TSS bench sheet and record the weight of the evaporating dish on the

Merit TDS bench sheet on the line indicating "Blank". If only TDS is needed record only the evaporating dish weight on the TDS bench sheet. Using tweezers place the filter in the filter holder with the wrinkled side up.

7.3 Place the filter holder assembly in the clean 150 mL side arm flask with the vacuum hose attached to the side arm.

7.4 Turn on the vacuum and filter 100 ml of deionized water through the filter until all of the water is drawn through. This is the Blank.

7.5 Record the 100 ml volume on the bench sheet(s) for the Blank.

7.6 Then remove the filter, if TSS is needed, and place it in its tin. Then place tin and filter in a drying oven at 103^{o}C for one hour or more. Note: If Filters are dried for more than four hours you can be confident they are dried to constant weight.

7.7 Transfer the filtrate to its weighed evaporating dish and dry in 103^{o}C oven overnight.

7.8 Then move the ceramic evaporating dish to a 180^{o}C oven for at least 1 hour until dried to a constant weight.

7.9 Remove the ceramic evaporating dish from the oven and place it in a desiccator to cool to room temperature.

7.10 Weigh it to the nearest 0.1 mg using an analytical balance.

7.11 Record the weight on the bench sheet for the blank.

7.12 Record on the bench sheet the tin number and the filter weight for another filter and place the prewieghed filter in the filter holder assembly with the wrinkled side up, apply vacuum and wet the filter with a little deionized water to ensure adhesion to the holder.

7.13 Record the Merit number on the bench sheet. Then mix a sample by shaking it violently and quickly pour about 150 ml to 250 ml into a plastic cup or beaker.

7.14 Place a Teflon covered magnetic stirring bar in the cup and place the cup on top of a magnetic stirrer. Stir for one minute or more.

7.15 Using a 25 ml serological pipette with a wide opening, remove 25.0 ml of well mixed sample from half way into the cup and halfway between the mixing vortex and the side of the cup. Then drain the pipette onto and through the filter.

7.16 Repeat pipetting (step 16) until 100 ml has been filtered. 50 ml can be used if you know there are a lot of dissolved solids in the sample (from historical testing information).

7.17 Note that shaking vigorously and quickly pouring the sample from the bottle into a graduated cylinder will be a better sampling procedure for some samples. When using this method, pour the sample on to the filter from the cylinder.

7.18 Record the volume you filtered on the bench sheet.

7.19 As you did with the Blank, remove the filter from the filter holder, place it back in its tin for TSS and dry it in a 103^{o}C oven for one hour or more.

7.20 Transfer the filtrate to its weighed evaporating dish and dry it at 103^{o}C overnight. Then dry the dish in a 180^{o}C oven to a constant weight.

7.21 Remove the tin from the oven and cool it to room temperature in a Desiccator. Carefully weigh it on an analytical balance to 0.1 mg.

7.22 Record the weight on the bench sheet.

7.23 Check the dryness of the sample by drying it for another 15 minutes. Then reweigh. The sample is dried to a constant weight if the two weights differ by no more than 4 % or 0.5 mg which ever is less.

7.24 Record the weight on the bench sheet.

7.25 Be sure to perform the QC analyses summarized in Section 8.0.

7.26 Repeat Steps 13 through 24 for each sample.

8.0 Calculations

8.1 TDS mg/l = [[(Grams of dish + residue) – (Grams dish)]/ml sample filtered] X 1000 ml/L X 1000 mg/Gram

9.0 Quality Control

9.1 Also perform the following Quality Control for each sample set. A sample set is a group of one to ten samples run at one time.

Quality Control

QC Sample	Frequency	Acceptable Limits	Corrective Action	Follow up Corrective Action
Blank	1/10 samples	-3 to +3 mg/l	Redry and Reweigh	Reset the entire set of samples with new filters
Laboratory Control Sample-ERA Small Lab Minerals	1/10 samples	Within Supplier's Limits	Redry and Reweigh	Reset the entire set of samples with new filters
Sample Duplicate	1/10 Samples	+/- 20 % of average	Reset sample duplicates	Footnote non-homogeneity
Analytical Balance Check with "S" Weights	1/day	For 1 gram Weight +/_ 0.0008 g	Recalibrate Balance and Reweigh	Call for Service
Constant Weight Verification	1/10 samples	4 % or 0.5 mg which ever is smaller	Dry longer and reweigh.	Dry longer and reweigh.

9.0 Documentation

9.1 Total Dissolved Solids Bench sheet
- 9.1.1 Date Started
- 9.1.2 Date Finished
- 9.1.3 Time
- 9.1.4 Analyst
- 9.1.5 Date Checked
- 9.1.6 Checked by
- 9.1.7 Batch #
- 9.1.8 Merit #
- 9.1.9 TSS (Yes/No)
- 9.1.10 Tin #
- 9.1.11 mLs of Sample
- 9.1.12 g Tin
- 9.1.13 g Dry Solids + Tin
- 9.1.14 g Weight after 15 Minutes
- 9.1.15 Ratio: TDS/ Conductivity
- 9.1.16 TDS (mg/L)
- 9.1.17 % Recovery
- 9.1.18 % RPD

9.2 Oven Temperature Log

9.3 TDS/TSS Excel File

10.0 References

10.1 *Standard Methods*, twentieth edition, Method 2540C, Solids.

11.0 Safety

11.1 Eye protection and gloves must be worn while performing TDS analyses.

11.2 Every Laboratory area has eyewash, emergency shower, and fire extinguisher. The metals lab also has dust masks available for use with dust samples.

11.3 The air system through out the laboratory area is on a 100% fresh air exchange system, this system exchanges 100% the air in the laboratory area with air from outside 6 times per hour and 30 times per hour when the emergency purge button is hit.

11.4 A reference file of material safety data sheets (MSDSs) is available to all personnel.

12.0 Waste Disposal and Pollution Prevention

12.1 All laboratory waste must be managed, stored, and disposed in accordance with all federal and state laws and regulations.

12.2 Additional information can be found in the Sample Disposal SOP and Merit's Waste Management Plan and Handbook.

13.0 Approval and Issue

13.1 This section indicates which personnel have read, accepted, and approved the SOP. All analysts involved with the SOP should acknowledge their comprehension of the SOP with a signature and a date.

_____

Analyst Date

_____

Andy Ball, QA Officer Date

_____

Maya V. Murshak, Technical Director Date

Revision: 4
Date: 06/19/08

Location: QA Officer's Office
SOP Files
Wet Chemistry Laboratory

1.0 SCOPE

1.1 This SOP is for the Persulfate-Ultraviolet Method for analyzing Total Organic Carbon. This SOP is a procedure used by Merit Laboratories for analyzing TOC. This method is applicable to drinking, surface, ground waters & treated mixed wastewater. Reporting limit 1.0 mg/L for water samples.

2.0 SUMMARY OF THE METHOD

2.1 This SOP is a procedure for evaluating Total Organic Carbon in liquid samples.

2.2 Organic Carbon is oxidized to carbon dioxide, CO_2, by persulfate in the presence of ultraviolet light. The CO_2 produced is measured by a non-dispersive infrared analyzer. Samples are introduced into a continuously gas-purged reactor with ultraviolet lamp and filled with persulfate solution. The CO_2 produced is sparged continuously from the solution and is carried in the gas stream to the infrared detector which is specifically tuned to the absorptive wavelength of CO_2. The area of the peak is calculated and compared to the area of the calibration standard stored in memory and prints out the calibrated organic carbon value in milligrams per liter.

3.0 INTERFERENCES

3.1 Excessive acidification of the sample, producing a reduction in pH of the persulfate solution to 1 or less, can result in sluggish and incomplete oxidation of the organic carbon. Highly turbid samples can lead to sluggish or incomplete oxidation as well. Some tannins, lignins and humic acid (complex molecules), may be oxidized slowly because persulfate oxidation is rate-limited. Samples with high chloride content can inhibit oxidation of organic molecules. Samples with greater than 0.1% chloride may prevent oxidation completely. Take care in sampling, handling, and analysis of samples below 1 mg/L, as they can be easily contaminated for trace analysis.

4.0 REAGENTS

4.1 Deionized (DI) water

4.2 Potassium Acid Phthalate ($C_8H_5O_4K$) / TOC Standard: Weigh 0.425g (dried) PAP into 100ml volumetric flask, add 60 or 70ml DI water, add 0.1ml concentrated phosphoric acid, bring to volume = 2,000ppm TOC (Store this solution in dark glass under refrigeration and replace monthly).

4.3 400 ppm C Standard: Dilute 20ml of 2,000ppm C into a 100ml volumetric flask and bring to volume (Store this solution in dark glass under refrigeration and prepare fresh weekly).

4.4 Phosphoric Acid (H_3PO_4) Concentrated

4.5 Potassium Persulfate Solution 2%: weigh 10g $K_2S_2O_8$ into 500ml beaker, add 400ml DI water, 1ml conc. H_3PO_4, dissolve. Pour into 500ml volumetric flask and bring to volume. (Store in a cool dark location. Shelf life is 1 month.

4.6 Potassium Persulfate-Mercuric Salt Reagent: This solution is used for samples with high chloride content. Prepare by dissolving 8.2g of reagent grade Mercuric Chloride ($HgCl_2$) and 9.6g of reagent grade Mercuric Nitrate, monohydrate ($Hg(NO_3)_2 \cdot H_2O$) in 400ml of DI water and 5 ml concentrated HNO_3. Add 20g of reagent grade Potassium Persulfate. Mix well and make to 1 L with DI water. Prepare monthly.

4.7 20% Phosphoric Acid: Dilute 4mls of reagent grade concentrated phosphoric acid to 20mls with the 2% potassium persulfate solution (prepared in 4.5).

4.8 Oxygen tank

4.9 Control ERA / TOC

5.0 APPARATUS & MATERIALS

5.1 Dohrmann DC-180 Carbon Analyzer

5.2 50ml centrifuge tubes with screw caps
5.3 100ml volumetric flasks
5.4 500ml volumetric flask

6.0 SAMPLE HANDLING AND PRESERVATION

6.1 Samples should be collected in amber glass bottles with TFE-lined cap and acidified to a pH $\leq$ 2 with H_2SO_4. Regulatory storage is 28 days under refrigeration (4 degrees C) and acidified.

7.0 PROCEDURE

7.1 DAILY STARTUP

7.1.1 Check to see that UV reactor is filled with reagent.
7.1.2 Make sure there is enough persulfate reagent in supply bottle to last through at least a day's operation.
7.1.3 Check to make sure Gas/Liquid separator is half filled with water. On a daily basis, the pH of the G/L liquid should be checked. A pH of less than 3 is necessary for maximum sparging efficiency.
7.1.4 Ensure water trap is less than half-full with water.
7.1.5 Make sure all plumbing is properly connected. Re-connect the Teflon line from the UV reactor and the G/L separator.
7.1.6 Check to see that waste container is empty.
7.1.7 Make sure the acid bottle has sufficient acid
7.1.8 Check to see that you have sufficient oxygen for the day's operation.

7.2 SYSTEM ON

7.2.1 Verify that the main power is on and that the system main menu is being displayed.
7.2.2 From "System On/Off" menu ([=/-] [1]), select "O_2/ UV/ Pump On".
7.2.3 Observe UV lamp is on, gas is bubbling in both the UV vessel and the G/L separator and the peristaltic pump is on.
7.2.4 Check each pump channel closely. Verify proper fluid movement through each line and replace any worn or weakly-pumping tubings. Refer to section 3.5 of manual for pump pressure adjustments.
7.2.5 Check the flow rate out the NDIR. Refer to the Gas Flow Rate Checks in section 3.5 of manual and verify proper gas flow rates for all modes you will be using.
7.2.6 From "Main Menu", select "Monitor baseline". Observe for stable baseline before starting an analysis.

7.3 INITIAL SET-UP

7.3.1 From "Analysis Modes" menu, ([+-] [2] [3]), select NPOC [1] (non-purgable organic carbon) (In most surface and ground waters the POC contribution is negligible. Therefore, in practice, the NPOC determination is substituted for TOC). Direct Inject NPOC (Y/N)? Press [No], NPOC w/Inj Loop.
7.3.2 Check attachment for sequence times and sampling parameters for NPOC.
7.3.3 From the "Main Menu" select "Monitor Baseline" [5].
7.3.4 Observe baseline in the bottom right corner of the screen. The system will be ready for calibration or analysis when the baseline becomes stable.

7.4 CALIBRATION

7.4.1 A calibration curve must be created once every year.
7.4.2 From " Calibration Mode" menu ([+/-] [2] [4]), select the NPOC w/ inject loop mode [1]. When [1] is selected, the appropriate volume (0.2ml) is displayed with a blinking cursor at the bottom of the screen. If the loop size is correct, press [ENTER]; otherwise, use [CLEAR] to erase the line and enter correct volume in ml and then press [ENTER].
7.4.3 Submerge sample pick-up line into container that has the standard solution of interest (400ppm TOC standard).
7.4.4 Press [CAL], enter the ppmC standard concentration (400), being used and then press [ENTER].

