RESOURCE CONSERVATION AND RECOVERY ACT FACILITY INVESTIGATION QUALITY ASSURANCE PROJECT PLAN FOR THE

FORMER GM POWERTRAIN DIVISION LIVONIA 12200 MIDDLEBELT ROAD, LIVONIA, MICHIGAN

USEPA ID #MID000718874

by

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for

Revitalizing Auto Communities
Environmental Response Trust
Ypsilanti, Michigan

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HALEY & ALDRICH

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ACRONYMS AND ABBREVIATIONS

CLP	Contract Laboratory Program
COC	Chain of custody
CQAP	Construction Quality Assurance Plan
CSMP	Containment System Monitoring Plan
CSOMP	Containment System Operation and Maintenance Plan
CSV	Comma separated value
DQO	Data Quality Objective
EDD	Electronic Data Deliverable
ft	Feet
GIS	Geographic Information System
HASP	Health and Safety Plan
IDW	Investigation-derived wastes
l	Liters
l/min	Liters per minute
MCL	Michigan Compiled Laws
MDEQ	Michigan Department of Environmental Quality
MI	Michigan
Michigan 10 Metals	Arsenic, Barium, Cadmium, Chromium, Copper, Lead, Mercury, Selenium, Silver, and Zinc
MLC	Motors Liquidation Company
MPI	Materials Processing Incorporated
MS	Matrix Spike
MSD	Matrix Spike Duplicate
NCP	National Contingency Plan
NEIC	National Enforcement Investigations Center
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
PLC	Programmable logic control
PPE	Personal protective equipment
QAC	QA Coordinator
QAPP	QA 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
SCB	Soil-cement-bentonite
SDG	Sample delivery group
SOP	Standard Operating Procedure
SOW	Scope of Work
SVOC	Semivolatile organic compound

USEPA	United States Environmental Protection Agency
USGS	United States Geological Survey
VOC	Volatile organic compound

1. INTRODUCTION

1.1 General

This document presents the Quality Assurance Project Plan (QAPP) for the monitoring environmental activities and sampling activities that Revitalizing Auto Communities Environmental Response Trust of Ypsilanti, Michigan (RACER) (formerly General Motors Corporation [GMC]) will conduct at the Former General Motors (GM) Livonia Powertrain Facility, located at 12200 Middlebelt Road, Livonia, Wayne County (the Site, see Figure 1). RACER has entered into negotiations with the Region 5 of the United States Environmental Protection Agency (USEPA) to undergo Corrective Action at the Site under a Performance Based Corrective Action Agreement, to be executed under the Resource Conservation and Recovery Act (RCRA). This agreement is being negotiated despite that hazardous waste has not been stored at the Site for more than 90 days, and the Site has not been subject to RCRA interim status. This QAPP has been developed on behalf of RACER by Haley & Aldrich of Michigan, Inc. (Haley & Aldrich) and is a supporting document to the RCRA Facility Investigation (RFI) Work Plan (RFI Work Plan) for the Site that has been prepared under a separate cover. Also supporting the RFI Work Plan under separate covers are the Field Sampling Plan (FSP) and the Public Involvement Plan (PIP).

This QAPP presents the 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. Appendix A of the FSP includes standard operating procedures (SOPs) (including associated field forms) associated with the Site RFI activities to be performed.

1.2 Overview

On June 1, 2009, GMC filed for Chapter 11 protection under United States bankruptcy code. On 10 July 2009, GMC was renamed Motors Liquidation Company (MLC), and on the same day, some of the operating assets of GMC were sold to a newly-formed company "General Motors Company". General Motors Company changed its name to General Motors LLC (GM LLC) on 16 October 2009. On 1 April 2011, the responsibility for environmental remediation of the property was transitioned from MLC to the RACER.

This QAPP addresses the QA/QC elements in the USEPA Region 5 QAPP policy presented in the USEPA RCRA QAPP Instructions, dated April 1998, as well as other relevant guidance documents, including "The Use of Field Methods to Support RFI Streamlining", USEPA Region 5 Memorandum, June 20, 1999. The QA/QC procedures described in this QAPP are consistent with USEPA guidance, including the following:

- American National Standard. Quality Systems for Environmental Data and Technology Programs – Requirements with Guidance for Use. ANSI/ASQC E4-2004. (American National Standard, 2004);

- United States Environmental Protection Agency (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
- MDEQ Remediation Redevelopment Division (RRD) Operational Memorandum No. 1, Part 201 Cleanup Criteria and Risk-Based Screening Levels, dated March 25, 2011 (MDEQ, 2011);
- MDEQ RRD Operational Memorandum No. 2, Sampling and Analysis, dated October 22, 2004 (MDEQ, 2004); and
- USEPA Guidance on Systematic Planning Using the Data Quality Objectives Process, USEPA QA/G-4 (USEPA, 2006);

1.3 QAPP Modifications

Under separate cover, RACER has submitted a RFI Work Plan to the USEPA for the initial phases of RFI work to be performed at the Site. Any future work plans submitted to USEPA 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. In accordance with USEPA guidance document entitled "USEPA Requirements for QA Project Plans, USEPA-QA/R-5" (USEPA, 2001a), established document revision procedures will be followed. 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 USEPA approval. Changes will only be implemented by RACER or RACER's contractors after acceptance by the USEPA. 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.

2. PROJECT ORGANIZATION AND RESPONSIBILITIES

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 brief organizational chart of project personnel and associated responsibilities of each member of the project team regarding 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 RFI Work Plan or as otherwise required by RACER to safely and effectively implement the investigation. Project direction will be provided by Haley & Aldrich, with oversight of certain sampling activities by the USEPA. The QAPP distribution list, which also represents the list of key project management personnel, is provided below.

Company / Organization	Title	Name	Phone Number
USEPA	Project Manager	Greg Rudloff	(312) 870-0455
USEPA	RCRA Corrective Action Unit Chief	George Hamper	(312) 886-0987
RACER	Project Manager	Grant Trigger	(313) 486-2908
RACER	Project Manager	David Favero	(271) 741-6235
Haley & Aldrich	Project Officer	James Little	(937) 530-1410
Haley & Aldrich	Project Manager	Derek Kaiding	(313) 348-5630
Haley & Aldrich	Project Task Manager	Sue Hoertt	(937) 530-1408
Merit Laboratories	Project Manager	Andy Ball	(517) 332-0167
Merit Laboratories	QA Manager	Barb 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 USEPA

Project Manager

- Oversight of all phases of the Corrective Action activity for the Site; and
- The Project Manager is responsible for submitting this QAPP and any subsequent revisions or amendments to the appropriate USEPA personnel for review and approval, and for providing approval of the QAPP.

USEPA RCRA Corrective Action Unit Chief

- The USEPA RCRA Corrective Action Chief has oversight responsibility for all Corrective Action activity for the Site.

2.2.2 RACER

Project Manager

- Provide overall direction of Site actions;
- Implementing the project, and has the authority to commit the resources necessary to meet project objectives and requirements;
- Ensure that technical, financial, and scheduling objectives are achieved successfully;
- Act as the major point of contact and control matters concerning the project and represent the project team at regulatory agency meetings and public hearings;
- Define project objectives;
- Direct RACER's contractors;
- Review the contractor work products, including data, memoranda, letters, reports, and all other documents transmitted to the USEPA; and
- Provide approval of the QAPP and will be responsible for submitting this QAPP to the regulatory personnel.

2.2.3 Haley & Aldrich Project Organization

Project Officer

- Provide approval for major project deliverables and may participate in technical meetings with the USEPA;
- Ensure that overall technical quality is maintained and will be actively involved in the direction of the project;
- Overall responsibility for ensuring that the project meets objectives;
- Acquire and apply technical and other resources as needed to ensure performance within budget and schedule restraints;
- Review work performed on each task to ensure quality, responsiveness, and timeliness; and
- Be responsible for the preparation and quality of interim and final reports.

Project Manager

- Develop a detailed project schedule;
- 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 Haley & Aldrich project manager;
- Verify that corrective actions are taken for deficiencies cited during any audits of Site activities;
- Procurement of project subcontractors and assisting in monitoring the work progress and quality;
- Providing technical support of project activities;
- Coordination of Haley & Aldrich's technical group; and
- Preparing updates of the QAPP and ensuring project personnel have the most current version.

Task Managers

- 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 quality assurance/quality control (QA/QC) of the relevant portions of the Site activities;
- Report data quality concerns to the Haley & Aldrich project manager;
- 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; and
- Maintain field and laboratory files of notebooks/logs, data reductions, and calculations.

- Transmit original files to the Project Manager.

Field Personnel

- Perform field procedures associated with the RFI as set forth in the RFI Work Plan;
- Perform field analyses and collect samples for laboratory analysis, including QA samples;
- Calibrate, operate, and maintain field equipment;
- Reduce field data;
- Maintain sample custody; and
- Prepare field records and logs.

Quality Assurance Coordinator

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

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; and
- Report any potential data quality concerns to the Haley & Aldrich Project Manager.

Project Manager

- 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; and
- Supervise laboratory chain-of-custody.

Quality Assurance Manager

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

3. PROJECT DESCRIPTION AND BACKGROUND

3.1 Site Location and Description

The Site is located at 12200 Middlebelt Road in Livonia, Michigan and is approximately 40 acres. The Site is a generally square-shaped tract of land that is situated in a mixed industrial / commercial / residential area. It is located east of Middlebelt Road between Industrial Road and Plymouth Road, in Wayne County, Michigan. The Site is bordered on the north by the CSX Railroad tracks. Commercial property is located beyond the railroad tracks to the north. The Site is bordered to the east and south by a residential and commercial area. The Site is bordered on the west by City of Livonia Fire Station and Middlebelt Road. Beyond Middlebelt Road, to the west, is a large industrial property.

Topographically, the Site is flat. The general area has a gradual gradient from east to southeast. Surface water flow in the areas of the building and the paved driveways and parking areas are largely controlled by drainage structures along roadways and in paved areas. The City of Livonia Municipal Water Department provides drinking water to the Site.

Previous reports associated with the Site state that surface soil texture in the area typically consists of fill and some sandy or silty deposits, generally less than ten feet thick. Underlying the surface soils is a thick firm silty clay layer, locally referred to as “blue clay”, with occasional sand lenses and pebbles (e.g. till). with occasional sand lenses and pebbles, which is locally referred to as “blue clay”. The “blue clay” layer is often greater than 100 feet thick in the Livonia area and has an inherently low hydraulic conductivity. Underlying the surface, shallow, and deep soils are bedrock deposits classified as Paleozoic Era, Devonian System and Upper Devonian Series.