7.4.5 After "Run Conditions" are printed, if ready, press [YES]. [NO] will exit from CAL mode and return the main menu.

7.4.6 The CAL factor for the mode selected will be automatically adjusted at the end of the analysis. Compare the results obtained with Table 5.5.1 of the manual. If your value falls outside the expected range, double-check your gas flow rate and pump tubes flows. If o.k., the baseline may not have been stable. Try calibrating again.

7.4.7 Expected raw count range for 0.2ml injection loop volume and 400ppm concentration is between 768000-1280000.

7.4.8 * Gas flow rate is approximately 200 $\pm$ cc/min.

7.5 SAMPLE RUN

7.5.1 An analysis can be started anytime after the baseline becomes stable. Usually a 30-minute warm-up time is used.

7.5.2 Always start a sample set with a blank (DI) and verify calibration with a standard (10ppm). (Use the calibration update function to make minor adjustments to the calibration factor, if necessary).

7.5.3 Mix sample bottle and pour approximately 50ml into plastic centrifuge tube.

7.5.4 Submerge sample pick-up line into centrifuge tube. Press [RUN] , enter ID#, Press [ENTER]. Sample run is approximately 7 minutes.

7.5.5 After sparging begins the pick-up line can be placed back into DI bottle to rinse line clean of sample.

7.5.6 The detector will calculate Cppm and display result.

7.5.7 If a sample contains a high concentration of TOC (> 50ppm), a DI blank is usually run between samples.

8.0 MAINTENANCE AND TROUBLESHOOTING

8.1 DAILY CHECKS

8.1.1 Oxygen supply

8.1.2 Persulfate supply

8.1.3 Acid supply

8.1.4 Printer paper supply

8.1.5 Check Cu and Sn scrubber

8.1.6 Check pH of G/L separator (< 3), add drop of concentrated phosphoric if not.

8.1.7 Connect output line on UV vessel to top port of GLS.

8.1.8 Printer on; O_2, UV vessel and pump on [+/-] [1] [1].

8.1.9 Carrier gas floe rate (approx. 200 cc/min.

8.1.10 Steady baseline [+/-] [5].

8.2 WEEKLY CHECKS

8.2.1 Daily checks, plus

8.2.2 Check liquid flow rate – pump tubing conditions.

8.2.3 Check for moisture in the LiOH tube.

8.2.4 Check for injection port septum if syringe analysis is used regularly.

8.3 BI-MONTHLY CHECKS

8.3.1 Daily and weekly checks, plus

8.3.2 Change pump tubings. (inspect for ware)

Questions on instrument operation can be found in DC-180 Operation Manual.

9.0 QUALITY CONTROL

9.1 See Table 1

9.2 A sample batch will consist of 20 samples or less. The QC samples that are analyzed per batch are:

- Method Blank
- Blank Spike
- Control (ERA or another outside known)

- LCS
- Matrix Spike
- Matrix Spike Dup (level 3 QC or requested)
- Matrix Duplicate

9.3 A Blank Spike, Matrix Spike, Matrix Duplicate are run every 10 samples.

Table 1. Quality Control Requirements (Sample Set = 20 samples)

QC Analysis	Required/ Frequency	Limits	Corrective Action	Corrective Action after Reanalyzing
Method (preparation) Blank	Yes One each set	<MDL or 1/10 Regulatory limit	Remove contamination and rerun	
Laboratory Control Sample (LCS) Soluble or insoluble	Yes One every 20 samples	85%-115%	Rerun	
Matrix Duplicate	Yes One each 10 samples	RPD<20%	Rerun entire set	
Matrix Spike	Yes One each 10 samples	85%-115%	Analyze by Method of Standard Additions	
Matrix Spike Duplicate	Level 3 One every 10 samples			
Dilution & Rerun	No except if result indicates suppressive interference	Does interference persist?	Yes. Rerun with Method of Standard Additions	

10.0 DOCUMENTATION

10.1 DC-180 Carbon Analyzer raw data printout

10.2 TOC Bench book

10.3 DC-180 Carbon Analyzer Maintenance Log

11.0 METHOD PERFORMANCE

11.1 Precision and accuracy studies are performed on as needed basis.

11.2 Method Detection Limit studies are performed annually.

12.0 REFERENCES

12.1 *Standard Methods*, twentieth edition, Method 5310C, Total Organic Carbon (TOC).

13.0 APPROVAL & ISSUE:

13.1 The following personnel have read, accepted and approved this standard operating practice.

_____

Analyst Date

_____

Andy Ball, QA Officer Date

_____

Maya V. Murshak, Technical Director Date

Location: QA Officer's Office
SOP Files
Wet Chemistry Laboratory

1.0 SCOPE

1.1 This SOP is applicable to drinking, surface, and saline waters. This procedure is based on method by HACH which states not approved for EPA reporting.

2.0 SUMMARY OF THE METHOD

2.1 This SOP is an spectrophotometric procedure for evaluating Turbidity in liquid samples.

3.0 INTERFERENCES

3.1 Presence of floating debris and coarse sediments that settle out rapidly will give low readings. Finely divided air bubbles will affect results in a positive manner.

4.0 APPARATUS AND MATERIALS

4.1 100 mL volumetric flask
4.2 Hach DR/3000 Spectrophotometer
4.3 2 clean cuvettes
4.4 Parafilm
4.5 Pipettes
4.6 Volumetric Flask

5.0 REAGENTS

5.1 Deionized (DI) water
5.2 Hydrazine Sulfate
5.3 Hexamethylenetetramine

6.0 SAMPLE HANDLING AND PRESERVATION

6.1 Turbidity is best analyzed as soon as possible from the time the sample is collected. Maximum holding time is 48 hours refrigerated at 4±2^{o}C.
6.2 Samples must be provided in unpreserved, clear plastic bottles.

7.0 PROCEDURE

7.1 Preparation of Standard Solution
- 7.1.1 Stir together 10.0 mL DI Water, 0.500 g Hydrazine Sulfate and 0.050 g Hexamethylenetetramine in a 100 mL volumetric flask until all particles are dissolved in the water.
- 7.1.2 Seal tightly with parafilm and leave it sit in a protected place overnight.
- 7.1.3 Bring standard solution to 100 mL before use.

7.2 Color Development and Measurement
- 7.2.1 Select the stored program for Turbidity by pressing 5 and 9 with the numeric keys and the Stored Program key then press enter.
- 7.2.2 Turn the wavelength dial to 450 nm.
- 7.2.3 Place 25.0 mL of sample in a 25 ml cuvette. If the sample is highly colored, dilute as needed. The upper limit for this analysis is 660 Formazin Turbidity Units (FTU).
- 7.2.4 Prepare a Blank by putting 25.0 mL of DI water in another cuvette.
- 7.2.5 Place the Blank in the spectrophotometer so as the 25 mL mark faces forward. Close the light shield.
- 7.2.6 Press the ZERO and then CONC keys. The spectrophotometer is zeroed for the analysis.
- 7.2.7 Place the sample into the cell holder and close the light shield. Results will be displayed in Formazin turbidity units (FTU).

8.0 QUALITY CONTROL

8.1 See Table 1

8.2 Samples are analyzed in batches of 20 or less per QC set. The QC samples that are analyzed per batch are:

- Standard Check
- LCS
- MS
- DUP
- MSD (optional)
- Method Blank

Table 1. Quality Control Requirements (Sample Set = 20 samples)

QC Analysis	Required/ Frequency	Limits	Corrective Action	Corrective Action after Reanalyzing
Method (preparation) Blank	Yes One each set	<MDL or 1/10 Regulatory limit	Remove contamination and rerun	Notify client. Flag data.
Laboratory Control Sample (LCS)	Yes One every 20 samples	90%-110%	Rerun	Notify client. Flag data.
Matrix Duplicate	Yes One each set	RPD<20%	Rerun entire set	Notify client. Flag data.
Matrix Spike	Yes One each set	80%-120%	Analyze by Method of Standard Additions	Notify client. Flag data.
Matrix Spike Duplicate	Yes One every 20 samples Level III	80%-120%	Analyze by Method of Standard Additions	Notify client. Flag data.
Dilution & Rerun	No except if result indicates suppressive interference	Does interference persist?	Yes. Rerun with Method of Standard Additions	Notify client. Flag data.

9.0 DOCUMENTATION

9.1 Turbidity Bench Sheet

9.1.1 Analyst
9.1.2 Analysis
9.1.3 Date Run
9.1.4 Detection Limit
9.1.5 Wavelength
9.1.6 Merit #
9.1.7 Dilution
9.1.8 Concentration (FTU)
9.1.9 Result
9.1.10 Spike Concentration
9.1.11 % Recovery
9.1.12 Batch ID

10.0 METHOD PERFORMANCE

10.1 Precision and accuracy studies are performed on as needed basis. (Ex. new instrument, etc.)
10.2 Method Detection limit studies are performed annually.

11.0 REFERENCES

11.1 *EPA Water NPDES*, Method 180.1, EPA Test Methods, Revision 1982, Turbidity (Nephelometric).
11.2 Hach DR/3000 Spectrophotometer Manual.

12.0 SAFETY

12.1 Every Laboratory area has eyewash, emergency shower, and fire extinguisher. The metals lab also has dust masks available for use with dust samples.

12.2 The air system through out the laboratory area is on a 100% fresh air exchange system, this system exchanges 100% the air in the laboratory area with air from outside 6 times per hour and 30 times per hour when the emergency purge button is hit.

12.3 A reference file of material safety data sheets (MSDSs) is available to all personnel.

13.0 WASTE DISPOSAL AND POLLUTION PREVENTION

13.1 All laboratory waste must be managed, stored, and disposed in accordance with all federal and state laws and regulations.

13.2 Additional information can be found in the Sample Disposal SOP and Merit's Waste Management Plan and Handbook.

14.0 APPROVAL & ISSUE

14.1 This section indicates which personnel have read, accepted and approved the SOP. All analysts involved with the SOP must acknowledge their comprehension of the SOP with a signature and a date.

_____

Analyst Date

_____

Andy Ball, QA Officer Date

_____

Maya V. Murshak, Technical Director Date

METHOD 8260B (VOCs) / 8015M (GRO)/8260SIM[1]

1.0 SCOPE AND APPLICATION

1.1 This sop is used to determine volatile organic compounds in a variety of matrices. This sop is applicable to nearly all types of samples, regardless of water content, including various air sampling trapping media, ground and surface water, aqueous sludges, caustic liquors, acid liquors, waste solvents, oily wastes, mousses, tars, fibrous wastes, polymeric emulsions, filter cakes, spent carbons, spent catalysts, soils, and sediments. See Table 1 for a list of compounds (along with their characteristic ions) that have been evaluated.

1.2 This sop is also used for the analysis of petroleum hydrocarbons, including gasoline range organics (GROs). GROs correspond to the range of alkanes from C_6 to C_{10} but ar not restricted to this range and covering a boiling point range of approximately 60°C - 170°C. The identification of specific fuel types may be complicated by environmental processes such as evaporation, biodegradation, or when more than one fuel type is present.

1.3 There are various techniques by which these compounds may be introduced into the GC/MS system. Purge-and-trap, by Methods 5030 (aqueous samples) and 5035 (solid, waste, and oil samples), is the most commonly used technique for volatile organic analytes. Method 5000 provides general information on the selection of other introduction methods.

1.4 The practical quantitation limit (PQL) of this sop for an individual compound is somewhat instrument dependent and also dependent on the choice of sample preparation/introduction method. Using standard quadrapole instrumentation and the purge-and-trap technique, limits should be approximately 50 µg/kg (wet weight) for solid samples and 1 µg/L for ground water (see Table 2a). When lower RDLs are required, the mass spectrometer (MS) can be set to selective ion monitoring (SIM) to achieve limits approximately 20 times lower then obtainable using the full scan method. The practical quantitation limit (PQL) of GROs is approximately 5 mg/kg (wet weight) for soil/sediment samples and is 0.2 mg/L for ground water samples (see Table 2b). Regardless of the sample matrix, PQLs will be proportionately higher for sample extracts and samples that require dilution or when a reduced sample size is used to avoid saturation of the detector.

1.5 This sop is restricted to use by, or under the supervision of, analysts experienced in the use of gas chromatograph/mass spectrometers, and skilled in the interpretation of mass spectra and their use as a quantitative tool.

1.6 This SOP is not for use with samples that come into the lab for OHIO VAP work.

2.0 SUMMARY OF METHOD

2.1 The volatile compounds are introduced into the gas chromatograph by the purge-and-trap method or by other methods. The analytes are introduced directly to a wide-bore capillary column. The column is temperature-programmed to separate the analytes, which are then detected with a mass spectrometer (MS) interfaced to the gas chromatograph (GC).

2.2 Analytes eluted from the capillary column are introduced into the mass spectrometer via a jet separator or a direct connection. Identification of target analytes is accomplished by comparing their mass spectra with the electron impact spectra of authentic standards. Quantitation is accomplished by comparing the response of a major (quantitation) ion relative to an internal standard using a five-point (or more) calibration curve.

2.3 The method includes specific calibration and quality control steps that supersede the general requirements provided in Method 8000.

[1] The SIM analysis is applicable for MDEQ low RDL level analytes.

3.0 INTERFERENCES

3.1 Major contaminant sources are volatile materials in the laboratory and impurities in the inert purging gas and in the sorbent trap. The use of non-polytetrafluoroethylene (PTFE) thread sealants, plastic tubing, or flow controllers with rubber components should be avoided, since such materials out-gas organic compounds which will be concentrated in the trap during the purge operation. Analyses of calibration and reagent blanks provide information about the presence of contaminants. Blank values are not subtracted from sample results.

3.2 Cross-contamination may occur when any sample is analyzed immediately after a sample containing high concentrations of volatile organic compounds. After the analysis of a sample containing high concentrations of volatile organic compounds, one or more blanks should be analyzed to allow the system to be cleaned as well as to demonstrate the ultimate absence of cross-contamination. Alternatively, if the sample immediately following the high concentration sample does not contain the volatile organic compounds present in the high level sample, freedom from contamination has been established.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph/mass spectrometer system

4.1.1 Gas chromatograph - An analytical system complete with a temperature-programmable gas chromatograph suitable for splitless injection and all required accessories, including syringes, analytical columns, and gases. The capillary column should be directly coupled to the source.

4.1.2 20 m × 0.18 mm ID capillary column coated with DB-624 (J&W Scientific), Rt_x-502.2 (RESTEK), or VOCOL (Supelco), 1-µm film thickness, or equivalent.

4.1.3 Mass spectrometer capable of scanning from 35 to 200 amu every 2 sec 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 4-bromofluorobenzene (BFB) which meets the criteria in Table 5.

4.1.4 GC/MS interface - The capillary column is interfaced through a direct connection to the GC/MS system.

4.1.5 Data system - A computer system is interfaced to the mass spectrometer. Hewlett-Packard Chemstation software (with environmental data analysis) is used to acquire and process GC/MS data.

4.2 Purge-and-trap device.

4.3 Microsyringes - 2 to 500-µL.

4.4 Balance - Analytical, capable of weighing 0.0001 g, and top-loading, capable of weighing 0.1 g.

4.5 Glass bottles - 40-mL, with PTFE-lined screw-caps.

5.0 REAGENTS

5.1 Reagent grade inorganic chemicals shall be used in all tests. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without introducing adverse interferences.

5.2 Organic-free reagent water - All references to water in this method refer to organic-free reagent water.

5.3 Stock standard solutions

5.3.1 Certified stock standard solutions are purchased when available for the bulk of desired analytes. They are typically available at concentrations of 1000 to 2000 mg/L.

5.3.2 Supplemental compounds added to calibration mixes are generally prepared gravimetrically from neat standard references (in order to create a high-concentration stock solution).

5.3.3 Stock standard solutions are stored in bottles with PTFE-lined screw-caps. They are refrigerated and protected from light, as recommended by the standard manufacturer.

5.3.4 Neat standard references are used in order to create a stock solution ~10000 mg/L for GRO standards.

5.3.5 Stock standard solutions are replaced prior to expiration, or sooner if comparison with quality control check samples indicates a problem.

5.4 Internal standard solutions - The internal standards used are pentafluorobenzene, 1,4-difluorobenzene, chlorobenzene-d_5, and 1,4-dichlorobenzene-d_4 (see Table 3). Internal standards are used at a working concentration of 25 mg/L and are added to samples, spikes, blanks, and calibration standards at a uniform concentration of 50 µg/L (i.e. 10µL per 5000µL purge volume). For SIM (selective ion monitoring) analysis, internal standards are the same, but with concentrations at 0.1 ppb (µg/L).

5.5 Calibration standards - A minimum of five calibration standards are prepared at different concentrations. The lowest calibration standard corresponds to a sample concentration at or below the standard reporting limit. The remaining standards should represent the working range of the GC/MS system. Each standard should contain each analyte for quantitation by this method.

5.6 Surrogate standards - The surrogates used are toluene-d_8, 4-bromofluorobenzene, and 1,2-dichloroethane-d_4. Surrogate standards are used at a working concentration of 25 mg/L and are added to samples, spikes, blanks, and calibration standards at a uniform concentration of 50 µg/L, or less.). For SIM (selective ion monitoring) analysis, surrogate standards are the same, but with concentrations at 0.1 ppb (µg/L).

5.7 Matrix spike and laboratory control standards - Matrix spiking solutions are prepared using stock solutions from a different vendor, relative to those used for calibration, where possible. The standards contain nearly the same list of compounds as those in the calibration standards. In any event, the matrix spike includes the minimally required compounds 1,1-dichloroethene, trichloroethene, chlorobenzene, toluene, and benzene.

5.1.1 Matrix spiking mixes for individual analytes are created at 100 mg/L and spiked into samples at 50 µg/L (*i.e.* 2.50µL per 5000µL purge volume).

5.1.2 For SIM (selective ion monitoring) analysis, compounds of interest are spiked at concentrations of 0.1 ppb (µg/L).

5.1.3 The matrix spiking mix for GRO is created at 10000 mg/L and spiked into samples at 1000 µg/L (*i.e.* 0.5µL per 5000µL purge volume).

5.8 Methanol, CH_3OH - Pesticide quality or equivalent, demonstrated to be free of analytes. Store apart from other solvents.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Unanalyzed samples are refrigerated in sealed vials.

6.2 Samples and target compound standards are refrigerated and stored separately.

6.3 Holding times for analysis depend on the sample type, method of collection, and type of preservation. See Method 5030B/5035 (SOP#075035) for details.

7.0 PROCEDURE

7.1 Sample introduction.

7.1.1 Direct injection - This method of introduction is used only rarely, generally when the compounds of interest exhibit poor purging efficiency. Quantitation in this case, if required, is generally subject to external standard calibration procedures (*cf.* Method 8000).

7.1.2 Purge-and-trap - This is the normal means of sample introduction for both soil and water samples. All samples, standards, spikes, and blanks are introduced into the GC/MS system in an identical manner (see Merit SOP#075035).

7.2 GC/MS operating conditions - see Table 4 for routine operating conditions for VOA analysis

7.2.1 For selective ion monitoring (SIM), the mass spec is put into the selective ion monitoring mode. Based on compounds of interest, the time windows are set within the run (i.e. for internal standards, surrogate standards, compounds). For each time window, corresponding to a compound, including internal and surrogate standards, a minimum of 3 ions are chosen for qualitative analysis. One ion (primary ion), generally the most abundant ion is used for quantitative analysis.

7.3 Initial calibration

7.3.1 Each GC/MS system must be hardware-tuned to meet the criteria in Table 5 for 4-bromofluorobenzene. Analyses does not begin until these criteria are met.

7.3.1.1 In the absence of any other manipulations, evaluate the mass spectrum of the peak apex or the scan immediately preceding or following from the total ion chromatogram for the BFB peak. This is the default approach used.

7.3.1.2 If the above evaluation is adversely affected by ion peak asymmetry, average the three highest intensity scans of the peak or average the mass spectrum ranging from the 10% initial peak intensity to the tailing 10% peak intensity level from the total ion chromatogram for the BFB peak.

7.3.1.3 If the above evaluation is adversely affected by background contamination, perform a background subtraction with a spectrum within 20 scans of the BFB peak which does not represent a target compound. Use of this procedure may be indicative of failing MS performance. The MS source should be cleaned and re-tuned.

7.3.1.4 The BFB mass intensity criteria in Table 5 are used as tuning acceptance criteria.

7.3.1.5 All subsequent standards, samples, MS/MSDs, and blanks associated with a BFB analysis must use the identical mass spectrometer instrument conditions, Exception: for selective ion monitoring (SIM), tune is run using full scan acquisition and subsequent samples are acquired using selective ion monitoring (SIM).

7.3.2 Purge and analyze each calibration standard (containing internal standards) and tabulate the area of the primary characteristic ion against concentration for each target analyte (as indicated in Table 1). A set of at least five calibration standards is necessary. The purge volume must be the same for all standards and sample extracts. Table 6 details the dilutions necessary to create a set of calibration standards. Figure 1 shows a chromatogram of a midpoint calibration standard.

7.3.3 Calculate response factors (*RF*s) for each target analyte relative to one of the internal standards as follows: $RF = A_s C_i / A_i C_s$. Here, A_s and A_i are the areas of the standard compound and corresponding internal standard, respectively. likewise, C_s and C_i are the respective concentrations (in any consistent set of units) of the standard compound and corresponding internal standard.

7.3.4 System performance check compounds (SPCCs)

7.3.4.1 A system performance check must be performed to ensure that minimum *RF*s are met before the calibration curve is used. For volatiles, the System Performance Check Compounds (SPCCs) are: chloromethane, 1,1-dichloroethane, bromoform, chlorobenzene, and 1,1,2,2-tetrachloroethane. (*cf.* Table 3). No response factor criteria are applied to selective monitoring SIM analysis,

7.3.4.2 The minimum acceptable average *RF* for these compounds is 0.1 (for chloromethane, 1,1-dichloroethane, and bromoform) and 0.3 (for chlorobenzene and 1,1,2,2-tetrachloroethane). These SPCCs typically have low *RF*s and tend to decrease

in response as the chromatographic system begins to deteriorate or the standard material begins to deteriorate. They are usually the first to show poor performance. Therefore, they must meet the minimum requirement when the system is calibrated.

7.3.4.3 If the minimum response factors are not met, the system must be evaluated, and corrective action must be taken before sample analysis begins. Possible problems include standard mixture degradation, contamination in the purge-and-trap system, excessively high or low purge flow rates, and active sites in the column or chromatographic system. Replacing the calibration standards, clipping and/or replacing the column will likely solve this problem.

7.3.5 Calibration check compounds (CCCs)

7.3.5.1 The purpose of the CCCs is to evaluate the calibration from the standpoint of the integrity of the system. High variability for these compounds may be indicative of system leaks or reactive sites on the column. Meeting the CCC criteria is in addition to the successful calibration of the target analytes using one of the approaches described in Section 7.0 of Method 8000.

7.3.5.2 Calculate the mean response factor and the relative standard deviation (RSD) of the response factors for each target analyte. The RSD should be less than or equal to 15% for each target analyte. However, the RSD for each individual CCC compound (1,1-dichloroethene, chloroform, 1,2-dichloropropane, toluene, ethylbenzene, and vinyl chloride; see Table 3) must be less than or equal to 30%.

7.3.5.3 If the RSD of any CCC is greater than 30%, then the chromatographic system is too reactive for analysis to begin. Clean or replace the injector liner and/or capillary column, then repeat the calibration procedure.

7.3.6 Evaluation of retention times - The relative retention time (RRT) of each target analyte in each calibration standard should agree within 0.06 RRT units. This is accomplished by setting the retention time extraction windows in the Chemstation software.

7.3.7 Linearity of target analytes - If the %RSD of any target analytes is 15% or less, then the relative response factor may be assumed to be constant over the calibration range, and the average relative response factor may be used for quantitation.

7.3.7.1 Refer to Method 8000 if a least-squares regression is used to determine a linear or quadratic fit to the calibration data. Note that quadratic polynomials are generally fit through the origin in order to prevent the symptomatic aphysical prediction of high concentrations at very low responses. . In any event, the COD for any regression fit should be ≥0.99. In addition, 6 calibration data points are required for a calibration fit with 3 free parameters, while 5 are required for a calibration fit with 1 or 2 free parameters.

7.3.7.2 When the RSD exceeds 15%, the plotting and visual inspection of a calibration curve can be a useful diagnostic tool. The inspection may indicate analytical problems, including errors in standard preparation, the presence of active sites in the chromatographic system, analytes that exhibit poor chromatographic behavior, *etc*.

7.3.7.3 The quality of the calibration fit for any particular compound is communicated to the data user via the Quality Control report for a given batch of samples. The calibration summary report includes: the concentration and RF for each standard in the calibration curve, the type of calibration fit, the calibration fit parameters (*i.e*. average RF or regression coefficients), and the appropriate calibration quality metric (*i.e*. %RSD or COD).

7.4 GC/MS calibration verification - Calibration verification consists of three steps that are performed at the beginning of each 12-hour analytical shift.

7.4.1 Prior to the analysis of samples or calibration standards, purge the BFB standard into the GC/MS system. The resultant mass spectrum for BFB must meet the criteria given in Table 5 before sample analysis begins. These must be *injected* within 12 hours of the injection time for the BFB.

7.4.2 The initial calibration for each compound of interest should be verified once every 12 hours prior to sample analysis, using the introduction technique and conditions used for samples. This is accomplished by analyzing a calibration standard at a concentration near the midpoint concentration for the calibration range of the GC/MS (50 µg/L; this represents 2.50 µL of the 100 mg/L calibration standard solution in a 5mL purge volume). A concentration of 0.1µg/L is analyzed for selective ion monitoring (SIM) procedures. The results from the calibration standard analysis must meet the verification acceptance criteria provided below for the SPCC and CCC compounds.

7.4.3 A method blank is run every 20 samples to ensure that the total system (preparation glassware, introduction device, transfer lines, and the GC/MS system itself) is free of contaminants. A method blank/wash sample is also run after calibration check/spike samples and prior to analytical samples in order to eliminate carryover contamination from the purge-and-trap system.