Previous reports for environmental investigations at the Site have described the stratigraphy as creating two groundwater systems: a perched system with a superficial layer, and a confined system within the bedrock. Previous reports have also indicated perched groundwater being encountered approximately three feet below ground surface, and groundwater flow direction generally to the west.

3.2 Site Background

A single building occupies the Site which, until June 2010, was used for machining operations associated with automotive manufacturing. There is approximately 1.2 million square feet under roof. Former operations included an engine plant, warehouse, and a wastewater treatment plant. The original building was constructed in 1971 and operated as Livonia Machining, which encompassed approximately 20 percent of the existing floor space. In 1984, there was a large expansion for engine work and a new warehouse.

Based on review of available records, investigations of the Site have been limited to the assessment and closure of underground storage tanks (USTs), as well as a more recent environmental assessment performed in general accordance with the American Society for Testing and Materials (ASTM) document E 1527-05.

3.3 Areas of Interest and Site Contaminants

Site-related areas of interest (AOIs) and potential contaminants and are detailed in the RFI Work Plan, and generally include areas where a potential release of hazardous constituents may have occurred involving constituents associated with automotive manufacturing operations (e.g., machining oils, solvents, adhesives, petroleum products, waste materials, etc.).

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.

4.2 Approach

The RFI of the AOIs presented in Table I will be undertaken in a phased approach. After each phase, adequacy of the data will be evaluated to determine whether additional data collection is warranted. When data of sufficient quality and quantity have been collected, the data will be used to support decisions regarding the need for interim or final corrective measures. The first field event (Phase I) includes the following:

- Additional research and review of available historic information and Site records , as appropriate, concerning select AOIs;
- Characterizing soil and/or groundwater quality at AOIs that have been identified for further investigation of potentially impacted media;
- Conducting ground surveying to establish sample and monitoring well location and elevation information;
- Evaluating the integrity of the sumps, pits, and subsurface waste and product lines, as appropriate, to determine if potential releases to the environment have occurred; and
- Conducting a preliminary assessment of potential human and ecological exposures to environmental media at and surrounding the Site by comparing results to screening criteria.

Subsequent field events will consist of soil boring and/or well installations at individual AOIs where a potential impact to soil and/or groundwater is indicated from Phase I results. The second event will also include additional soil and groundwater sampling, as necessary, to achieve RFI goals, as discussed above.

Overall, the RFI activities will be implemented with the following considerations:

- Soil boring/monitoring well installations and soil and groundwater sampling and analysis will be implemented in an phased approach for data collection;
- To the extent possible, data evaluation concerning AOIs that are clustered geographically and/or functionality will be combined;

- Characterization of a suspected release will be biased toward areas of highest potential impacts by positioning borings/wells within or downgradient of likely release areas such as primary/surrogate components (sumps, pits, trenches, etc.) of each AOI or group of AOIs.
- Initially during Phase I activities, all soil borings will be converted temporary monitoring wells (screen and riser installation with sand pack, but no pack/surface seal or surface mount) to facilitate initial borehole groundwater sampling;
- Temporary monitoring wells will be converted to permanent installations during Phase II efforts, pending the results of Phase I efforts.

4.3 Project Schedule

It is expected that the RFI will be completed by the end of 2012.

5. QUALITY OBJECTIVES AND CRITERIA FOR MEASUREMENT DATA

The Data Quality Objectives (DQO) process, as described in Guidance on Systematic Planning using the Data Quality Objectives Process (USEPA, 2006), 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: Study Goals

Step 3: Information Inputs

Step 4: Define Boundaries

Step 5: Analytical Approach

Step 6: Performance of Acceptance Criteria

Step 7: Develop Plan for Obtaining Data

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.

A DQO summary for the investigation monitoring activities presented in the 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 allow rapid identification and quantitation, although the quantitation 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. 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.

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.

For this project, all groundwater or soil samples collected for laboratory chemical analysis will require full documentation equivalent to USEPA Contract Laboratory Program (CLP) format including all sample analysis performed by RACER's contracted Laboratory, Merit Laboratories (Merit). The analytical results will be reported by Merit in the electronic data deliverable (EDD) format and in a PDF format (from data sheets) within 10 working days from the date of sample receipt. The full CLP data packages will be due from the laboratory within 30 calendar days from the date of sample receipt.

5.2 Environmental Sample Analysis

Monitoring and sampling activities will be conducted to support the DQOs associated with the investigation performance objectives.

Data Use – The data to be collected as described in Section 5.3 the Work Plan will be used to ensure the performance objectives of the investigation are met.

Data Quantity – The sample quantities and parameter specific requirements for chemical monitoring are presented in the RFI Work Plan.

Sampling and Analytical Methods – Sampling methods for groundwater chemical monitoring will be as specified in Section 9. The analytical methods are 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 Work Plan. Data comparability is intended to be achieved through the use of standard USEPA-approved methods.

6. SPECIAL TRAINING REQUIREMENTS/CERTIFICATION

Haley & Aldrich 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 OSHA 8-Hour Supervisory Training.

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 sample type and digits indicating the sequential sample number collected starting at 100, followed by the date the sample was collected. For monitoring wells, 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 – "DP"
- 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 feet). 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. Field forms are included in Appendix A of the FSP.

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

Sample Labels – Sample labels will be used to designate each environmental sample collected. Labels are provided by the laboratory and are waterproof with a sticker back so that they will adhere to the sample jars and bottles without falling off or smearing if they get wet. Each sample label will have pertinent information about the sample collected. This includes the sample ID, date and time collected, sampler name, sample location, laboratory analysis to be performed, and name of client requesting analysis.

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 A. 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, Haley & Aldrich, and the USEPA, 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 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 Haley & Aldrich.

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 full CLP-equivalent (Level 3) data packages for all laboratory analysis. Total PCBs are calculated by adding all of the PCB Aroclor detected results together. Non-detect PCB Aroclors are not included in the summation.

Data reports 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;
- Corrective actions taken including description of any reanalysis; and
- 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.

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 for CLP-equivalent reporting will be expanded to include supporting documentation necessary to provide a CLP-equivalent package and will consist of the information presented on the inorganic and organic checklists presented in Appendix A.

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 calendar 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 Haley & Aldrich's 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.

These activities are detailed in Section 3 of the RFI Work Plan.

9. SAMPLE METHOD REQUIREMENTS

9.1 Groundwater Sampling

Groundwater samples will be collected for baseline chemical analysis from the newly install 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 are presented in the FSP. All samples will be collected in accordance with MDEQs Remediation and Redevelopment Division (RRD) Operational Memorandum No. 2, Sampling and Analysis (Op Memo 2) (MDEQ, 2004). Sample analytical results will be compared to MDEQ's RRD Operational Memorandum No. 1, Part 201 Cleanup Criteria and Risk-Based Screening Levels (Part 201 Criteria) (MDEQ, 2011). Groundwater samples 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 MDEQs RRD Op Memo 2 (MDEQ, 2004). Soil samples for laboratory analysis will be collected from soil borings based on field PID readings and visual observations. Sample analytical results will be compared to MDEQ's RRD Operational Memorandum No. 1, Part 201 Criteria (MDEQ, 2011).

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 purchased pre-cleaned according to USEPA Office of Solid Waste and Emergency Response (OSWER) Directive 9240.05A requirements. 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. Soil samples obtained for the analysis of volatile organic compounds (VOC) will be collected in laboratory supplied pre-weighed and pre-preserved methanol containers. Approximately ten (10) grams of soil will be weighed and added to the containers via plastic syringes. For more detailed information, see the "Extraction/Preservation of Soil/Sediment for VOCs" SOP presented in Appendix A of the FSP.

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 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:

- 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. See Appendix A of the FSP for more details on the COC forms.

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:

1. Securely affix the sample label to the container with clear packing tape.
2. Check the cap on the sample container to confirm that it is properly sealed.
3. Wrap the sample container with clear packing tape to prevent the label from becoming loose.
4. 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.
5. Using duct tape, secure the outside drain plug at the bottom of the cooler.
6. Wrap sample containers in bubble wrap or other cushioning material.
7. Place 1 to 2 inches of cushioning material at the bottom of the cooler.

8. Place the sealed sample containers into the cooler.
9. Place ice in plastic bags and seal. Place loosely in the cooler.
10. Fill the remaining space in the cooler with cushioning material.
11. Place COC forms in a plastic bag and seal. Tape the forms to the inside of the cooler lid.
12. Close the lid of the cooler, lock, and secure with duct tape.
13. Wrap strapping tape around both ends of the cooler at least twice.
14. 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.
15. Place a signed custody seal over the sample cooler lid.

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 48 hours of the time of collection. 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. See Appendix A of the FSP for more details on the packing, handling and shipping procedures.

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 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 Haley & Aldrich

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. An 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 over a maximum of 7 calendar days and must be processed through the laboratory (preparation, analysis, and reporting) as a group. Every SDG must include a minimum of one Site-specific MS/MSD pair, which shall be received by the laboratory at the start of the SDG assignment.

10.5.4 Sample Storage Following Analysis

Samples will be maintained by the laboratory for at least 1 month after the final CLP-equivalent 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 are 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 A. These documents include "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods," SW-846, U.S.EPA 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. In addition, Merit's "Quality Assurance Manual" which summarizes specific details related to laboratory procedures and quality assurance is also included in Appendix A.

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. The RFI Work Plan presents 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.

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

QC procedures for field instruments will include calibrating the instruments as described in Sections 13.1 and 14 of this QAPP, measuring duplicate samples and checking the reproducibility of the measurements by taking multiple readings on a single sample, or the measurement reference standards. Assessment of field sampling precision and bias will be made by collecting field duplicates and equipment rinseate blanks for laboratory analysis.

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 Equipment Rinseate Blank Samples

Equipment rinseate blank samples are used to monitor the cleanliness of the sampling equipment and the effectiveness of the cleaning procedures. Equipment rinseate blanks will be prepared and submitted for analysis once per day per matrix. Equipment rinseate 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. The presence of analytes in the equipment rinseate blank samples will be indicative of potential cross contamination. When dedicated sampling devices or sample containers are used to collect the samples, rinseate blanks will not be necessary.

12.2.5 Field Blanks

Field blanks will be collected only for the analysis of 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 of mercury by USEPA method 1631E and VOCs. 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 program. The blank samples are used to assess whether contamination of VOC samples has occurred due to the contamination migration during sample shipment and storage. The frequency of the trip blank sample will be at least one sample per cooler.

12.3 Analytical Laboratory Quality Control Checks

12.3.1 General

The laboratory identified in Section 2.2.4 of this QAPP has QC programs they use to ensure the reliability and validity of the analysis performed at the laboratory. 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. All data will be properly recorded and the data package will include a summary of QC data. Any samples analyzed in nonconformance with QC criteria will be re-analyzed by the laboratory, if sufficient volume is available. In addition, Merit's "Quality Assurance Manual" which summarizes specific details related to laboratory procedures and quality assurance is included in Appendix A.