7.4.4 System performance check compounds (SPCCs)

7.4.4.1 A system performance check must be made during every 12-hour analytical shift. Each SPCC in the calibration verification standard must meet the minimum response factors given above. This is the same check that is applied during the initial calibration (see §7.3.4.2).

7.4.4.2 If the minimum response factors are not met, the system must be evaluated, and corrective action must be taken before sample analysis begins.

7.4.5 Calibration check compounds (CCCs)

7.3.5.1 After the system performance check is met, the CCCs listed in Table 3 are used to check the validity of the initial calibration. Percent drift is used to evaluate the CCC response and it must be ≤20%.

7.3.5.2 If the percent drift for each CCC is ≤20%, then the initial calibration is assumed to be valid. If the criterion is not met for any one CCC, then corrective action must be taken prior to the analysis of samples (see previous). Drift is defined as the normalized deviation of the measured from the spike value of a target component: $\%D = \left|C - C_{spike}\right| / C_{spike}$.

7.3.5.3 Problems similar to those listed under SPCCs could affect the CCCs. If the problem cannot be corrected by other measures, a new initial calibration must be generated. The CCC criteria must be met before sample analysis begins.

7.5 GC/MS analysis of samples

7.5.1 Samples are screened at a diluted state via GC/MS whenever possible prior to analysis within a 12-hour QC batch. This can identify potentially low surrogate recoveries, high target compound concentrations, non-target matrix interferences. This will minimize contamination of the GC/MS system from unexpectedly high concentrations of organic compounds.

7.5.2 Use a 5 mL syringe to take a 5 mL aliquot from the sample vial. Be sure to eliminate any air bubbles from within the syringe. Table 6 has a list of commonly used dilutions as well as the required amount of sample, water, and internal standard for each dilution.

7.5.3 Add 10 µL of 25 mg/L internal/surrogate standard mixture to each sample. If the sample also represents a matrix spike, add 2.50 µL of 100 mg/L target compound matrix spiking mixture to the sample (or 0.5µL of the 10000 mg/L GRO spiking mixture, as appropriate). For SIM analysis, internal and surrogate standards are spliked at 0.1µg/L.

7.5.4 If the response for any quantitation ion exceeds the initial calibration range of the GC/MS system, the sample extract should be diluted and reanalyzed. In any event, a result based on an extrapolation of calibration curve beyond the working range is flagged on the analytical report.

7.5.5 The Extracted Ion Current Profile (EICP) area for all of the internal standards in all spikes, blanks, and samples is monitored relative to the most recent calibration verification standard. Changes by more than a factor of two (*i.e.* 50% to 200%) can indicate adverse matrix effects (in the case of an isolated sample) or degrading MS performance (in the case of a systematic low bias). A single-sample matrix effect is documented either via screening or re-analysis and is noted on the analytical report (see Table 7). Similarly, the retention times for all of the internal standards in all spikes, blanks, and samples is monitored relative to the most recent calibration verification standard. The change in retention time for any internal standard by more than 30 seconds of the most recent calibration verification standard is indicative of the same potential problems listed above and should be flagged/corrected as appropriate.

7.6 Qualitative analysis

7.6.1 The qualitative identification of compounds determined by this method is based on retention time and on comparison of the sample mass spectrum, after background correction, with characteristic ions in a reference mass spectrum. The reference mass spectrum must be generated by the laboratory using the conditions of this method. The characteristic ions from the reference mass spectrum are given in Tables 1a and 1b. Compounds are identified when the following criteria are met.

7.6.1.1 Initial selection of a target compound peak is performed by the Chemstation data system search routine. The search is based on the presence of a target chromatographic peak containing ions specific for the target compound at a compound-specific retention time.

7.6.1.2 The RRT of the sample component is within ± 0.06 RRT units of the RRT of the standard component. This is accomplished using retention time extraction windows within the Chemstation data system.

7.6.1.3 The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum. (Example: For an ion with an abundance of 50% in the reference spectrum, the corresponding abundance in a sample spectrum can range between 20% and 80%.)

7.6.1.4 Structural isomers that produce very similar mass spectra are identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

7.6.1.5 Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When gas chromatographic peaks obviously represent more than one sample component (*i.e.*, a broadened peak with shoulder(s) or a valley between two or more maxima), appropriate selection of analyte spectra and background spectra is important.

7.6.1.6 Examination of extracted ion current profiles of appropriate ions can aid in the selection of spectra and in qualitative identification of compounds. When analytes coelute (*i.e.*, only one chromatographic peak is apparent), the identification criteria may be met, but each analyte spectrum will contain extraneous ions contributed by the coeluting compound.

7.6.1.7 In the two previous cases, analyst expertise as well as knowledge of site history may be important in accepting/rejecting the identification of a compound. In the event of

continued uncertainty, the analyst should preferentially make a conservative judgement and accept an identified hit, allowing the potential for a false positive.

7.6.2 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 purpose of the analyses being conducted. Only after visual comparison of sample spectra with the nearest library searches may the analyst assign a tentative identification. Guidelines for 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%.
- 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.

7.7 Quantitative analysis

7.7.1 Once a compound has been identified, the quantitation of that compound will be based on the integrated abundance of the primary characteristic ion from the EICP.

7.7.2 The curve fit applied in the initial calibration is the same as that used to compute the concentration of a target analyte in a sample. All curve fits are evaluated by the data system and are of the form: $A_s/A_i = k_0 + k_1[C_s/C_i] + k_2[C_s/C_i]^2$. Here A_s and A_i are the areas of the target and internal standard, C_s and C_i are the concentrations of the target and internal standard, and k_i is the i^{th}-order regression coefficient. Note that for a mean RF fit to the calibration data, $k_1 \equiv$ <RF>, while k_0, $k_2 \equiv 0$.

7.7.3 The concentration of any non-target analytes identified in the sample may be estimated by assuming a mean RF of 1 and by using the TIC areas for the nearest internal standard and target compound. The resulting concentration should be reported indicating: (1) that the value is an estimate, and (2) which internal standard was used to determine concentration. Use the nearest internal standard free of interferences.

7.7.4 Structural isomers that produce very similar mass spectra should be quantitated as individual isomers if they have sufficiently different GC retention times. Otherwise, structural isomers are quantitated as isomeric pairs (such as p- and m-xylene).

7.8 Special procedures for gasoline range organics (GROs) - The following items detail the differences in the calibration procedures for multicomponent, gasoline range organics from the general, single component procedures outlined above.

7.8.1 A set of at least five calibration standards per §7.2 and §7.3.2. Figure 2 represents a GRO chromatogram.

7.8.2 The measured response from the TIC is used to represent the GRO calibration with an internal standard calibration.

7.8.3 Calculate the response factor (*RF*) for the TIC relative to one of the internal standards as follows: $RF = A_s C_i / A_i C_s$. Here, A_s and A_i are the area of the TIC and characteristic mass over its respective time range and corresponding internal standard, respectively. Likewise, C_s and C_i are the respective concentrations (in any consistent set of units) of the *total fuel* and corresponding internal standard. The characteristic time ranges for each mass depend upon current

chromatographic conditions. The time ranges used for the sample chromatograms in Figures 1 and 2 are listed in the respective figure.

The relative area response vs. relative concentration for the TIC and characteristic mass is calibrated in the same manner as described in §7.3.7 and §7.7.

7.8.4 In addition to the routine SPCC/CCC check standard, a GRO check standard is analyzed in order to characterize the efficiency of the present GRO calibration in terms of recovery and retention times.

8.0 QUALITY CONTROL

8.1 All of the quality control items employed and evaluated are listed in Table 7. In addition, the table indicates the frequency of each QC item along with appropriate courses of corrective action.

8.2 Control limits for surrogate and matrix spikes are listed in Table 9.

8.3 Quality control items are inspected by the analyst as the data becomes available. At the conclusion of the analytical batch, all of the samples, spikes, standards, *etc*. are processed and evaluated automatically and stored electronically for future reference/retrieval.

9.0 METHOD PERFORMANCE

9.1 Laboratory-specific performance data is provided in this document

9.2 Table 2a and 2b present the results for detection limit studies. The MDL, PQL and ratio of PQL/MDL is given for each analyte in the target compound list.

9.3 Table 9 presents the lower and upper acceptance limits for all surrogate and matrix spiking compounds.

10.0 REFERENCES

1. SW-846, 1996, Revision 3; Methods 3500, 3510, 3550, 8000, 8015, 8260, 624.

11.0 SAFETY

11.1 Eye protection and gloves must be worn while performing Volatile analyses.

11.2 Every Laboratory area has eyewash, emergency shower, and fire extinguisher. The metals lab also has dust masks available for use with dust samples.

11.3 The air system through out the laboratory area is on a 100% fresh air exchange system, this system exchanges 100% the air in the laboratory area with air from outside 6 times per hour and 30 times per hour when the emergency purge button is hit.

11.4 A reference file of material safety data sheets (MSDSs) is available to all personnel.

11.5 Specific attention be paid (but not limited) to

11.5.1 Hydrochloric acid is corrosive, extreme heat or contact with metals can release flammable hydrogen gas, stable under ordinary conditions of use and storage, and incompatible with many substances and highly reactive with strong bases, metals, metal oxides, hydroxides, amines, carbonates, cyanides, sulfides, sulfites, and formaldehyde.

11.5.2 Methanol may react violently with acids, acid chlorides, acid anhydrides, oxidizing agents, reducing agents and alkali metals. Protect from moisture. Highly flammable.

12.0 WASTE DISPOSAL AND POLLUTION PREVENTION

12.1 All laboratory waste must be managed, stored, and disposed in accordance with all federal and state laws and regulations.

12.2 Additional information can be found in the Sample Disposal SOP and Merit's Waste Management Plan and Handbook.

13.0 APPROVAL AND ISSUE

13.1 This section indicates which personnel have read, accepted and approved the SOP. All analysts involved with the SOP must acknowledge their comprehension of the SOP with a signature and a date.

_____

Analyst Date

_____

Andy Ball, QA Officer Date

_____

Maya V. Murshak, Technical Director Date

14.0 TABLES AND FIGURES

Table 1. Summary of Retention Times† and Characteristic Ions for Volatile Organics

#	**Compound**	t_R (*min*)	$t_R/t_{R,I}$ (-)	t_R-$t_{R,I}$ (*min*)	1^0 *m/z*	2^0 *m/z*	3^0*m/z*	4^0 *m/z*
1)	PENTAFLUOROBENZENE	3.58	1.000	0.00	168	99	37	
2)	1,2-DICHLOROETHANE-D4	3.8	1.061	0.22	65	102	104	
3)	1,1,2-Trichloro-1,2,2-trif	1.9	0.531	-1.68	101	151	103	
4)	Diethyl ether (*)	1.7	0.475	-1.88	74	59	45	
5)	Acetone (*)	1.89	0.528	-1.69	58	43	44	
6)	Methyl iodide (iodomethane	1.97	0.550	-1.61	142	141	127	
7)	Carbon disulfide (*)	2.01	0.561	-1.57	76	78	44	
8)	Methyl Acetate	2.09	0.584	-1.49	43	74	59	
9)	tert-Methyl butyl ether (M	2.37	0.662	-1.21	73	57	41	43
10)	Acrylonitrile (*)	2.39	0.668	-1.19	52	53	54	
11)	2-Butanone (MEK) (*)	3.23	0.902	-0.35	43	72	57	
12)	Dichlorodifluoromethane	1.17	0.327	-2.41	85	87	50	
13)	Chloromethane (SPCC)	1.25	0.349	-2.33	50	52	49	
14)	Vinyl Chloride (CCC)	1.32	0.369	-2.26	62	64	61	
15)	Bromomethane	1.44	0.402	-2.14	94	96	81	
16)	Chloroethane	1.46	0.408	-2.12	64	66	49	51
17)	Acrolein	1.82	0.508	-1.76	56	55	53	
18)	Trichlorofluoromethane	1.66	0.464	-1.92	101	103	66	105
19)	1,1-Dichloroethene (CCC/MS	1.86	0.520	-1.72	61	96	63	98
20)	Methylene Chloride	2.19	0.612	-1.39	84	49	86	51
21)	trans-1,2-Dichloroethene	2.38	0.665	-1.20	61	96	63	98
22)	1,1-Dichloroethane (SPCC)	2.73	0.763	-0.85	63	65	83	
23)	cis-1,2-Dichloroethene	3.21	0.897	-0.37	96	61	98	
24)	Tetrahydrofuran	3.42	0.955	-0.16	42	41	71	
25)	Chloroform (CCC)	3.46	0.966	-0.12	83	85	47	
26)	Bromochloromethane	3.4	0.950	-0.18	130	49	93	128
27)	1,1,1-Trichloroethane	3.57	0.997	-0.01	97	99	61	
28)	1,1-Dichloropropene	3.67	1.025	0.09	75	77	110	
29)	Cyclohexane	3.63	1.014	0.05	56	84	41	
30)	1,4-DIFLUOROBENZENE	4.07	1.000	0.00	114	88	57	
31)	TOLUENE-D8	4.95	1.216	0.88	98	100	70	
32)	4-Methyl-2-pentanone (MIBK	4.9	1.204	0.83	58	85	100	43
33)	2-Hexanone (*)	5.37	1.319	1.30	58	43	85	100
34)	2-chloroethylvinyl ether	4.73	1.162	0.66	63	106	65	
35)	Carbon Tetrachloride	3.67	0.902	-0.40	117	119	121	
36)	Benzene (MS)	3.82	0.939	-0.25	78	77	51	
37)	1,2-Dichloroethane	3.85	0.946	-0.22	62	98	100	64
38)	Trichloroethene (MS)	4.23	1.039	0.16	95	132	130	134
39)	1,2-Dichloropropane (CCC)	4.38	1.076	0.31	63	76	62	
40)	Bromodichloromethane	4.56	1.120	0.49	83	85	127	129
41)	Methyl Cyclohexane	4.33	1.064	0.26	55	83	41	98
42)	Dibromomethane	4.47	1.098	0.40	174	93	172	79
43)	cis-1,3-Dichloropropene	4.82	1.184	0.75	75	77	110	
44)	Toluene (CCC/MS)	4.99	1.226	0.92	91	92	65	
45)	trans-1,3-Dichloropropene	5.13	1.260	1.06	75	110	77	
46)	1,1,2-Trichloroethane	5.24	1.287	1.17	83	97	99	85