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 encompass 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 batch 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 (1 MS/MSD for every 20 samples or at least once per sampling round, if less than 20 samples are collected).

When MS recoveries are outside QC limits, associated control sample and surrogate spike recoveries will be evaluated, as applicable, 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

Instruments and equipment used to gather, generate, or measure environmental data will be calibrated as specified in the field SOPs. 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. Satisfactory completion of the pre-operation inspection will be recorded in the Field Book or Field Sampling Record, along with the results of each field measurement.

The field instruments will include dissolved oxygen meters, pH meters, turbidity meters, specific conductance meters, and photo-ionization detectors (PIDs). Field instruments will be used for real-time sample measurement during monitoring well sampling and organics screening for both on-Site screening of soil samples and for health and safety air monitoring. On-Site air monitoring for health and safety purposes and the screening of soil samples may be accomplished using PIDs.

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 they are 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 is a measure of the amount of valid (usable) data obtained from a measuring system compared to the amount that was expected to be obtained under normal conditions. The completeness goal for all data uses is that a sufficient amount of valid data be generated so that determinations can be made related to the intended data use with a high degree of confidence. The assessment of completeness will require professional judgment to determine data usability for intended purposes. 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.

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

The field completeness and lab completeness objective for this project will be 90 percent. The evaluation of the data completeness will be performed at the conclusion of each sampling and analysis effort. Corrective actions such as revised sample handling procedures will be implemented if problems

are noted. The completeness of the data generated will be determined by comparing the amount of valid data, based on independent validation, with the total data set. The sampling design of this investigation is sufficient that the completeness goal of 90% will provide enough usable data to assess the DQOs at the Site

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, Haley & Aldrich, and the USEPA 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). In addition, Merit's "Quality Assurance Manual" which summarizes specific details related to laboratory procedures and quality assurance is also included in Appendix A.

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, as noted in the attached SOPs (Appendix A). For analyses governed by SOPs, see the appropriate SOP for the required calibration procedures and frequencies in Appendix A. 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. In addition, Merit's "Quality Assurance Manual" which summarizes specific details related to laboratory procedures and quality assurance is also included in Appendix A.

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. Field personnel will be responsible for inspecting supplies and consumables and accepting them for use in the project. Inspection will consist of visually assessing supplies and consumables for noticeable defects (i.e., tears in packaging, opened/dirty containers/bottles, etc.). All defected materials will be returned or discarded and not used. 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. Additional information related to the laboratory is presented in Merit's "Quality Assurance Manual" in Appendix A.

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; and
- Survey EDD.

These deliverables will be uploaded to the database maintained by Haley & Aldrich and ensures consistency with the Laboratory EDD. Although these documents are typically generated by hand using Microsoft Excel, after the sample event, an alternative solution offered by RACER's Information Management group, that may be used, is a program called EDGE. This system is utilized by a pocket PC with custom software which will record the necessary information and generate the EDDs during field activities. EDGE is installed to complement the field notebook documentation.

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 Haley & Aldrich 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 Haley & Aldrich Project Manager) on the following day.

When analytical data are received from the laboratory, the 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 Haley & Aldrich 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 5 data management system. This database will allow Haley & Aldrich 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 EQulS 5 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 EQulS 5 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 EQulS 5 and/or Microsoft® Excel and Microsoft® Word. These software products will be upgraded as necessary to maintain industry 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 USEPA 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. 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. Additional information related to the laboratory is presented in Merit's "Quality Assurance Manual" in Appendix A.

In addition to the chain of custody record, the final laboratory data report format shall consist of the following:

1. Case Narrative:
   - Date of issuance;
   - Laboratory analysis performed;
   - Any deviations from intended analytical strategy;
   - Laboratory batch number;
   - Number of samples and respective matrices;
   - Cross-reference table of laboratory sample to project sample identification numbers;
   - Definition of data qualifiers to be used;
   - Methods of sample preparation and analyses for samples;
   - QC procedures utilized and also references to the acceptance criteria;
   - Laboratory report contents;
   - Project name and number;
   - Condition of samples "as received";
   - Discussion of whether or not sample holding times were met;
   - Discussion of technical problems or other observations which may have created analytical difficulties;
   - Discussion of laboratory QC checks which failed to meet project criteria; and
   - Signature of the Laboratory QA Officer or his designee.

2. Chemistry Data Package:
   - Sample results with quantitation (report) limits (RL), reporting MDLs and estimated values between the RL and MDL;
   - Raw data for sample results and laboratory quality control samples;
   - Results of (dated) initial and continuing calibration checks, GC/MS tuning results;
   - Internal standard response and retention time summaries;
   - Matrix spike and matrix spike duplicate recoveries, laboratory control samples, method blank results, surrogate recoveries, calibration check compounds and system performance check compound results (organics);

- Matrix spike recoveries and matrix duplicate relative percent differences, laboratory control sample, serial dilutions, method blank results, and reagent blank results (inorganics);
- Labeled and dated chromatograms, quantitation reports and mass spectra of sample results and laboratory quality control checks; and
- All sample preparation forms and other related instrumental data.

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 and can still be entered into the database.

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 EPA.

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. The project files, including all relevant records, reports, logs, field notebooks, pictures, subcontractor reports, and data reviews will be maintained in a secured, limited access area and under custody of the Haley & Aldrich Project Manager, or his designee. The project file shall be maintained for a period of six (6) years after project completion. The USEPA shall be offered the file prior to disposal. The final project file will be maintained in Haley & Aldrich's project files located at 3840 Packard Road Suite 130, Ann Arbor, Mi 48108.

The laboratory will be responsible for maintaining analytical logbooks, laboratory data and sample chain of custody documents. Raw laboratory data files and copies of hard copy reports will be inventoried and maintained by the laboratory for a period of five (5) years at which time the laboratory will contact Haley & Aldrich regarding the disposition of the project related 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 Field Performance and System Audits

17.2.1 Internal Field Audit Responsibilities

Internal audits of field activities include the review of sampling and field measurements conducted by the Field QA Coordinator. The audits will verify that all procedures are being followed. Internal field audits will be conducted once during each phase of the sampling and at the conclusion of the project. The audits will include examination of the following:

- Sampling equipment decontamination procedures;
- Field sampling records, screening results, instrument operating records
- Sample collection
- Handling and packaging in compliance with procedures
- Maintenance of QA procedures; and
- COC reports.

Follow up audits will be conducted to correct deficiencies and to verify that procedures are maintained throughout the investigation. An example of the field audit checklist is included in **Appendix B**.

17.2.2 External Field Audit Responsibilities

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 Haley & Aldrich 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 Work Plan.

External audits may be conducted by the USEPA at any time during the field operations. These audits may or may not be announced and are at the discretion of the USEPA QA 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 Performance and System Audits

17.3.1 Internal Laboratory Audit Responsibilities

The laboratory system audits will be conducted by the Haley & Aldrich QA Coordinator or designee and performed on an annual basis. Laboratory performance audits will be conducted prior to field activities or on an annual basis, depending on the duration of the project.

The system audit will include an examination of laboratory documentation including: sample receiving logs, sample storage, chain-of-custody procedures, sample preparation and analysis, and instrument operating records. System audits are qualitative and consist of an on-Site review of a laboratory's quality assurance system and physical facilities for calibration and measurement.

The performance audits after project startup will include submittal of blind performance evaluation samples along with project samples. The Haley & Aldrich QA Coordinator will evaluate the analytical results to ensure the lab is maintaining acceptable QC performance.

At the conclusion of internal or external system audits, reports are provided to the laboratory's operating divisions for appropriate comment and remedial/corrective action where necessary. Written response to internal as well as external audits will be required. Records of audits and corrective actions are maintained by the Laboratory QA Coordinator. Additional information related to the laboratory is presented in Merit's "Quality Assurance Manual" in Appendix A.

17.3.2 External Laboratory Audit Responsibilities

External audits will be conducted as required, by appropriate QA personnel of the USEPA Region 5 and may be conducted at least once prior to sampling and analysis activities. Additional information related to the laboratory is presented in Merit's "Quality Assurance Manual" in Appendix A.

External audits may include any of the following:

- Review of laboratory analytical procedures;
- Laboratory on-Site visits; and

- 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:

- Sample receipt procedures;
- Custody, sample security, and log-in procedures;
- Review of instrument calibration logs;
- Review of QA procedures;
- Review of log books;
- Review of analytical SOPs; and
- Personnel interviews.

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

- Comparison of resulting data to the SOP or method
- Verification of initial and continuing calibrations within control limits
- Verification of surrogate recoveries and instrument timing results
- Review of extended quantitation reports for comparisons of library spectra to instrument spectra, where applicable; and
- 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 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. In addition, Merit's "Quality Assurance Manual" which summarizes specific details related to laboratory procedures and quality assurance is included in Appendix A.

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 Investigation 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

The field team leader or designee will prepare summary field reports at the end of each sampling event. The reports will document field progress and any concerns in the field. Adjustments to the field scope of work and other problems will be reported immediately. The report will be provided to the Task Manager or designee for review prior to submitting to the project file.

18.3 Audit Reports

Audit reports will be prepared by the audit team leader immediately after completion of the audit. The report will list findings and recommendations and will be provided to the Project Manager, Task Manager, and Project Chemist.

18.4 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.

18.5 Project Status Reports

Project status reports will be completed by the Task Manger or other designee to document the overall assessment of the project on a monthly basis. The Haley & Aldrich Project Manager, Task Manager, or other designee will use the reports to track the overall quality of performance on projects in regard to schedule, budgets, and other issues.

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 Haley & Aldrich 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 analytical 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) modified in accordance with SW-846 methodology for data validation criteria available at the time of project initiation, where appropriate. The data review (Tier III) utilizing M-3 (organic) and M2 (inorganic) will be performed on 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 USEPA.

The Haley & Aldrich 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 Haley & Aldrich 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 Haley & Aldrich 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 Haley & Aldrich Project Manager at this point. Data Useability reports will be kept in the project file.

Tier III data validation will be performed on 10% of the laboratory quality control summary data deliverables and will consist of the following components:

1. Organic Analysis
    - Technical holding times;
    - GC/MS instrument performance check;
    - Initial and continuing calibration;
    - Internal standard performance;
    - Method, trip and equipment rinseate blanks;
    - System monitoring compounds (surrogate spikes);
    - MS/MSD results;
    - Laboratory control samples; and
    - Field duplicate samples.

2. Inorganic Analysis
    - Technical holding times;
    - Initial calibration;
    - Initial and continuing calibration verification;
    - Calibration and method blanks;

- ICP interference check samples;
- ICP/MS internal standards;
- ICP serial dilutions;
- Laboratory control samples;
- MS/MSD results; and
- Field duplicate.