#	**Compound**	t_R (*min*)	$t_R/t_{R,I}$ (-)	t_R-$t_{R,I}$ (*min*)	1^0 *m/z*	2^0 *m/z*	3^0 *m/z*	4^0 *m/z*
47)	Tetrachloroethene	5.29	1.300	1.22	166	129	164	
48)	CHLOROBENZENE-D5	5.76	1.000	0.00	82	117	119	
49)	4-BROMOFLUOROBENZENE	6.38	1.108	0.62	174	95	176	
50)	trans-1,4-Dichloro-2-buten	6.49	1.127	0.73	53	89	124	75
51)	Dibromochloromethane	5.46	0.948	-0.30	129	127	79	
52)	1,2-Dibromoethane	5.52	0.958	-0.24	107	109	81	
53)	Chlorobenzene (SPCC/MS)	5.77	1.002	0.01	112	77	114	
54)	1,1,1,2-Tetrachloroethane	5.82	1.010	0.06	131	133	117	119
55)	Ethylbenzene (CCC)	5.82	1.010	0.06	91	106	77	
56)	p,m-Xylene	5.88	1.021	0.12	106	91	77	
57)	o-Xylene	6.09	1.057	0.33	91	106	77	
58)	Styrene	6.1	1.059	0.34	104	78	103	
59)	Isopropylbenzene	6.28	1.090	0.52	105	120	77	
60)	Bromoform (SPCC)	6.23	1.082	0.47	173	171	175	
61)	1,1,2,2-Tetrachloroethane	6.47	1.123	0.71	83	85	131	133
62)	1,2,3-Trichloropropane	6.49	1.127	0.73	110	75	97	61
63)	n-Propylbenzene	6.5	1.128	0.74	91	120	105	
64)	Bromobenzene	6.46	1.122	0.70	156	77	158	
65)	1,3,5-Trimethylbenzene	6.59	1.144	0.83	120	105	77	
66)	tert-Butylbenzene	6.76	1.174	1.00	91	119	134	
67)	1,2,4-Trimethylbenzene	6.79	1.179	1.03	120	105	77	
68)	1,4-DICHLOROBENZENE-D4	6.99	1.000	0.00	152	150	115	
69)	sec-Butylbenzene	6.87	0.983	-0.12	105	134	91	
70)	p-Isopropyltoluene	6.95	0.994	-0.04	119	91	134	
71)	1,3-Dichlorobenzene	6.95	0.994	-0.04	146	148	111	
72)	1,4-Dichlorobenzene	7	1.001	0.01	146	148	111	
73)	1,2-Dichlorobenzene	7.2	1.030	0.21	146	148	111	
74)	1,2,3-Trimethylbenzene	7.01	1.003	0.02	105	120	77	
75)	n-Butylbenzene	7.16	1.024	0.17	91	92	134	
76)	Hexachloroethane	7.32	1.047	0.33	201	117	166	
77)	1,2-Dibromo-3-Chloropropan	7.61	1.089	0.62	157	155	75	159
78)	1,2,4-Trichlorobenzene	8.02	1.147	1.03	182	180	145	109
79)	Hexachlorobutadiene	8.09	1.157	1.10	225	227	223	190
80)	1,2,3-Trichlorobenzene	8.27	1.183	1.28	180	182	145	109
81)	Naphthalene	8.15	1.166	1.16	128	102	127	129
82)	2-Methylnaphthalene	8.72	1.247	1.73	142	141	115	

†: Absolute retention times (t_R) listed are from calibration FT060808.M. Absolute and relative retention times ($t_R/t_{R,I}$) may shift with the present condition of the column (*i.e*. new, clipped, *etc*.), but the differential retention times (t_R - $t_{R,I}$) tend to remain constant given the same chromatographic temperature program.

Table 2a. Summary of Practical Quantitation Limits for Volatile Organics †

Compound	Water Matrix			Soil Matrix		
	PQL_w (ug/l)	MDLw (ug/l)	P/M_w (-)	PQLs (ug/l)	MDLs (ug/l)	P/Ms (-)
1,1,2-Trichloro-1,2,2-trif	1	0.2	6.3	50	8.9	5.6
Diethyl ether (*)	1	0.3	3.2	50	13.3	3.8
Acetone (*)	10	4.0	2.5	500	126.0	4.0
Methyl iodide (iodomethane	1	0.1	12.3	50	6.0	8.4
Carbon disulfide (*)	1	0.1	11.3	50	9.6	5.2
Methyl Acetate	1	0.3	3.5	50	35.1	1.4
tert-Methyl butyl ether (M	1	0.1	12.4	50	5.3	9.5
Acrylonitrile (*)	1	0.4	2.4	50	14.1	3.6
2-Butanone (MEK) (*)	10	1.4	7.2	500	53.6	9.3
Dichlorodifluoromethane	1	0.3	3.9	50	9.0	5.6
Chloromethane (SPCC)	1	0.2	6.2	50	6.1	8.2
Vinyl Chloride (CCC)	1	0.2	4.1	50	6.2	8.0
Bromomethane	1	0.4	2.7	50	12.6	4.0
Chloroethane	1	0.2	5.3	50	11.3	4.4
Acrolein	10	0.9	10.6	500	46.1	10.8
Trichlorofluoromethane	1	0.1	10.8	50	7.1	7.1
1,1-Dichloroethene (CCC/MS	1	0.1	8.4	50	7.6	6.6
Methylene Chloride	1	0.2	4.6	50	7.9	6.3
trans-1,2-Dichloroethene	1	0.1	15.9	50	6.3	7.9
1,1-Dichloroethane (SPCC)	1	0.1	9.6	50	4.9	10.3
cis-1,2-Dichloroethene	1	0.1	8.5	50	3.6	13.9
Tetrahydrofuran	10	1.2	8.6	500	34.1	14.7
Chloroform (CCC)	1	0.1	11.5	50	5.3	9.4
Bromochloromethane	1	0.2	5.3	50	12.7	3.9
1,1,1-Trichloroethane	1	0.1	9.8	50	3.8	13.1
1,1-Dichloropropene	1	0.1	8.5	50	4.8	10.5
Cyclohexane	1	0.1	7.5	50	5.7	8.7
4-Methyl-2-pentanone (MIBK	10	0.1	68.2	500	11.2	44.7
2-Hexanone (*)	10	0.3	30.9	500	17.0	29.5
2-chloroethylvinyl ether	1	0.1	8.4	50	9.5	5.3
Carbon Tetrachloride	1	0.1	7.7	50	2.8	18.0
Benzene (MS)	1	0.1	18.5	50	4.6	10.9
1,2-Dichloroethane	1	0.2	4.5	50	4.9	10.2
Trichloroethene (MS)	1	0.2	6.6	50	9.1	5.5
1,2-Dichloropropane (CCC)	1	0.1	11.2	50	7.4	6.8
Bromodichloromethane	1	0.2	5.1	50	4.8	10.5
Methyl Cyclohexane	1	0.2	5.4	50	6.0	8.3
Dibromomethane	1	0.2	5.2	50	9.2	5.4
cis-1,3-Dichloropropene	1	0.1	8.1	50	2.6	19.0
Toluene (CCC/MS)	1	0.1	14.4	50	3.5	14.4
trans-1,3-Dichloropropene	1	0.1	8.2	50	5.6	8.9
1,1,2-Trichloroethane	1	0.2	4.1	50	8.2	6.1
Compound	Water Matrix			Soil Matrix		

	PQL_w (ug/l)	MDLw (ug/l)	P/M_w (-)	PQLs (ug/l)	MDLs (ug/l)	P/Ms (-)
Tetrachloroethene	1	0.1	13.2	50	25.7	1.9
trans-1,4-Dichloro-2-buten	1	0.3	3.8	50	14.3	3.5
Dibromochloromethane	1	0.2	5.5	50	7.5	6.7
1,2-Dibromoethane	1	0.2	5.8	50	2.7	18.5
Chlorobenzene (SPCC/MS)	1	0.1	16.7	50	4.4	11.4
1,1,1,2-Tetrachloroethane	1	0.1	7.3	50	7.5	6.6
Ethylbenzene (CCC)	1	0.1	11.3	50	3.1	16.3
p,m-Xylene	1	0.1	8.4	50	5.3	9.4
o-Xylene	1	0.1	8.6	50	3.4	14.9
Styrene	1	0.1	16.0	50	4.0	12.4
Isopropylbenzene	1	0.1	10.9	50	4.4	11.3
Bromoform (SPCC)	1	0.2	5.0	50	6.2	8.1
1,1,2,2-Tetrachloroethane	1	0.2	5.6	50	8.2	6.1
1,2,3-Trichloropropane	1	0.4	2.4	50	16.5	3.0
n-Propylbenzene	1	0.1	12.1	50	3.4	14.8
Bromobenzene	1	0.1	13.2	50	7.8	6.4
1,3,5-Trimethylbenzene	1	0.1	8.1	50	4.0	12.4
tert-Butylbenzene	1	0.1	17.4	50	5.7	8.7
1,2,4-Trimethylbenzene	1	0.1	9.8	50	4.0	12.5
sec-Butylbenzene	1	0.1	9.7	50	7.6	6.6
p-Isopropyltoluene	1	0.1	9.5	50	5.4	9.3
1,3-Dichlorobenzene	1	0.1	7.2	50	7.3	6.8
1,4-Dichlorobenzene	1	0.1	7.7	50	6.1	8.2
1,2-Dichlorobenzene	1	0.1	6.9	50	7.7	6.5
1,2,3-Trimethylbenzene	1	0.1	7.6	50	5.7	8.7
n-Butylbenzene	1	0.1	11.1	50	4.8	10.3
Hexachloroethane	1	0.1	10.0	50	4.9	10.3
1,2-Dibromo-3-Chloropropan	1	0.1	7.6	50	27.6	1.8
1,2,4-Trichlorobenzene	1	0.2	5.0	50	8.0	6.2
Hexachlorobutadiene	1	0.2	6.2	50	10.3	4.8
1,2,3-Trichlorobenzene	1	0.1	8.5	50	7.6	6.6
Naphthalene	1	0.1	10.4	50	8.4	6.0
2-Methylnaphthalene	1	0.3	3.4	50	14.8	3.4

†: Data are from 03/04/06 (water) and 03/03/06 (soil).

Table 2b. Practical Quantitation Limits for Gasoline Range Organics†

COMPOUND	PQL_W (mg/L)	PQL_S (mg/kg)	MDL_W (mg/L)	MDL_S (mg/kg)	PQL_W/MDL_W	PQL_S/MDL_S
Gasoline Range Organics	0.2	5	0.0207	0.899	9.7	5.6

†: Data are from 07/13/2006.

Table 3. Summary of Applicable Performance Compounds - Volatile Organics Analysis

#†	COMPOUND	CCC	SPCC	ISD	SSD	MS
1	PENTAFLUOROBENZENE			✔		
2	1,2-DICHLOROETHANE-D4				✔	
11	Chloromethane (SPCC)		✔			
12	Vinyl Chloride (CCC)	✔				
16	1,1-Dichloroethene (CCC/MS)	✔				✔
19	1,1-Dichloroethane (SPCC)		✔			
21	Chloroform (CCC)	✔				
25	1,4-DIFLUOROBENZENE			✔		
26	TOLUENE-D8				✔	
30	Benzene (MS)					✔
32	Trichloroethene (MS)					✔
33	1,2-Dichloropropane (CCC)	✔				
37	Toluene (CCC/MS)	✔				✔
42	CHLOROBENZENE-D5			✔		
43	4-BROMOFLUOROBENZENE				✔	
47	Chlorobenzene (SPCC/MS)		✔			✔
49	Ethylbenzene (CCC)	✔				
54	Bromoform (SPCC)		✔			
55	1,1,2,2-Tetrachloroethane (SPCC)		✔			
62	1,4-DICHLOROBENZENE-D4			✔		

†: Compound identification numbers listed are from calibration FR010910.M.

Key

CCC: Calibration Check Compound
SPCC: System Performance Check Compound
ISD: Internal Standard Compound
SSD: Surrogate Standard Compound
MS: Matrix Spiking Compound

Table 4. GC/MS Operating Conditions - Volatile Organics Analysis

Operating Parameter	**Volatiles Analysis**
Chromatographic Column	DB 624, L = 20 *m*, ID = 0.18 *mm*
Carrier Gas	Helium (He)
Temperature Program	T_0 = 30°C, hold 2.0 *min* dT/dt_1 = 32°C/*min* T_1 = 195°C dT/dt_2 = 30°C/*min* T_2 = 235°C
Injector Temperature	250°C
Detector Temperature	280°C
Purge Volume	5 *mL*
Mass Scanning Range	35 *m/z* - 250 *m/z*
Mass Scanning Rate	2.0 *Hz*

Note: the above is subject to change based on GC and/or sample conditions.

Table 5. BFB Tune Evaluation Criteria

Target *m/z*	**Relative *m/z***	**LCL (%)**	**UCL (%)**
50	95	8	40
75	95	30	66
95	95	100	100
96	95	5.0	9.0
173	174	0	2.0
174	95	50	120
175	174	4.0	9.0
176	174	93	101
177	176	5.0	9.0

Table 6.Commonly Used Dilutions for Sample Preparation

Dilution	Sample Volume (µL)	H_2O Volume (µL)	ISD/SSD Volume (µL)	Total Volume (µL)
1:1	5000	0	10.0	5010
2:1	2500	2500	10.0	5010
5:1	1000	4000	10.0	5010
10:1	500	4500	10.0	5010
20:1	250	4750	10.0	5010
50:1	100	4900	10.0	5010
100:1	50	4950	10.0	5010
200:1	25	4975	10.0	5010
500:1	10	5000	10.0	5020
1000:1	5.0	5000	10.0	5015
2500:1	2.0	5000	10.0	5012

General "*n*:1" dilution: (5000/*n*) µL of Sample
(5000 - 5000/*n*) µL H_2O
10 µL Internal/Surrogate Standard (ISD/SSD) at 25 mg/L

Table 7. Quality Control Items, Frequency, and Corrective Action

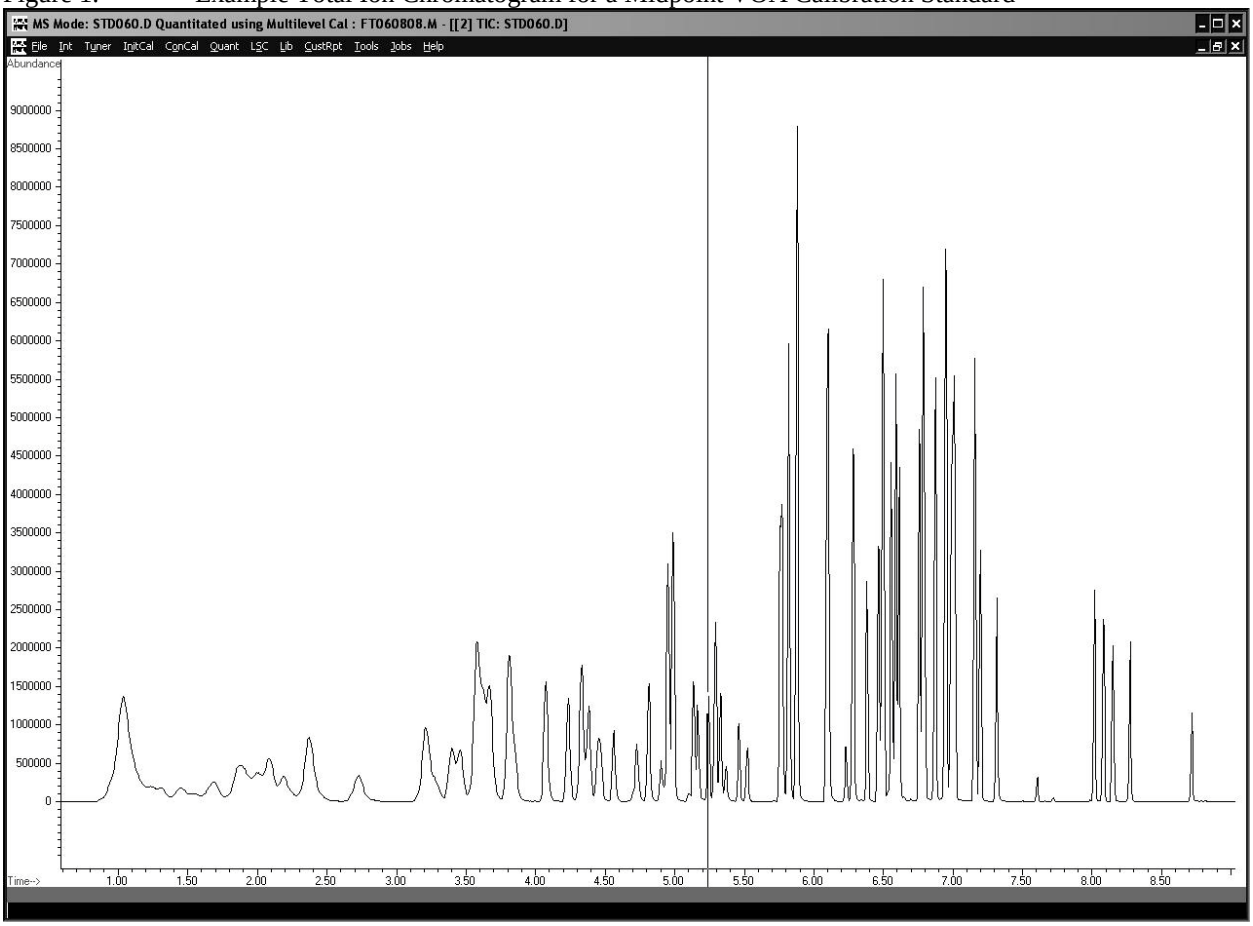
QC Item	Frequency	Acceptance Criteria	Corrective Action
Initial Calibration	Prior to all analytical runs	Method-based	Examine the entire analytical system; some or all of the following: clean MS source, re-tune, clip/replace column, replace calibration standards, re-calibrate.
BFB	12-hour	Method-based	Re-attempt injection; clean MS source, re-tune; failure requires the re-analysis of all associated analytical runs.
SPCC/CCC	12-hour	Method-based	Re-attempt injection; some or all of the following: clean MS source, re-tune, clip/replace column, replace calibration standards, re-calibrate; failure requires the re-analysis of all associated analytical runs.
LCS and MS	20 samples	Lab-based	A failed LCS should be re-extracted and re-analyzed. A failed MS requires no action provided that the LCS is acceptable. If additional sample exists, the samples associated with a failed LCS should be re-extracted and re-analyzed.
Duplicate or MSD	20 samples	n/a	Relative Percent Differences (RPDs) are computed and included in the QC report
Method Blank	20 samples	n/a	Method blank contamination is flagged on the analytical report for any identified target compound. Blanks indicative of contaminated analytical system (typically the purge-and-trap system) should result in a thorough cleansing of the affected system and sample/blank re-analysis.
Internal Standard	All samples	Method-based	Adverse matrix effects on areas/recoveries are demonstrated either by screening the extract of re-analyzing the sample within a 12-hour QC batch. The resulting analytical report is flagged appropriately. A negative bias unrelated to matrix effects indicates the need to: clean the MS source, re-tune, and re-calibrate
Surrogate Standard	All samples	Lab-based	Adverse matrix effects on areas/recoveries are demonstrated either by screening the extract of re-analyzing the sample within a 12-hour QC batch. The resulting analytical report is flagged appropriately. If additional sample exists, the sample should be re-extracted prior to re-analysis if a matrix effect cannot be demonstrated.
Target Compound	All samples	Method-based	Target compounds beyond the calibration range are diluted and re-analyzed and/or flagged as estimated on the analytical report.

Table 8. Summary of Control Limits: Surrogate and Matrix Spiking Compounds Percent Recovery†

#‡	COMPOUND	Water Matrix		Solid Matrix	
		LCL (%)	UCL (%)	LCL (%)	UCL (%)
2	1,2-DICHLOROETHANE-D4	66.4	124.8	70.0	136.3
26	TOLUENE-D8	82.5	118.4	84.0	138.0
43	4-BROMOFLUOROBENZENE	78.4	119.6	59.0	122.8
16	1,1-Dichloroethene (CCC/MS)	59.9	145.0	59.0	172.0
30	Benzene (MS)	73.7	127.0	66.0	142.0
32	Trichloroethene (MS)	71.0	121.2	62.0	137.0
37	Toluene (CCC/MS)	71.4	127.6	59.0	139.0
47	Chlorobenzene (SPCC/MS)	75.0	130.0	60.0	133.0
n/a	Gasoline Range Organics	70.0	130.0	70.0	130.0

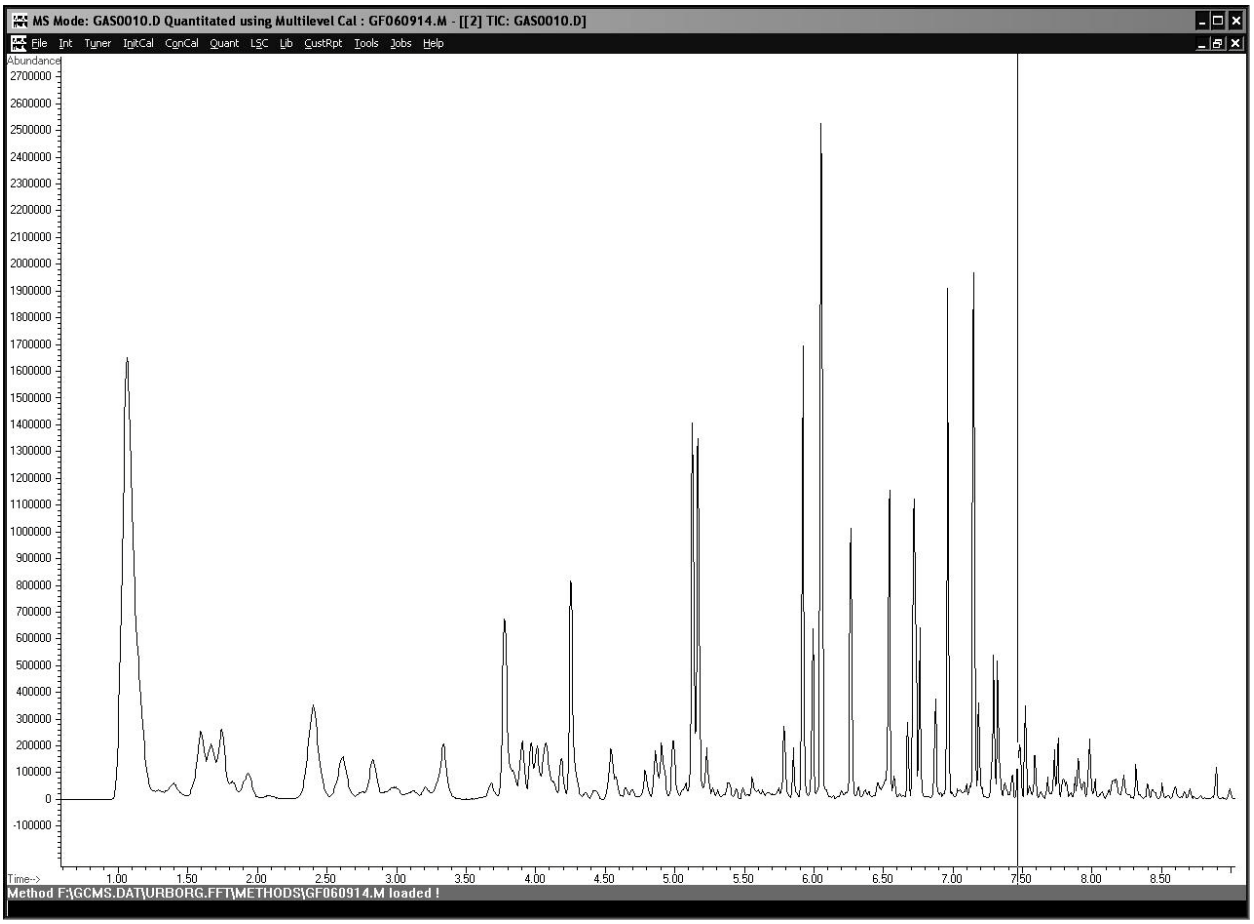
†: Results based on recovery data from 2001.
‡: Compound identification numbers listed are from calibration FR010910.M.

Figure 1. Example Total Ion Chromatogram for a Midpoint VOA Calibration Standard†



†: Data file Std060.D (60 µg/L). GC/MS acquisition parameters are given by Table 4.

Figure 2. Example Total Ion Chromatogram for a Gasoline Range Organics Calibration Standard†



†: Data file GAS_010.D from calibration GF060914.M (1.0 mg/L). GC/MS acquisition parameters are given by Table 4.

METHOD 5030B/5035

1. SCOPE AND APPLICATION

1.1. This Sop describes a purge-and-trap procedure for the analysis of volatile organic compounds (VOCs) in aqueous samples and water miscible liquid samples. It also describes the analysis of low and high concentration soil and waste sample extracts prepared in Method 5035. The method is applicable to GC/MS Method 8260.