The Tier III validation will include the evaluation of all raw data and mass spectra to validate the above components as well as verify sample results.

21. DATA VALIDATION AND VERIFICATION

The data results will be examined to determine the performance that was achieved for each data usability criterion. The performance will then be compared with the project objectives and DQOs. Deviations from objectives will be noted. Additional action may be warranted when performance does not meet performance objectives for critical data. Options for corrective action relating to incomplete information, questionable results, or inconsistent data may include any or all of the following:

- Retrieval of missing information;
- Request for additional explanation or clarification;
- Reanalysis of sample from extract (when appropriate); and
- Recalculation or reinterpretation of results by the laboratory.

These actions may improve the data quality, reduce uncertainty, and eliminate the need to qualify or reject data. If these actions do not improve the data quality to an acceptable level, the following additional actions may be taken:

- Extrapolation of missing data from existing data points;
- Use of historical data; and
- Evaluation of the critical/non-critical nature of the sample.

If the data gap cannot be resolved by these actions, an evaluation of the data bias and potential for false negatives and positives can be performed. If the resultant uncertainty level is unacceptable, additional samples will be collected and analyzed.

REFERENCES

1. American National Standard. 2004. Quality Systems for Environmental Data and Technology Programs – Requirements with Guidance for Use. ANSI/ASQC E4-2004.

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3. MDEQ. 2004. Operational Memorandum No. 2 (October 22, 2004).

4. State of Michigan, R299.5526, Part 201, of Michigan's Natural Resources and Environmental Protection Act 451

5. USEPA. 1986. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods. SW-846 EPA. USEPA Office of Solid Waste (3rd Edition and promulgated updates).

6. USEPA. 1992. Specifications and Guidance for Obtaining Contaminant-Free Sample Containers, Office of Solid Waste and Emergency Response (OSWER) Directive #9240.0-0.5A.

7. USEPA. 1992. Guide to Management of Investigation-Derived Wastes, 9345.3-03FS. January 1992.

8. USEPA. 1995. Innovative Approaches to Data Validation. USEPA Region III (June 1995).

9. USEPA. 1999a. Data Quality Objectives Process for Hazardous Waste Site Investigations. EPA QA/G-4HW, Peer Review Draft (June 1999).

10. USEPA. 1999b. Contract Laboratory Program National Function Guidelines for Organic Data Review. EPA 540/R-99/008. (October 1999).

11. USEPA. 2001. EPA Requirements for Quality Assurance Project Plans. EPA QA/R-5. (March 2001).

12. USEPA. 2002a. Contract Laboratory Program National Function Guidelines for Inorganic Data Review. EPA 540/R-01/008. (July 2002).

13. USEPA. 2002b. Guidance for Quality Assurance Project Plans. EPA QA/G-5 (December 2002).

14. USEPA. 2006. Guidance on Systematic Planning Using the Data Quality Objectives Process. EPA QA/G-4. (February 2006).

TABLE 1
QUALITY ASSURANCE PROJECT PLAN
DATA QUALITY OBJECTIVES (DQOS) FOLLOWING USEPA 7-STEP PROCESS
FORMER GENERAL MOTORS POWERTRAIN PROPERTY
LIVONIA, MICHIGAN

Data Type	Problem Statement	Study Goals	Information Inputs	Define Boundaries	Analytic Approach	Performance or Acceptance Criteria	Develop Plan for Obtaining Data
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. In addition, paired wells (shallow and deep) may need to be installed to evaluate the vertical component of flow .	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, 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, 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
QUALITY ASSURANCE PROJECT PLAN
SAMPLE QUANTITIES AND QUALITY CONTROL FREQUENCIES
FORMER GENERAL MOTORS POWERTRAIN PROPERTY
LIVONIA, 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 PAHs	1/cooler	5	NC	--	1/10	1	1/20	1	1/20	1	NC	--	8
Metals (arsenic, barium, cadmium, chromium, copper, 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
General Water Quality Parameters[4]	NC	--	NC	--	1/10	1	1/20	1	1/20	1	1/20	1	4
Soil													
VOCs and PAHs	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, copper, 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

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, for a total of 9 and that soil sample counts are 2 per boring for a total of 18 samples.
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
QUALITY ASSURANCE PROJECT PLAN
SAMPLE CONTAINERS, PRESERVATION, HOLDING TIMES, METHODS, AND DETECTION LIMITS
FORMER GENERAL MOTORS POWERTRAIN PROPERTY
LIVONIA, MICHIGAN

Parameter	Analytical Method[1]	Merit Reporting Detection Limit	Target Detection Limit[2]	Sample Container and Volume[3]	Preservation[4]	Maximum Holding Time[5]
GROUNDWATER SAMPLES (ug/L)						
Volatile Organic Compounds (VOCs)						
1,2-Dichlorobenzene	8260B	1	1	2-40 ml VOA vials	cool to 4˚ C, HCl to pH<2 no headspace	14 days
1,2-Dichloroethane	8260B	1	1	2-40 ml VOA vials	cool to 4˚ C, HCl to pH<2 no headspace	14 days
1,2-Dichloropropane	8260B	1	1	2-40 ml VOA vials	cool to 4˚ C, HCl to pH<2 no headspace	14 days
Acetone	8260B	20	50	2-40 ml VOA vials	cool to 4˚ C, HCl to pH<2 no headspace	14 days
Benzene	8260B	1	1	2-40 ml VOA vials	cool to 4˚ C, HCl to pH<2 no headspace	14 days
cis-1,2-Dichloroethene	8260B	1	1	2-40 ml VOA vials	cool to 4˚ C, HCl to pH<2 no headspace	14 days
Chlorobenzene	8260B	1	1	2-40 ml VOA vials	cool to 4˚ C, HCl to pH<2 no headspace	14 days
Ethylbenzene	8260B	1	1	2-40 ml VOA vials	cool to 4˚ C, HCl to pH<2 no headspace	14 days
m,p-Xylene	8260B	1	2	2-40 ml VOA vials	cool to 4˚ C, HCl to pH<2 no headspace	14 days
Merthyl(tert)butylether (MTBE)	8260B	5	5	2-40 ml VOA vials	cool to 4˚ C, HCl to pH<2 no headspace	14 days
Methylene chloride	8260B	5	5	2-40 ml VOA vials	cool to 4˚ C, HCl to pH<2 no headspace	14 days
Naphthalene	8260B	5	5	2-40 ml VOA vials	cool to 4˚ C, HCl to pH<2 no headspace	14 days
o-Xylene	8260B	1	1	2-40 ml VOA vials	cool to 4˚ C, HCl to pH<2 no headspace	14 days
Styrene	8260B	1	1	2-40 ml VOA vials	cool to 4˚ C, HCl to pH<2 no headspace	14 days
Tetrachloroethene	8260B	1	1	2-40 ml VOA vials	cool to 4˚ C, HCl to pH<2 no headspace	14 days
Toluene	8260B	1	1	2-40 ml VOA vials	cool to 4˚ C, HCl to pH<2 no headspace	14 days
Trichloroethene	8260B	1	1	2-40 ml VOA vials	cool to 4˚ C, HCl to pH<2 no headspace	14 days
Vinyl chloride	8260B	1	1	2-40 ml VOA vials	cool to 4˚ C, HCl to pH<2 no headspace	14 days
Xylenes, total	8260B	3	3	2-40 ml VOA vials	cool to 4˚ C, HCl to pH<2 no headspace	14 days

TABLE 3
QUALITY ASSURANCE PROJECT PLAN
SAMPLE CONTAINERS, PRESERVATION, HOLDING TIMES, METHODS, AND DETECTION LIMITS
FORMER GENERAL MOTORS POWERTRAIN PROPERTY
LIVONIA, MICHIGAN

Parameter	Analytical Method[1]	Merit Reporting Detection Limit	Target Detection Limit[2]	Sample Container and Volume[3]	Preservation[4]	Maximum Holding Time[5]
Polycyclic Aromatic Hydrocarbons (PAHs)						
Acenaphthene	8270C	5	5	2-1 liter amber glass	cool to 4˚ C	7 days to extraction 40 days to analysis
Fluoranthene	8270C	1	1	2-1 liter amber glass	cool to 4˚ C	7 days to extraction 40 days to analysis
Fluorene	8270C	5	5	2-1 liter amber glass	cool to 4˚ C	7 days to extraction 40 days to analysis
Phenanthrene	8270C	2	2	2-1 liter amber glass	cool to 4˚ C	7 days to extraction 40 days to analysis
Acenaphthylene	8270C	5	5	2-1 liter amber glass	cool to 4˚ C	7 days to extraction 40 days to analysis
Anthracene	8270C	5	5	2-1 liter amber glass	cool to 4˚ C	7 days to extraction 40 days to analysis
Benzo(a)anthracene	8270C	1	5	2-1 liter amber glass	cool to 4˚ C	7 days to extraction 40 days to analysis
Benzo(a)pyrene	8270C	1	5	2-1 liter amber glass	cool to 4˚ C	7 days to extraction 40 days to analysis
Benzo(b)fluoranthene	8270C	1	5	2-1 liter amber glass	cool to 4˚ C	7 days to extraction 40 days to analysis
Benzo(k)fluoranthene	8270C	1	5	2-1 liter amber glass	cool to 4˚ C	7 days to extraction 40 days to analysis
Benzo(ghi)perylene	8270C	1	5	2-1 liter amber glass	cool to 4˚ C	7 days to extraction 40 days to analysis
Chrysene	8270C	1	5	2-1 liter amber glass	cool to 4˚ C	7 days to extraction 40 days to analysis
Dibenzo(ah)anthracene	8270C	2	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	5	2-1 liter amber glass	cool to 4˚ C	7 days to extraction 40 days to analysis
Naphthalene	8270C	5	5	2-1 liter amber glass	cool to 4˚ C	7 days to extraction 40 days to analysis
Pyrene	8270C	5	5	2-1 liter amber glass	cool to 4˚ C	7 days to extraction 40 days to analysis
Metals						
Mercury	1631E [7]	0.00050 [7]	0.001	2-40 ml VOA vials	cool to 4˚ C	28 days
Arsenic	6020 [8]	1	5	125 ml plastic	cool to 4˚ C, HNO_3 to pH<2	6 months
Chromium (hexavalent)	7196A	10	10	125 ml plastic	cool to 4˚ C	24 hours
Chromium (total)	6020 [8]	5	10	125 ml plastic	cool to 4˚ C, HNO_3 to pH<2	6 months
Cadmium	6020 [8]	0.5	1	125 ml plastic	cool to 4˚ C, HNO_3 to pH<2	6 months
Copper	6020 [8]	5	100	125 ml plastic	cool to 4˚ C, HNO_3 to pH<2	6 months
Barium	6020 [8]	5	100	125 ml plastic	cool to 4˚ C, HNO_3 to pH<2	6 months
Lead	6020 [8]	3	3	125 ml plastic	cool to 4˚ C, HNO_3 to pH<2	6 months
Selenium	6020 [8]	5	5	125 ml plastic	cool to 4˚ C, HNO_3 to pH<2	6 months
Silver	6020 [8]	0.20	0.20	125 ml plastic	cool to 4˚ C, HNO_3 to pH<2	6 months

TABLE 3
QUALITY ASSURANCE PROJECT PLAN
SAMPLE CONTAINERS, PRESERVATION, HOLDING TIMES, METHODS, AND DETECTION LIMITS
FORMER GENERAL MOTORS POWERTRAIN PROPERTY
LIVONIA, MICHIGAN

Parameter	Analytical Method[1]	Merit Reporting Detection Limit	Target Detection Limit[2]	Sample Container and Volume[3]	Preservation[4]	Maximum Holding Time[5]
Zinc	6020 [8]	5	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 mg/l	1 L plastic	cool to 4˚ C	28 days
Sulfate	300.0	1 mg/l	1 mg/l	1 L plastic	cool to 4˚ C	28 days
Nitrate	300.0	0.1 mg/l	0.1 mg/l	1 L plastic	cool to 4˚ C	48 hours
Nitrite	300.0	0.1 mg/l	0.1 mg/l	1 L plastic	cool to 4˚ C	48 hours
Hardness	2340 Std Mtd	1 mg/l	2 mg/l	125 ml plastic	cool to 4˚ C, HNO_3 to pH<2	6 months
Alkalinity	2320B	1 mg/l	1 mg/l	1 L plastic	cool to 4˚ C	14 days
Ammonia	4500-NH3 D	0.02 mg/l	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 mg/l	1 L plastic	cool to 4˚ C	7 days
Total Organic Carbon	EPA 415	1 mg/l	1 mg/l	2-40 ml VOA vials	cool to 4˚ C, H_2SO_4 to pH<2	28 days
SOIL SAMPLES (ug/kg)						
Volatile Organic Compounds (VOCs)						
1,2-Dichlorobenzene	8260B	50	100	1-40 ml VOA vial 1-4 oz glass, wide mouth	cool to 4˚ C, MeOH in VOA	14 days
1,2-Dichloroethane	8260B	50	50	1-40 ml VOA vial 1-4 oz glass, wide mouth	cool to 4˚ C, MeOH in VOA	14 days
1,2-Dichloropropane	8260B	50	50	1-40 ml VOA vial 1-4 oz glass, wide mouth	cool to 4˚ C, MeOH in VOA	14 days
Acetone	8260B	750	1000	1-40 ml VOA vial 1-4 oz glass, wide mouth	cool to 4˚ C, MeOH in VOA	14 days
Benzene	8260B	50	50	1-40 ml VOA vial 1-4 oz glass, wide mouth	cool to 4˚ C, MeOH in VOA	14 days
cis-1,2-Dichloroethene	8260B	50	50	1-40 ml VOA vial 1-4 oz glass, wide mouth	cool to 4˚ C, MeOH in VOA	14 days
Chlorobenzene	8260B	50	250	1-40 ml VOA vial 1-4 oz glass, wide mouth	cool to 4˚ C, MeOH in VOA	14 days
Ethylbenzene	8260B	50	50	1-40 ml VOA vial 1-4 oz glass, wide mouth	cool to 4˚ C, MeOH in VOA	14 days
m,p-Xylene	8260B	50	100	1-40 ml VOA vial 1-4 oz glass, wide mouth	cool to 4˚ C, MeOH in VOA	14 days
Merthyl(tert)butylether (MTBE)	8260B	250	250	1-40 ml VOA vial 1-4 oz glass, wide mouth	cool to 4˚ C, MeOH in VOA	14 days
Methylene chloride	8260B	100	100	1-40 ml VOA vial 1-4 oz glass, wide mouth	cool to 4˚ C, MeOH in VOA	14 days
Naphthalene	8260B	330	330	1-40 ml VOA vial 1-4 oz glass, wide mouth	cool to 4˚ C, MeOH in VOA	14 days
o-Xylene	8260B	50	50	1-40 ml VOA vial 1-4 oz glass, wide mouth	cool to 4˚ C, MeOH in VOA	14 days
Styrene	8260B	50	50	1-40 ml VOA vial 1-4 oz glass, wide mouth	cool to 4˚ C, MeOH in VOA	14 days
Tetrachloroethene	8260B	50	50	1-40 ml VOA vial 1-4 oz glass, wide mouth	cool to 4˚ C, MeOH in VOA	14 days
Toluene	8260B	50	100	1-40 ml VOA vial 1-4 oz glass, wide mouth	cool to 4˚ C, MeOH in VOA	14 days

TABLE 3
QUALITY ASSURANCE PROJECT PLAN
SAMPLE CONTAINERS, PRESERVATION, HOLDING TIMES, METHODS, AND DETECTION LIMITS
FORMER GENERAL MOTORS POWERTRAIN PROPERTY
LIVONIA, MICHIGAN

Parameter	Analytical Method[1]	Merit Reporting Detection Limit	Target Detection Limit[2]	Sample Container and Volume[3]	Preservation[4]	Maximum Holding Time[5]
Trichloroethene	8260B	50	50	1-40 ml VOA vial 1-4 oz glass, wide mouth	cool to 4˚ C, MeOH in VOA	14 days
Vinyl chloride	8260B [6]	40 [6]	40	1-40 ml VOA vial 1-4 oz glass, wide mouth	cool to 4˚ C, MeOH in VOA	14 days
Xylenes, total	8260B	150	150	1-40 ml VOA vial 1-4 oz glass, wide mouth	cool to 4˚ C, MeOH in VOA	14 days
Polycyclic Aromatic Hydrocarbons (PAHs)						
Acenaphthene	8270C	330	330	1- 4 oz. glass, wide mouth	cool to 4˚ C	14 days to extraction 40 days to analysis
Fluoranthene	8270C	330	330	1- 4 oz. glass, wide mouth	cool to 4˚ C	14 days to extraction 40 days to analysis
Fluorene	8270C	330	330	1- 4 oz. glass, wide mouth	cool to 4˚ C	14 days to extraction 40 days to analysis
Phenanthrene	8270C	330	330	1- 4 oz. glass, wide mouth	cool to 4˚ C	14 days to extraction 40 days to analysis
Acenaphthylene	8270C	330	330	2-1 liter amber glass	cool to 4˚ C	14 days to extraction 40 days to analysis
Anthracene	8270C	330	330	2-1 liter amber glass	cool to 4˚ C	14 days to extraction 40 days to analysis
Benzo(a)anthracene	8270C	330	330	2-1 liter amber glass	cool to 4˚ C	14 days to extraction 40 days to analysis
Benzo(a)pyrene	8270C	330	330	2-1 liter amber glass	cool to 4˚ C	14 days to extraction 40 days to analysis
Benzo(b)fluoranthene	8270C	330	330	2-1 liter amber glass	cool to 4˚ C	14 days to extraction 40 days to analysis
Benzo(k)fluoranthene	8270C	330	330	2-1 liter amber glass	cool to 4˚ C	14 days to extraction 40 days to analysis
Benzo(ghi)perylene	8270C	330	330	2-1 liter amber glass	cool to 4˚ C	14 days to extraction 40 days to analysis
Chrysene	8270C	330	330	2-1 liter amber glass	cool to 4˚ C	14 days to extraction 40 days to analysis
Dibenzo(ah)anthracene	8270C	330	330	2-1 liter amber glass	cool to 4˚ C	14 days to extraction 40 days to analysis
Indeno(1,2,3-cd)pyrene	8270C	330	330	2-1 liter amber glass	cool to 4˚ C	14 days to extraction 40 days to analysis
Naphthalene	8270C	330	330	2-1 liter amber glass	cool to 4˚ C	14 days to extraction 40 days to analysis
Pyrene	8270C	330	330	2-1 liter amber glass	cool to 4˚ C	14 days to extraction 40 days to analysis
Polychlorinated Biphenyls (PCBs)						
Total PCBs	8082A	330	330	1- 4 oz. glass, wide mouth	cool to 4˚ C	14 days to extraction 40 days to analysis

TABLE 3
QUALITY ASSURANCE PROJECT PLAN
SAMPLE CONTAINERS, PRESERVATION, HOLDING TIMES, METHODS, AND DETECTION LIMITS
FORMER GENERAL MOTORS POWERTRAIN PROPERTY
LIVONIA, MICHIGAN

Parameter	Analytical Method[1]	Merit Reporting Detection Limit	Target Detection Limit[2]	Sample Container and Volume[3]	Preservation[4]	Maximum Holding Time[5]
Metals						
Mercury	7471A	50	50	1- 4 oz. glass, wide mouth	cool to 4˚ C	28 days
Arsenic	6020 [8]	100	100	1- 4 oz. glass, wide mouth	cool to 4˚ C	6 months
Chromium (total)	6020 [8]	2,000	2,000	1- 4 oz. glass, wide mouth	cool to 4˚ C	6 months
Copper	6020 [8]	1,000	1,000	1- 4 oz. glass, wide mouth	cool to 4˚ C	6 months
Barium	6020 [8]	1,000	1,000	1- 4 oz. glass, wide mouth	cool to 4˚ C	6 months
Cadmium	6020 [8]	200	200	1- 4 oz. glass, wide mouth	cool to 4˚ C	6 months
Lead	6020 [8]	1,000	1,000	1- 4 oz. glass, wide mouth	cool to 4˚ C	6 months
Selenium	6020 [8]	200	200	1- 4 oz. glass, wide mouth	cool to 4˚ C	6 months
Silver	6020 [8]	100	100	1- 4 oz. glass, wide mouth	cool to 4˚ C	6 months
Zinc	6020 [8]	1,000	1,000	1- 4 oz. glass, wide mouth	cool to 4˚ C	6 months
Inorganics						
Cyanide	335.4/4500-CN-E	100	100	1- 4 oz. glass, wide mouth	cool to 4˚ C	14 days

Notes:
(1) United States Environmental Protection Agency. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, Edition 3 (SW-846), Office of Solid Waste & Emergency Response.
(2) 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.
(3) Sample container will be new, precleaned, and certified by manufacturer.
(4) Whenever possible, pre-preserved bottles will be used.
(5) Holding time measured from date of collection.
(6) Lab will need to perform Selective Ion Monitoring (SIMs) runs or will need to report down to the method detection limit to achieve target detection limit.
(7) Lab will need to subcontract a different lab to achieve required detection limits.
(8) If the lab uses Method 6020, a post digest spike will be run if the matrix spike/matrix spike duplicate exceeds acceptance limits.
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
QUALITY ASSURANCE PROJECT PLAN
ANALYTICAL QUALITY CONTROL LIMITS
FORMER GENERAL MOTORS POWERTRAIN PROPERTY
LIVONIA, MICHIGAN