1.2. Method 5030 can be used for 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, quantitation limits (by GC or GC/MS) are approximately ten times higher because of poor purging efficiency. The method is also limited to compounds that elute as sharp peaks from a GC column packed with graphitized carbon lightly coated with a carbowax or a coated capillary column. Such compounds include low molecular weight halogenated hydrocarbons, aromatics, ketones, nitriles, acetates, acrylates, ethers, and sulfides.

1.3. Water samples can be analyzed directly for volatile organic compounds by purge-and-trap extraction and gas chromatography. Higher concentrations of these analytes in water can be determined by direct injection of the sample into the chromatographic system or by dilution of the sample prior to the purge-and-trap process.

1.4. This method is restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with this method.

1.5. This SOP is not for use with samples that come into the lab for OHIO VAP work.

2. SUMMARY OF METHOD

2.1. Aqueous Samples: An inert gas is bubbled through a portion of the aqueous sample at ambient temperature, 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.

2.2. High Concentration Extracts from Method 5035: An aliquot of the extract prepared in Method 5035 is combined with organic free reagent water in the purging chamber. It is then analyzed by purge-and-trap GC or GC/MS following the normal aqueous method.

2.3. Low Concentration Soils: An aliquot of the soil is combined with organic free reagent water in the purging chamber. It is then analyzed by purge-and –trap GC or GC/MS.

2.4. Air samples in Tedlar Bags: A volume of air is extracted from the Tedlar Bag using a gas tight syringe and is introduced to a vial of reagent water. An inert gas is bubbled through a portion of the aqueous sample at ambient temperature. 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.

3. INTERFERENCES

3.1. Impurities in the purge gas, and from organic compounds out-gassing from the plumbing ahead of the trap, account for the majority of contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running laboratory reagent blanks. The use of non-polytetrafluoroethylene (non-PTFE) plastic coating, non-PTFE thread sealant, or flow controllers with rubber components in the purging device must be avoided, since such materials out-gas organic compounds which will be concentrated in the trap during the purge operation. These compounds will result in interferences or false positives in the determinative step.

3.2. Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride and fluorocarbons) through the septum seal of the sample vial during shipment and storage. A trip blank prepared from organic-free reagent water and carried through sampling and handling protocols serves as a check on such contamination.

3.3. Contamination by carryover can occur whenever high-concentration and low-concentration samples are analyzed sequentially. Whenever an unusually concentrated sample is analyzed, it should be followed by an analysis of organic-free reagent water to check for cross-contamination. The trap and other parts of the system are subject to contamination. Therefore, frequent bake-out and purging of the entire system may be required.

3.4. The laboratory where volatiles analysis is performed should be completely free of solvents. Special precautions must be taken to determine methylene chloride. The analytical and sample storage areas should be isolated from all atmospheric sources of methylene chloride. Otherwise random background levels will result. Since methylene chloride will permeate through PTFE tubing, all GC carrier gas lines and purge gas plumbing should be constructed of stainless steel or copper tubing. Laboratory workers' clothing previously exposed to methylene chloride fumes during common liquid/liquid extraction procedures can contribute to sample contamination. The presence of other organic solvents in the laboratory where volatile organics are analyzed will also lead to random background levels and the same precautions must be taken.

4. APPARATUS AND MATERIALS

4.1. Microsyringes - 10-µL, 25-µL, 100-µL, 250-µL, and 500-µL

4.2. Gas tight 5ml syringes.

4.3. Vials – 40-mL, for GC autosampler (Archon).

4.4. Magnetic stir bars.

4.5. Scale capable of displaying weight to the nearest hundredth of a gram.

4.6. Purge-and-trap device (Tekmar 3000). The purge-and-trap device consists of three separate pieces of equipment: the sample purger, the trap, and the desorber.

4.6.1. The Vocarb3000 trap by Supelco is used. It is preconditioned at 270°C for 60 minutes upon installment as suggested by supplier.

4.7. Gas Chromatograph (HP5890).

5. REAGENTS

5.1. Organic-free reagent water - All references to water in this method refer to organic-free reagent water.

5.2. Purge and Trap grade methanol.

5.3. Sodium Bisulfate

5.4. See method 8260B SOP for specifications on internal and surrogate standards.

6. SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1. Aqueous Samples

6.1.1. Samples should be stored in capped bottles, with minimum headspace, at (4 +/- 4)°C in an area free of solvent fumes.

6.1.2. All samples should be analyzed within 14 days of collection. Samples not analyzed within this period must be noted and data are considered minimum values. The pH of the samples is checked with pH strips after the sample has been prepared for the autosampler. If the pH is greater than 2 as determined by the pH strip the fact is noted. If the sample with pH > 2 is not analyzed within seven days of the collection date then it is noted on the report that the sample was not properly preserved.

6.2. Soil Samples

6.2.1. High concentration soil samples collected and preserved in the field. The following steps apply to the preparation of vials used in the collection of high concentration soil samples to be preserved in the field with methanol and analyzed by the aqueous purge-and-trap equipment described in Method 5030B SOP.

6.2.1.1. Add 10 mL of methanol to each vial. Seal the vial with the screw-cap and septum seal. Affix a label to each vial. This eliminates the need to label the vials in the field and assures that the tare weight of the vial includes the label. (The weight of any markings added to the label in the field is negligible). Weigh the prepared vial to the nearest 0.01g, record the tare weight, and write it on the label.

6.2.1.2. (10 ± 0.5)g of sample are weighed out and added to the vial in the field.

6.2.1.3. Upon arrival to the lab, samples are stored at (4 ±2)°C.

6.2.2. High concentration soil samples collected without a preservative.

6.2.2.1. When high concentration soil samples are collected without the use of a preservative, an EnCore sample container/sampler is employed.

6.2.2.1.1. The EnCore sampler has not been thoroughly evaluated by the EPA as a sample storage device. Preliminary results indicate that storage in the EnCore device may be appropriate for up to 48 hours, and so samples collected this way should be preserved in methanol within 48 hours of the sampling date. This preservation is documented in the Methanol Prep. Log.

6.2.2.2. Weigh out (10 ±0.5)g of soil sample into a 40-mL vial and add 10-mL of Methanol.

6.2.2.3. Sonicate for twenty minutes.

6.2.2.4. Sample extracts are transferred to 4 ml vials and stored at (4 ± 2)°C.

6.2.2.5. Frozen samples are not acceptable for all OHIO VAP samples.

6.2.3. Low concentration soil samples collected and preserved in the field. The following steps apply to the preparation of vials used in the collection of low concentration soil samples to be preserved in the field with sodium bisulfate and reagent water and analyzed by the aqueous purge-and-trap equipment described in Method 5030B SOP. Note: The sampling and preservation techniques required for low concentration analysis vary widely by state and regulating agency. The end-use of the data should be considered before selecting a sampling and preservation technique and may include procedures not in Method 5035 SOP.

6.2.3.1. Add 5 mL of reagent water and a magnetic stir bar to each vial as well as 0.2g of sodium bisulfate for every 1g of sample to be collected. Seal the vial with the screw-cap and septum seal. Affix a label to each vial. This eliminates the need to label the vials in the field and assures that the tare weight of the vial includes the label. (The weight of any markings added to the label in the field is negligible). Weigh the prepared vial to the nearest 0.01g, record the tare weight, and write it on the label.

6.2.3.2. (1-5 ± 0.5)g of sample are weighed out and added to the vial in the field.

6.2.3.3. Upon arrival to the lab, samples are stored at (4 ±2)°C.

6.2.4. Low concentration soil samples collected without a preservative.

6.2.4.1. When low concentration soil samples are collected without the use of a preservative, an EnCore sample container/sampler is employed.

6.2.4.1.1. The EnCore sampler has not been thoroughly evaluated by the EPA as a sample storage device. Preliminary results indicate that storage in the EnCore device may be appropriate for up to 48 hours, and so samples collected this way should be preserved with sodium bisulfate within 48 hours of the sampling date. This preservation is documented in the Prep. Log.

6.2.4.2. Weigh out (1-5 ±0.5)g of soil sample into a 40-mL vial and add 5ml of reagent water and 0.2g of sodium bisulfate for every 1g of sample.

6.2.4.3. The preserved samples are stored at (4 ± 2)°C.

7. PROCEDURE

7.1. The purge-and-trap technique for aqueous samples is found in Sec. 7.2 and method for analysis of solvent extracts from the High Concentration Method in Method 5035 is found in Sec. 7.3. The gas chromatographic determinative steps are found in Methods 8260B SOP. The method is also applicable to the analysis of gasoline, using Method 8015M SOP.

7.2. This section provides guidance on the analysis of aqueous samples and samples that are water miscible, by purge-and-trap analysis.

7.2.1. Initial calibration.

7.2.2. Prior to using this introduction technique for any GC method, the system must be calibrated. General calibration procedures are discussed in Method 8260B SOP.

7.2.3. Sample screening

7.2.3.1. Screening of the sample prior to purge-and-trap analysis may provide guidance on whether sample dilution is necessary and may prevent contamination of the purge-and-trap system.

7.2.4. Sample introduction and purging

7.2.4.1. Assemble the purge-and-trap device. The operating conditions for the GC and GC/MS are given in method 8260B SOP.

7.2.4.2. GC or GC/MS calibration verification criteria must be met (Method 8260B SOP) before analyzing samples.

7.2.4.3. Adjust the purge gas flow rate to provide the best response for chloromethane and bromoform, if these compounds are analytes. Excessive flow rate reduces chloromethane response, whereas insufficient flow reduces bromoform response.

7.2.4.4. Use a 5-mL syringe to take a 5-mL aliquot of the sample. Care must be taken to remove any bubbles from the syringe. This process of taking an aliquot destroys the validity of the liquid sample for future analysis. Re-analysis should be done with duplicate VOA.

7.2.4.5. Add 10.0 µL of surrogate and internal spiking solution as well as any matrix spike if applicable as described in method 8260B SOP.

7.2.4.6. Inject the aliquot into a 40-mL VOA and immediately place cap with septum and tighten.

7.2.4.7. Purge for 11.0 minutes at room temperature in the 40ml vial.

7.2.5. Sample desorption

7.2.5.1. Non-cryogenic interface - After the recommended purge (see above), place the purge-and-trap system in the desorb mode and preheat the trap without a flow of carrier gas passing through the trap. Start the flow of the carrier gas, begin the GC temperature program, and start GC data acquisition.

7.2.6. Trap Reconditioning

7.2.6.1. After desorbing the sample, recondition the trap by baking it.

7.3. This section provides guidance on the analysis of solvent extracts from High Concentration Samples prepared by Method 5035.

7.3.1. The GC or GC/MS system should be set up as in specific determinative method (8260B SOP).

7.3.2. Take 5mL's of organic-free reagent water and add 10.0 µL of surrogate and internal spiking solution as well as any matrix spike if applicable as described in method 8260B SOP.

7.3.3. Measure out a 100µL aliquot of the methanol phase of the sample.

7.3.4. Quickly inject the 5-mL reagent water with standard mixture and 100µL of sample into a 40-mL vial and place cap with septum on it and tighten.

7.3.5. Purge for 11.0 minutes at room temperature in the 40ml vial.

7.3.6. Desorb the sample and recondition the trap (see 7.2.5 and 7.2.6).

7.4. This section provides guidance on the analysis of Low Concentration Samples prepared by Method 5035.

7.4.1. The GC or GC/MS system should be set up as in specific determinative method (8260B SOP).

7.4.2. Internal standards, surrogates and matrix spikes (if applicable) should be added automatically by the autosampler or manually by puncturing the septum using a small gauge needle.

7.4.3. Prior to purging the sample is preheated to 40°C for 1.0 minute while being agitated by the magnetic stir bar.

7.4.4. Purge for 11.0 minutes at 40°C while being agitated by the magnetic stir bar in the 40ml vial.

7.4.5. Desorb the sample and recondition the trap (see 7.2.5 and 7.2.6).

7.5. Tedlar Bag Air Analysis

7.5.1. The GC or GC/MS system should be set up as in specific determinative method (8260B SOP).

7.5.2. To a 40 ml VOA bottle add 5 ml reagent water and add 10.0 µL of surrogate and internal spiking solution as well as any matrix spike if applicable as described in method 8260B SOP.

7.5.3. Take a gas tight syringe with a niddle fixed to the tip. Draw in a small volume of DI water into the syringe. This will provide a bubbling effect to show air is being drawn in from the bag.

7.5.4. Insert the needle of the syringe through the septa of the Tedlar Bag and with draw 5 cc into the syringe.

7.5.5. Bubble into 40 ml VOA bottle with 5 ml of DI water and surrogates and internal standards then cap promptly.

7.5.6. Purge for 11.0 minutes at room temperature in the 40ml vial.

7.5.7. Desorb the sample and recondition the trap (see 7.2.5 and 7.2.6).

7.6. Sample analysis. The samples prepared by this method will be analyzed according to method 8260B SOP.

8. QUALITY CONTROL

8.1. Refer to method 8260B SOP for specific quality control procedures.

9. METHOD PERFORMANCE

10. Refer to the determinative methods for performance data.

11.0 APPROVAL AND ISSUE

11.1 This section indicates which personnel have read, accepted and approved the SOP. All analysts involved with the SOP must acknowledge their comprehension of the SOP with a signature and a date.