			Water (µg/L)				Soil (µg/kg)			
			RDL	Accuracy		Precision	RDL	Accuracy		Precision
Compound	EPA Method	SW-846 Method	µg/L	LCL %	UCL %	RPD %	µg/L	LCL %	UCL %	RPD %
Volatiles										
Acetone	624	8260B	20	28.1%	121.9%	20	750	13.2%	200.8%	20
Benzene	624	8260B	1.0	73.7%	127.0%	20	50	66.0%	142.0%	20
Chlorobenzene	624	8260B	1.0	75.0%	130.0%	20	50	60.0%	133.0%	20
1,2-Dichlorobenzene	624	8260B	1.0	66.8%	120.0%	20	50	72.4%	120.0%	20
1,2-Dichloroethane	624	8260B	1.0	74.3%	124.3%	20	50	71.3%	122.5%	20
cis-1,2-Dichloroethene	624	8260B	1.0	80.0%	120.5%	20	50	68.9%	122.8%	20
1,2-Dichloropropane	624	8260B	1.0	80.0%	120.0%	20	50	78.3%	122.0%	20
Ethylbenzene	624	8260B	1.0	78.9%	120.0%	20	50	80.0%	120.0%	20
Methyl tert-butyl ether	624	8260B	5.0	74.6%	136.5%	20	250	58.5%	136.9%	20
Methylene Chloride	624	8260B	5.0	57.7%	150.1%	20	250	45.3%	136.7%	20
Styrene	624	8260B	1.0	76.0%	120.0%	20	50	78.8%	120.1%	20
Naphthalene	624	8260B	5.0	80.0%	120.0%	20				
Tetrachloroethene	624	8260B	1.0	70.2%	122.9%	20	50	72.2%	129.1%	20
Toluene	624	8260B	1.0	71.0%	127.6%	20	50	59.0%	139.0%	20
Trichloroethene	624	8260B	1.0	71.0%	121.2%	20	50	62.0%	137.0%	20
Vinyl Chloride	624	8260B	1.0	54.3%	120.7%	20	100	33.1%	126.3%	20
m&p-Xylene	624	8260B	1.0	72.1%	120.0%	20	50	77.8%	127.2%	20
o-Xylene	624	8260B	1.0	80.0%	120.0%	20	50	80.0%	121.2%	20
Xylenes (total)	624	8260B	3.0	72.1%	120.0%	20	150	77.8%	127.2%	20
Polycyclic Aromatic Hydrocarbons										
Acenaphthene	625	8270C	5.0	36.9%	124.4%	20	330	36.9%	124.4%	20
Acenaphthylene	625	8270C	5.0	35.4%	127.7%	20	330	35.4%	127.7%	20
Anthracene	625	8270C	5.0	32.3%	142.4%	20	330	32.3%	142.4%	20
Benzo(a)anthracene	625	8270C	1.0	36.7%	134.7%	20	330	36.7%	134.7%	20
Benzo(a)pyrene	625	8270C	1.0	39.6%	131.8%	20	330	39.6%	131.8%	20
Benzo(b)fluoranthene	625	8270C	1.0	29.0%	152.7%	20	330	29.0%	152.7%	20
Benzo(g,h,i)perylene	625	8270C	1.0	45.2%	130.7%	20	330	45.2%	130.7%	20
Benzo(k)fluoranthene	625	8270C	1.0	29.8%	136.0%	20	330	29.8%	136.0%	20
Chrysene	625	8270C	1.0	38.7%	137.1%	20	330	38.7%	137.1%	20
Dibenzo(a,h)anthracene	625	8270C	2.0	45.3%	130.8%	20	330	45.3%	130.8%	20
Fluoranthene	625	8270C	1.0	35.5%	144.5%	20	330	35.5%	144.5%	20
Fluorene	625	8270C	5.0	37.8%	127.8%	20	330	37.8%	127.8%	20
Indeno(1,2,3-cd)pyrene	625	8270C	2.0	39.2%	137.4%	20	330	39.2%	137.4%	20
Naphthalene	625	8270C	5.0	38.2%	120.0%	20	330	38.2%	120.0%	20
Phenanthrene	625	8270C	2.0	36.4%	143.0%	20	330	36.4%	143.0%	20
Pyrene	625	8270C	5.0	35.4%	138.1%	20	330	35.4%	138.1%	20
PCBs (Aroclor-Specific)										
Aroclor-1016	N/A					20	330	52.9%	123.7%	20
Aroclor-1242						20	330	59.1%	123.7%	20
Aroclor-1248						20	330	59.1%	123.7%	20
Aroclor-1254						20	330	59.1%	123.7%	20
Aroclor-1260						20	330	59.1%	123.7%	20
Total PCBs						20	NA	59.1%	123.7%	20

TABLE 4
QUALITY ASSURANCE PROJECT PLAN
ANALYTICAL QUALITY CONTROL LIMITS
FORMER GENERAL MOTORS POWERTRAIN PROPERTY
LIVONIA, MICHIGAN

Compound	EPA Method	SW-846 Method	Water (µg/L) RDL µg/L	Water (µg/L) Accuracy LCL %	Water (µg/L) Accuracy UCL %	Water (µg/L) Precision RPD %	Soil (µg/kg) RDL µg/L	Soil (µg/kg) Accuracy LCL %	Soil (µg/kg) Accuracy UCL %	Soil (µg/kg) Precision RPD %
Metals										
Arsenic	200.8	6020	1.0	85%	115%	20	100	85%	115%	20
Barium	200.8	6020	5.0	85%	115%	20	1000	85%	115%	20
Cadmium	200.8	6020	0.5	85%	115%	20	200	85%	115%	20
Chromium	200.8	6020	5.0	85%	115%	20	2000	85%	115%	20
Copper	200.8	6020	5.0	85%	115%	20	1000	85%	115%	20
Lead-Total (Water)	200.8	6020	3.0	85%	115%	20	1000	85%	115%	20
Lead - Fine	N/A	6020	NA	N/A	N/A	N/A	1000	85%	115%	20
Lead - Course	N/A	6020	NA	N/A	N/A	N/A	1000	85%	115%	20
Mercury	245.1	7471	0.1	85%	115%	20	50	85%	115%	20
Nickel	200.8	6020	5.0	85%	115%	20	1000	85%	115%	20
Selenium	200.8	6020	5.0	85%	115%	20	200	85%	115%	20
Silver	200.8	6020	0.2	85%	115%	20	100	85%	115%	20
Zinc	200.8	6020	5.0	85%	115%	20	1000	85%	115%	20
Hexavalent Chromium										
Hexavalent Chromium		7196	10	90.0%	110%	15	1000	90.0%	110%	15
Conventional										
Nitrate	300.00		100	90.0%	110%	15				
Nitrite	300.00		100	90.0%	110%	15				
Sulfate	300.00		1,000	90.0%	110%	15				
Chloride	300.00		1,000	90.0%	110%	15				
Hardness	2340 Std Mth		1,000	90.0%	110%	15	N/A			
Alkalinity	2320B Std Mth		1,000	90.0%	110%	15				
Total Dissolved Solids	2540C Std Mth		1,000	90.0%	110%	15				
Total Organic Carbon	EPA 415.1		1,000	80.0%	120%	20				
Ammonia Nitrogen	4500-NH3D		20	90.0%	110%	20				

Notes:
LCL Lower control limit.
NS Not specified in the analytical method. Laboratory derived MDLs (adjusted for dilution and percent solids) will be used.
NA Not applicable or Not available.
RPD Relative Percent Deviation.
UCL Upper control limit.
µg/L Micro-grams per liter.
µg/kg Micro-grams per kilogram.

* To meet the reporting limit of 1000 ug/kg Encore sampling is required

1. Analysis for groundwater pH, groundwater conductivity, and oxidation/reduction potential will be analyzed using field methods only.

2. Target detection limits as defined in MDEQ Environmental Response Division Operational Memorandum #6, Revision 6 (January, 2001). In some cases, due to sample matrix interferences, the laboratory may use other RDLs.

3. Target detection limits as defined in MDEQ Environmental Response Division Operational Memorandum #2, Revision 1 (October 22, 2004) additional.

4. The target detection limits for soil / sediment are based on high level for volatile organics.

LEGEND

APPROXIMATE PROPERTY BOUNDARY

NOTES

1. AERIAL PHOTOGRAPH TAKEN FROM GOOGLE EARTH DATED 5-10-2010.
2. COORDINATES 42° 22' 26.44"N 83° 19'46.26"W

N
W E
S

0 300' 600'

SCALE" 1" = 300'

HALEY & ALDRICH

GMPT - LIVONIA SITE ID: 1195
LIVONIA, MICHIGAN

SITE PLAN

SCALE: 1" = 300'
DECEMBER 2011

FIGURE 1

Drawing Name: G:\37290-GMPTLivonia\009\CAD\37290-009-02.dwg Plot Date: December 16, 2011 Layout: Site Plan (1)
Operator Name: LUCIDO, SAM

APPENDIX A

Laboratory Standard Operating Procedures and Quality Assurance – Merit Laboratories (On CD-ROM)

STANDARD OPERATING PROCEDURE

SEPARATORY FUNNEL LIQUID-LIQUID EXTRACTION FOR PCB/PESTICIDES USEPA METHOD 3510C

APPROVALS:

Barbara Richardson 6/3/11

QA Officer Date

Maya Mushaben 6/3/11

Technical Director Date

Number	Description of Change	Date
001-009	Previous changes were not documented	
010	Updated to comply with DoD QSM and ISO 17025 standards.	6/3/11
011		
012		
013		
014		
015		
016		
017		
018		
018		
020		

1.0 SCOPE AND APPLICATION

This SOP is a procedure for isolating organic compounds from aqueous samples. This SOP is applicable to the isolation and concentration of water-insoluble and slightly water-soluble organics in preparation for a variety of chromatographic procedures, specifically polychlorinated biphenyls (PCBs) and Pesticides. 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. This SOP is not applicable for OHIO VAP samples.

2.0 SUMMARY OF METHOD

A measured volume of sample, up to 1 liter, at a pH 5-9, is extracted with methylene chloride using a separatory funnel. The extract is concentrated and exchanged into hexane solvent, which is also compatible with the cleanup procedures utilized for PCBs. Clean glassware and matrix cleanup procedures are used to obtain the optimum analytical chromatograms.

3.0 INTERFERENCES

The decomposition of some analytes has been demonstrated under basic extraction conditions. Organochlorine pesticides may de-chlorinate. Degradation of PCBs, as well as more complex matrices (e.g., oil, tar, sulfur, etc.), can interfere with the “clarity” of the chromatograms.

4.0 APPARATUS AND MATERIALS

Separatory funnel - 2-liter, with polytetrafluoroethylene (PTFE) stopcock.

Evaporation tubes, 250-ml volume, Zymark with end point of 0.5 ml.

Zymark Turbo Vap II Concentration Station with temperature control water bath.

Vials – 4 ml, glass with PTFE-lined screw caps.

pH indicator paper - pH range including the desired extraction pH.

Glass beakers, 250 ml.

Glass funnel.

Filter paper, coarse grade.

Adhesive labels.

Syringe - 5-mL NIST certified.

Graduated cylinder - 1-liter.

250 mL Erlenmeyer flasks.

Pipettors.

Automated Shakers.

5.0 REAGENTS

Note: Reagent grade chemicals must be used in all tests. Unless otherwise indicated, it is intended that all reagents must conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades can 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 must be stored in glass to prevent the leaching of contaminants from plastic containers.

Deionized (DI) water.

Sodium sulfate (granular, anhydrous), Na_2SO_4.

Sulfuric acid, concentrated.

Extraction/exchange solvents - All solvents must be pesticide quality or equivalent.

- Methylene chloride, CH_2Cl_2, boiling point 49°C
- Hexane, C_6H_{14}, boiling point 68.7°C
- Ethyl ether (6%)
- Nonchromix, used when contamination is detected.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

All aqueous samples for the analysis of Pesticides and PCBs must be stored in Amber glass containers only. Approximately 1L volume of sample is needed for extraction. Refrigerate at $4^o \pm 2°$ C. The holding time for samples is 7 days from collection until extraction and 40 days until analysis.

Note: If samples contain significantly less volume then 1L, Quality Assurance Manager & client need to be notified. Higher detection limits will be applied to low volume extracts.

7.0 PROCEDURE

1. All glassware must be kept immaculate. Glassware must be cleaned as soon as possible after extraction. Glassware washing procedures are found in SOP # GEN-002.

2. Mark the level of sample on the outside of the bottle. Pour the sample into the 2 liter separatory funnel. After step 5, 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.

3. Check the pH of the sample with wide-range pH paper and adjust the pH, if necessary, to a pH between 5 – 9. Do not place pH paper into sample container.

4. Pipette 1.0 ml of the surrogate spiking solution into the funnel and swirl the sample. For matrix spike samples and LCS, add 1ml surrogate and 1 ml matrix spike standard.

5. Add 60 ml of methylene chloride into the sample bottle to rinse it and transfer this rinse solvent to the separatory funnel.

6. Venting prior to the 3 minute shake: Place cap on funnel, tip up/down five to 10 times, release vent into paper towel (to prevent cross contamination). Initial venting must be done immediately after the separatory funnel has been sealed and shaken once. Seal the separatory funnel and shake vigorously for 3 minutes on a horizontal placement at a motor speed 70 in accordance with Table 1 shake program. The separatory funnel must 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. *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 can include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods.*

7. Drain the extract through a filter filled with approximately 10g of Na_2SO_4 into a 250-ml glass Zymark evaporation tube.

8. Repeat step 6 twice more with 60 ml methylene chloride each in accordance with Table 1 shake program.

9. 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 48°C ± 2°C and 29 psi. Allow the sample to evaporate down to 0.5 ml methylene chloride or until the evaporation station signals completion.

10. Add 30 ml hexane and evaporate down to 0.5 ml final volume under the same conditions as above.

11. 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 compressed air to evaporate to the 1 ml mark.

12. Final 1 ml adjustment: if the transfer is greater than 1 ml, use compressed air 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 than 1 ml, add final extract solvent to the meniscus.

13. The vials are calibrated per Lot # of vials with a NIST traceable syringe. One vial is filled with exactly 1 ml for comparison.

14. Follow with clean-up procedures as appropriate for PCB analysis. See Document # ORL-002 for details.

- Sulfuric Acid Clean-up
- Sulfur Clean-up
- Alumina Column Clean-up.

8.0 QUALITY CONTROL

Samples are extracted in batches of 20 samples or less. For every batch there must be an blank, LCS, MS, and MSD/DUP depending on the client's request. All the reagent blanks, matrix spikes, or replicate samples must 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.

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 0.03 mg/l.

The MS/MSD and LCS spikes will contain a mixture of Aroclor 1016/1260. MS/MSD spike must 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 0.05 ppm.

New lot blanks are analyzed to ensure the purity of the materials and reagents.

Note: The working standards are prepared every six months or when evidence of bias or trends are observed to show that the standards need to be replaced.

For DoD projects the MS/MSD and LCS spike solution must contain ALL target compounds.

All pertinent information is entered into an extraction bench sheet (Figure 1).

9.0 METHOD PERFORMANCE

Laboratory specific data are provided in Document #'s ORL-001 and ORL-002. The MDLs and PQLs can be found in Merit's LIMS system are from the most recent detection limit studies.

10.0 EQUIPMENT MAINTENANCE AND TROUBLESHOOTING

Each instrument is assigned a maintenance logbook. All maintenance performed on the instrument must be recorded. Additionally, any modifications to the instrument settings shall be noted in the specific instrument logbook. Maintenance procedures provided in the equipment manual shall be followed.

11.0 SAFETY

Eye protection and gloves must be worn while performing the analyses. Every laboratory area has eyewash, emergency shower, and fire extinguisher. The metals lab also has dust masks available for use with dust samples. The air system throughout 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. A reference file of material safety data sheets (MSDSs) is available to all personnel.

Specific attention be paid (but not limited) to:

- Sodium sulfate is mildly toxic by ingestion, not considered an explosion hazard, and oxides of sulfur and sodium may form when heated to decomposition. Keep in a tightly closed container, stored in a cool, dry, ventilated area. Protect against physical damage. Isolate from incompatible substances. Containers of this material may be hazardous when empty since they retain product residues (dust, solids); observe all warnings and precautions listed for the product.

- Methylene chloride is harmful if swallowed, inhaled or absorbed through skin. Methylene chloride affects central nervous system, liver, cardiovascular system, and blood. Also, it can cause irritation to skin, eyes, and respiratory tract. Risk of cancer depends on level and duration of exposure. Vapor may form flammable mixture in atmosphere that contains a high percentage of oxygen. Sealed containers may rupture when heated. Emits highly toxic fumes of phosgene when heated to decomposition. Decomposes in a flame or hot surface to form toxic gas phosgene and corrosive mists of hydrochloric acid. Carbon dioxide and carbon monoxide may form when heated to decomposition.

- Hexane is extremely flammable liquid and vapor, causes irritation to skin, eyes, and respiratory tract, and overexposure may cause lightheadedness, nausea, headache, and blurred vision. Above flash point, vapor-air mixtures are explosive within flammable limits. Contact with oxidizing materials may cause extremely violent combustion. Sensitive to static discharge.

12.0 WASTE DISPOSAL AND POLLUTION PREVENTION

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

13.0 DEFINITIONS

Sample Batch: samples of the same or similar matrix; for this method, a sample batch consists of 20 samples or less.

Method Blank: an analyte-free matrix to which all reagents are added in the same volumes or proportions as used in the sample processing. The method blank is carried through the complete sample preparation and analytical procedure. The method blank is used to document contamination resulting from the analytical process.

Laboratory Control Sample (LCS) (also known as Laboratory Fortified Blank, Spiked Blank, or QC Check Sample): a Sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes. It is generally used to establish intra-laboratory or analyst-specific precision and bias or to assess the performance of all or a portion of the measurement system.

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

Matrix Spike Duplicate (also known as Spiked Sample or Fortified Sample Duplicate): a second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

Surrogate: An organic compound which is similar to the target analytes in chemical composition and behavior in the analytical process, but which is not normally found in environmental samples. Its use is to monitor the performance of the extraction, cleanup (as needed), the analytical system, and the effectiveness of the method.

14.0 REFERENCES

Department of Defense, *Quality Systems Manual for Environmental Laboratories* (DoD QSM), DoD Environmental Data Quality Workgroup, Department of Navy, Lead Service, Based on NELAC Voted Revision 5 June 2003, Version 4.1, April 22, 2009.

USEPA, SW-846, Revision 3; Method 3510C.

Table 1. Extraction Funnel Shake Program

Stage	Solvent Volume	pH	Funnel Position	Shaker Time	Shaker Intensity
1a	60 ml	5-9	Vertical/open	5 to 10 times	to vent
1b			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

(1) Solvent – Methylene chloride.

(2) *Funnel Position* indicates whether the funnel is horizontally or vertically situated in the automatic shaker and whether the stopcock is open or closed.

(3) *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).

(4) *Shaker Intensity* is the dial setting on the automatic shaker unit. A higher number indicates a more vigorous shake.

Figure 1: Extraction Bench Sheet

$MeCl_2$_____		PCB/Pesticide Extraction											
Hexane_____									Date _____				
Na_2SO_4 _____		Method 3510C							Time Procedure Started _____				
H_2SO_4_____									Time Procedure Ended _____				
SSD# _____ Ethyl Ether _____									Prep Batch ID#_____				
PCB MS ID#_____Pest MS ID#_____													

#	Merit #	Matrix	Sample Vol (ml)	Solvent	Solvent Vol (ml)	Final Vol (ml)	SSD Vol (ml)	MS Vol (ml)	Analyst	Alumina Cleanup	Dioxin Cleanup	Sep Funnel ID	Notes
Initial Q.C.	BLANK	D.I.		$MeCl_2$/Hex	180	1	1						
	LCS	D.I.						1					
	LCSD	D.I.						1					
	MS												
	MSD												
1													
2													
3													
4													
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18													
19													
20													
	Reviewed by: _____		On: _____						Prepared by: Merit Laboratories, Inc.				

STANDARD OPERATING PROCEDURE

ULTRASONIC EXTRACTION FOR PCBS/PESTICIDES USEPA METHOD 3550B

APPROVALS:

6/3/11

QA Officer — Date

6/3/11

Technical Director — Date

Number	Description of Change	Date
001-008	Previous changes were not documented	
009	Updated to comply with DoD QSM and ISO 17025 standards.	6/3/11
010		
011		
012		
013		
014		
015		
016		
017		
018		
019		

1.0 SCOPE AND APPLICATION

This SOP is used for extracting polychlorinated biphenyls (PCBs) and pesticide 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. 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. This SOP is not applicable for OHIO VAP samples.

2.0 SUMMARY OF METHOD

For most samples, 1g - 30g of sample (depending on the matrix; typically 0.3g 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. The extract is separated from the sample and concentrated. Clean glassware is used to obtain the optimum analytical chromatograms.