12.0 SAFETY

12.1 Eye protection and gloves must be worn while performing Volatile analyses.

12.2 Every Laboratory area has eyewash, emergency shower, and fire extinguisher. The metals lab also has dust masks available for use with dust samples.

12.3 The air system through out the laboratory area is on a 100% fresh air exchange system, this system exchanges 100% the air in the laboratory area with air from outside 6 times per hour and 30 times per hour when the emergency purge button is hit.

12.4 A reference file of material safety data sheets (MSDSs) is available to all personnel.

12.5 Specific attention be paid (but not limited) to

12.5.1 Hydrochloric acid is corrosive, extreme heat or contact with metals can release flammable hydrogen gas, stable under ordinary conditions of use and storage, and incompatible with many substances and highly reactive with strong bases, metals, metal oxides, hydroxides, amines, carbonates, cyanides, sulfides, sulfites, and formaldehyde.

12.5.2 Methanol may react violently with acids, acid chlorides, acid anhydrides, oxidizing agents, reducing agents and alkali metals. Protect from moisture. Highly flammable.

13.0 WASTE DISPOSAL AND POLLUTION PREVENTION

13.1 All laboratory waste must be managed, stored, and disposed in accordance with all federal and state laws and regulations.

13.2 Additional information can be found in the Sample Disposal SOP and Merit's Waste Management Plan and Handbook.

14.0 APPROVAL & ISSUE:

14.1 This section indicates which personnel have read, accepted and approved the SOP. All analysts involved with the SOP must acknowledge their comprehension of the SOP with a signature and a date.

_____

Analyst Date

_____

QA Officer Date

_____

Maya V. Murshak, Technical Director Date

15.0 REFERENCES

15.1 U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.

15.2 Bellar, T., "Measurement of Volatile Organic Compounds in Soils Using Modified Purge-and-Trap and Capillary Gas Chromatography/Mass Spectrometry", U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Cincinnati, OH, November, 1991.

	Finished?	Written By	Last Revised	SOP Number	Revision #
Administrative	**00**				
Archival of Electronic Data	X	Pat Q.	10/27/09	000001	3
Complaints	X	Maya M.	05/17/10	000002	2
Electronic Deliverables	X	Maya M.	10/27/09	000003	3
Faxing	X	Rosanne A.	10/26/09	000004	3
Invoice	X	Paula S./Barb R.	10/25/09	000005	2
Method Validation	X	Mike G.	02/19/02	000006	1
Phone System	X	Mike G.	10/23/09	000007	2
QA Manual Updates	X	Maya M.	10/29/09	000008	3
Reports	X	Paula S./Barb R.	10/26/09	000009	3
Sending Reports/Invoices	X	Paula S./Barb R.	10/21/09	000010	4
How to Write SOPs	X	Maya M.	10/26/09	000011	6
Training Records	X	Mike G./Maya M.	10/27/09	000012	2
Validation	X	Maya M.	09/17/00	000013	2
Changing SOPs	X	Chris D.	10/21/09	000014	2
Document Control	X	Chris D.	10/21/09	000015	2
Sample Custody and Data Flow	X	Chris D.	10/07/09	000016	2
Visitors	X	Chris D.	10/21/09	000017	2
Internal Audits	X	Chris D.	07/19/10	000018	3
SOP Distribution	X	Chris D.	10/27/09	000019	2
Standard Tracking	X	Joesph K.	11/03/05	000020	1
CRA-GM-Remediation	X	GM	02/23/05	000021	1
Data Integrity	X	Joesph K	10/21/09	000022	2
Flow of Consumable Materials	X	Paula S./Barb R.	05/18/10	000023	3
Ordering Reagents and Supplies	X	Kara T./Violetta M.	06/29/10	000024	3
Chain of Custody Preparation	X	Paula S./Barb R.	10/26/09	000025	2
Sample Handling	**01**				
Bottle Prep/Cooler Shipping	X	Rosanne A.	10/22/09	010001	4
Cooler Cleaning	X	Rosanne A.	10/22/09	010002	5
Disposal	X	Mike G./Isaak M.	01/03/04	010003	4
Log In	X	Paula S./Barb R.	10/22/09	010006	3
Sample Receiving	X	Paula S./Barb R.	10/21/09	010007	6
Thermometer Calibration	X	Mike G.	04/15/03	010008	1
Sample pH	X	Mike G.	10/22/09	010009	2
Pipet Calibration	X	Mike G.	06/04/10	010010	2
Sterilization of Regulated Samples	X	Kara T.	05/19/10	010011	2
Safe Handling of Hazardous Materials	X	Mike G./Andy B.	08/18/09	010012	1
Sub Sampling of Solids, Waste, and Semi-Solid Ma	X	Maya M./Isaak M.	10/15/10	010013	1
Field Services	**02**				
Drum Sampling	X	Mike G.	11/26/01	020001	3
Low-level Mercury Sampling	X	Maya M./Mike G.	04/16/03	020002	1
Sample Splitting	X	Mike G.	01/02/02	020003	2
Sampling Utility Manholes	X	Mike G.	01/02/02	020004	3
Solid Sampling	X	Mike G.	01/02/02	020005	2
Wastewater Sampling	X	Mike G.	11/26/01	020006	2
Field pH	X	Mike G.	10/16/03	021501	1

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Residual Chlorine Field	X	Mike G.	01/17/05	024500C	1
Inorganics	**03**				
Acidity	X	Mike C.	05/21/10	033101A	4
Alkalinities	X	Kara T.	07/20/10	033101B	3
Ammonia	X	Mike C.	07/19/10	033503	8
BOD5/CBOD - SM5210B	X	Megan H.	07/15/10	034051	6
BOD5/CBOD - New Method	X	Kara T.	05/25/10	0310360	2
Winkler Method Modified	X	Mike G.	03/17/08	033602M	2
Carbon Dioxide	X	Mike C.	05/25/10	034500A	2
Chloride (titration)	X	Kara T.	05/21/10	033253	3
COD	X	Mike C.	06/01/10	034104	3
Conductivity	X	Kara T.	05/20/10	031201	2
Cyanide (colorimetric)	X	Jeff P.	05/09/08	033354	9
Cyanide Distillation	X	Jeff P.	05/08/08	03LACHATCN	4
Density solids	X	Kara T.	06/01/10	032710	3
Density liquids and powders	X	Kara T.	06/01/10	032710B	3
Dissolved Oxygen - New Method	X	Kara T.	06/04/10	0310360DO	2
Dissolved Sulfide Prep	X	Jeff P.	06/03/10	034500S2	2
DO Meter Calibration	X	Mike G.	05/12/10	030001	2
Ferrous Iron	X	Jeff P.	05/27/10	03HACHA	2
Hardness	X	Kara T.	05/21/10	032340	5
Hexavalent Cr	X	Kara T./Isaak M.	03/30/05	032184	4
Hexavalent Cr Digestion	X	Jeff P./Isaak M.	07/21/03	033060	4
Ion Chromatography	X	Jeff P.	05/12/10	033000	6
MBAS	X	Mike C./Jeff P.	05/27/10	034251	3
Nitrite (colorimetric)	X	Jeff P.	01/27/06	034500B	4
Phenols	X	Jeff P.	06/02/10	034201	6
Phenols Distillation	X	Jeff P.	06/02/10	03LACHETA	3
Phosphorus	X	Mike C.	06/03/10	033652	6
Reactive Cyanide	X	Jeff P.	09/24/01	039010	1
Residual/Total Chlorine	X	Jeff P.	05/21/10	038167	3
Silica	X	Jeff P.	05/27/10	034500	3
Sulfide Analysis	X	Jeff P.	06/01/10	033762	6
Sulfide Distillation	X	Jeff P.	06/01/10	03LACHATB	3
Sulfite	X	Barb R./Jola B.	06/01/10	030004	1
TKN	X	Mike C.	06/01/10	033514	7
TOC	X	Jeff P.	01/29/02	034151	2
Turbidity	X	Kara T.	06/01/10	03HACH	2
pH (Liquid)	X	Mike G.	06/01/10	031501	6
pH (Solid)	X	Joesph K.	06/01/10	039045D	2
Specific Gravity by Hydrometer	X	Kara T.	06/01/10	03D891	2
Total Dissolved Solids	X	Mike G.	05/25/10	031601	5
Total Solids/Total Volatile Solids/Ash	X	Mike G.	06/02/10	031603	6
Total Suspended Solids/ Volatile Suspended Solids	X	Mike G.	06/02/10	031602	5
Total Solids in Water	X	Mike G.	06/02/10	031603B	6
Viscosity	X	Kara T.	06/01/10	034212	2
FOC by Walkley Black	X	Jeff P. / Andy B.	05/27/10	030002	2

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Determination of H2O2 with KMnO4	X	Mike G./Andy B.	12/14/09	030003	1
Extractions	**04**				
BNA/Herbs (soil)	X	Steve P./Andy H.	03/03/06	043550B	5
BNA/TCLP Micro Ext.	X	Andy H.	08/05/02	043510M	1
MBAS	X	Jola B./Kara T.	01/26/04	044251	2
Oil & Grease (Freon, Grav.)	X	Ken M.	05/08/02	044131A	1
Oil & Grease (Hexane, Grav.)	X	Ken M.	07/16/10	041664A	4
Oil & Grease Soxhlet	X	Chris D.	07/15/03	049071	1
Oily Waste Extraction	X	Troy S.	06/21/07	041330A	1
PCB (water)	X	Brent W./Ken M.	12/12/06	043510	9
PCB (soil)	X	Brent W./Ken M.	12/12/06	043550	8
PNA/BNA/TCLP/Herbs	X	Brent W./Ken M.	03/03/06	043510C	6
PCB-Silica Gel Clean-Up	X	Troy S.	03/06/06	043630C	1
TPH (Hexane, Grav.)	X	Ken M.	05/08/02	041664B	1
TCLP/Waste Analyses	**05**				
%Oil and % Water	X	Andy H.	04/21/10	059688	2
BTU and Total Halogens	X	Kara T.	06/04/10	055050	2
Flash Point for liquids	X	Kara T.	05/11/10	05D3278	2
Flash Point for solids	X	Kara T./Andy H.	05/25/10	051030	2
Paint Filter Test	X	Mike G.	06/02/10	059095	2
SPLP Extraction	X	Andy H./Isaiah M.	06/03/10	050608	2
TCLP Extraction	X	Andy H./Isaiah M.	06/04/10	051311	7
Sample Preparation	**06**				
Analysis Calculations	X	Steve P.	10/26/09	060001	2
Batch Number Tracking	X	Steve P.	06/06/02	060002	1
Glassware Washing	X	Mike G.	05/19/10	060003	2
Method Detection Limits	X	Steve P.	10/23/09	060004	5
Scale/Weight Calibration	X	Mike G.	10/27/09	060005	3
Significant Digits	X	Steve P./Maya M.	01/04/02	060006	1
Organics	**07**				
5035 Prep.	X	Megan H./Josh H.	06/03/10	075035	4
5035 Prep. - VAP	X	Megan H./Josh H.	10/09/06	075035-VAP	3
Formaldehyde (HPLC & Ext.)	X	Mike C.	01/22/02	078315	1
PCBs by GC (Method 608)	X	Janusz B./Maya M.	06/01/04	070608	1
PCBs	X	Janusz B./Maya M.	04/29/08	078082	10
Pests	X	Janusz B. /Joe K.	06/01/10	078081	3
Peak Integration	X	Steve P.	01/05/07	070001	3
SVOCs/DRO	X	Steve P./Brent W.	11/04/10	078270	10
VOCs/GRO	X	Josh H./Steve P.	06/03/10	078260	11
VOCs/GRO - VAP	X	Josh H./Steve P.	03/25/08	078260-VAP	10
Drinking Water VOCs	X	Josh H./Andy B.	06/03/10	075242	2
Metals	**08**				
Digestion (Liquid)	X	Emil B.	09/27/10	083015	7

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Digestion (Liquid) - VAP	X	Andy B./Sarah S.	10/01/10	083015-VAP	6
Digestion (Soil)	X	Emil B.	09/27/10	083050B	8
Digestion (Soil) - VAP	X	Andy B./Sarah S.	10/04/10	083050B-VAP	7
Hg (Digestion & Analysis)	X	Emil B.	05/18/08	087470	8
Hg Drinking Water	X	Emil B.	06/03/10	082451	9
ICPMS 200.8/6020	X	Emil B.	11/30/07	082008	10
ICPMS 6020A	X	Andy B./Barb R	07/21/10	086020A	1
ICPMS 6020A - VAP	X	Andy B./Barb R	07/15/10	086020A-VAP	1
Maintenance	**09**				
Emergency Showers		Eugene B. Mike G.	01/22/03		
General Maintenance		Eugene B. Mike G.	01/22/03		
Hood Airflow		Eugene B. Mike G.	01/22/03		
Reagent Handling		Eugene B. Mike G.	01/22/03		
Refrigerator	X	Barb R. Andy B.	03/26/10	090001	1
Water Purity (DI)	X	Mike G. Barb R.	03/26/10	090002	1