3.0 INTERFERENCES

The decomposition of some analytes has been demonstrated under basic extraction conditions. Organochlorine pesticides may de-chlorinate. 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

Apparatus for grinding/crushing solid waste samples (i.e. drill press or hammer).

Ultrasonic device – Branson Sonifier, Model 450.

Ultrasonic Disrupter - power wattage of 300 watts, with pulsing.

- 3/4" horn
- Sonabox – (Ultrasonics #432B).

Zymark Evaporation Station.

Evaporation tubes.

Water bath - Heated, capable of temperature control (± 5ºC).

Balance - capable of accurately weighing to the nearest 0.01 g.

Vials – 4 ml, with polytetrafluoroethylene (PTFE)-lined screw caps.

Glass scintillation vials - 20-mL, with PTFE-lined screw caps.

Tongue depressors, disposable.

Drying column - 50ml Pyrex chromatographic column with Pyrex glass wool at bottom.

Syringe - 5-mL NIST Certified.

Beakers – 250 ml.

Glass funnel.

Filter paper, coarse grade.

Adhesive labels.

250 mL Erlenmeyer flasks.

Pipettors.

5.0 REAGENTS

Note: Reagent grade chemicals must be used in all tests. Unless otherwise indicated, it is intended that all reagents must conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades must 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 must be stored in glass to prevent the leaching of contaminants from plastic containers.

Deionized (DI) water.

Sodium sulfate (granular, anhydrous), Na_2SO_4.

Extraction - All solvents must be pesticide quality or equivalent.

- Hexane, C_6H_{14}, boiling point 68.7°C
- Ethyl Ether (6%)
- Nonchromix used when contamination is detected.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

All soil samples for the analysis of Pesticides and PCBs must be stored in non-preserved glass containers only. Approximately 0.3g to 30g (depending on the matrix) of sample is needed for extraction. Refrigerate at 4° ± 2°C. Holding Time for solid samples is 14 days from collection to extraction and 40 days after extraction until analysis.

7.0 PROCEDURE

1. All glassware must be kept immaculate. Glassware must be cleaned as soon as possible after extraction. Glassware washing procedures are found in SOP #GEN-002.

2. The extraction device has a minimum of 300 watts of power and is equipped with ¾" size disrupter horns.

   - 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.
   - Samples are prepared by thorough mixing with sodium sulfate so that it forms a free-flowing solid prior to the addition of the solvent.
   - Three extractions are performed with 60ml hexane solvent for 3 minutes each.
   - 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.
   - 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 ensure that the placement of the horn is correct.

3. Sample handling

   - 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.
   - 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.
   - Solid waste samples amenable to grinding - Drill or hammer until uniform matrix is achieved.
   - 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.

4. Extraction method

- Weigh approximately 0.3 - 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.

- 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 can be added. After addition of sodium sulfate, the sample must be free flowing.

- Add 1.0 ml of the surrogate standard solution to all samples, spiked samples, QC samples, and blanks.

- For the sample in each batch selected for spiking (*i.e.* LCS, MS, MSD), add 1.0 ml of the matrix spiking solution.

- Add 60 ml of Hexane to the beaker.

- 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.

- 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).

- Decant through a conical gravity filter (Whatman No. 41 filter paper or equivalent) and sodium sulfate to catch any excess water into an evaporation tube.

- Repeat the extraction two 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.

5. Evaporation method

- Place the concentrator tube in the TurboVap Evaporation Station, that has the water bath @ 48ºC ± 2°C, 29 psi, until 0.5 ml final volume.

- Transfer the sample extract to a 4 ml vial rinse evaporation tube with 0.5 ml Hexane. Adjust up to 1 ml final volume.

- Final 1 ml adjustment: if the transfer is greater than 1 ml, use the compressed air 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 than 1 ml, add final extract solvent to the meniscus.
    - The vials are calibrated per Lot # of vials with a NIST traceable syringe. One vial is filled with exactly 1 ml for comparison.
- Follow with clean–up procedures as appropriate for PCB analysis. See Document # ORL-002 for details.
    - Sulfuric Acid Clean-up
    - Sulfur Clean-up
    - Alumina Column Clean-up.

8.0 QUALITY CONTROL

Samples are extracted in batches of 20 samples or less. For every batch there must be an blank, LCS, MS, and MSD/DUP depending on the client's request. All the reagent blanks, matrix spikes, or replicate samples must 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.

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 0.03 mg/l.

The MS/MSD and LCS spikes will contain a mixture of Aroclor 1016/1260. MS/MSD spike must 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 0.05 ppm.

The MS/MSD and LCS spikes contain a mixture of Pesticides. This spike must be prepared at a concentration at or below the medium level of the Pesticide curve. The MS/MSD and LCS standard is prepared by the GC analyst at a concentration of 0.1mg/l.

New lot blanks are analyzed to ensure the purity of the materials and reagents.

For DoD projects, the MS/MSD and LCS spike solution must contain ALL target compounds.

All pertinent information is entered into an extraction bench sheet (Figure 1).

Note: The working standards are prepared every six months or when evidence of bias or trends are observed to show that the standards need to be replaced.

9.0 METHOD PERFORMANCE

Laboratory specific data are provided in SOPs #0708081 and #0708082. The MDLs and PQLs can be found in Merit's LIMS system are from the most recent detection limit studies.

10.0 EQUIPMENT MAINTENANCE AND TROUBLESHOOTING

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. When cavities are observed, horns are cleaned and/or replaced.

Each instrument is assigned a maintenance logbook. All maintenance performed on the instrument must be recorded. Additionally, any modifications to the instrument settings shall be noted in the specific instrument logbook. Maintenance procedures provided in the equipment manual shall be followed.

11.0 SAFETY

Eye protection and gloves must be worn while performing the analyses. Every laboratory area has eyewash, emergency shower, and fire extinguisher. The metals lab also has dust masks available for use with dust samples. The air system throughout 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. A reference file of material safety data sheets (MSDSs) is available to all personnel.

Specific attention be paid (but not limited) to:

- Sodium sulfate is mildly toxic by ingestion, not considered an explosion hazard, and oxides of sulfur and sodium may form when heated to decomposition. Keep in a tightly closed container, stored in a cool, dry, ventilated area. Protect against physical damage. Isolate from incompatible substances. Containers of this material may be hazardous when empty since they retain product residues (dust, solids); observe all warnings and precautions listed for the product.

- Hexane is extremely flammable liquid and vapor, causes irritation to skin, eyes, and respiratory tract, and overexposure may cause lightheadedness, nausea, headache, and blurred vision. Above flash point, vapor-air mixtures are explosive within flammable limits. Contact with oxidizing materials may cause extremely violent combustion. Sensitive to static discharge.

12.0 WASTE DISPOSAL AND POLLUTION PREVENTION

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

13.0 DEFINITIONS

Sample Batch: samples of the same or similar matrix; for this method, a sample batch consists of 20 samples or less.

Method Blank: an analyte-free matrix to which all reagents are added in the same volumes or proportions as used in the sample processing. The method blank is carried through the complete sample preparation and analytical procedure. The method blank is used to document contamination resulting from the analytical process.

Laboratory Control Sample (LCS) (also known as Laboratory Fortified Blank, Spiked Blank, or QC Check Sample): a Sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes. It is generally used to establish intra-laboratory or analyst-specific precision and bias or to assess the performance of all or a portion of the measurement system.

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

Matrix Spike Duplicate (also known as Spiked Sample or Fortified Sample Duplicate): a second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

Surrogate: an organic compound which is similar to the target analytes in chemical composition and behavior in the analytical process, but which is not normally found in environmental samples. Its use is to monitor the performance of the extraction, cleanup (as needed), the analytical system, and the effectiveness of the method.

14.0 REFERENCES

Department of Defense, *Quality Systems Manual for Environmental Laboratories* (DoD QSM), DoD Environmental Data Quality Workgroup, Department of Navy, Lead Service, Based on NELAC Voted Revision 5

June 2003, Version 4.1, April 22, 2009.

USEPA, SW-846, Revision 3, Method 3550B.

Figure 1: PCB/Pesticide Extraction Bench Sheet

Hexane_____			PCB/Pesticide Extraction									
Ethyl Ether_____									Date _____			
Na_2SO_4 _____			Method 3550B						Time Procedure Started _____			
H_2SO_4_____									Time Procedure Ended _____			
SSD# _____									Prep Batch ID#_____			
PCB MS ID#_____Pest MS ID#_____												
#	Merit #	Matrix	Sample Wt. (g)	Solvent	Solvent Vol (ml)	Final Vol (ml)	SSD Vol (ml)	MS Vol (ml)	Analyst	Alumina Cleanup	Dioxin Cleanup	Notes
Initial Q.C.	BLANK			Hexane	180	1	1					
	LCS							1				
	LCSD							1				
	MS											
	MSD											
1												
2												
3												
4												
5												
6												
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	Reviewed by: _____		On: _____						Prepared by: Merit Laboratories, Inc.			

STANDARD OPERATING PROCEDURE

ULTRASONIC EXTRACTION FOR BNAS/PNAS/DRO EPA METHOD 3550B

APPROVALS:

Barbara Richardson 6/9/11

QA Officer Date

Maya Mushahwar 6/9/11

Technical Director Date

Number	Description of Change	Date
001-005	Previous changes were not documented	
006	Updated to comply with DoD QSM and ISO 17025 standards.	6/9/11
007		
008		
010		
011		
012		
013		
014		
015		
016		
017		

1.0 SCOPE AND APPLICATION

This SOP is used for extracting nonvolatile and semivolatile base/neutral/acid (BNA), polynuclear aromatic hydrocarbon (PNA) and diesel range organics (DRO) organic compounds from solids such as soils, sludges, and wastes. The ultrasonic process ensures intimate contact of the sample matrix with the extraction solvent. 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. This SOP is not applicable for OHIO VAP samples.

2.0 SUMMARY OF METHOD

For most of samples, 0.5g - 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. The extract is separated from the sample and concentrated. Clean glassware is used to obtain the optimum analytical chromatograms.

3.0 INTERFERENCES

The decomposition of some analytes has been demonstrated under basic extraction conditions. Organochlorine pesticides may de-chlorinate. Degradation of sample matrix (i.e. oil, tar, sulfur, etc.), can interfere with the “clarity” of the chromatograms.

4.0 APPARATUS AND MATERIALS

Apparatus for grinding/crushing solid waste samples (i.e. drill press or hammer).

Ultrasonic device - Branson Sonifier, Model 450.

Ultrasonic Disrupter - power wattage of 300 watts, with pulsing.

- 3/4" horn
- Sonabox - (Ultrasonics #432B).

Zymark Evaporation Station.

Evaporation tubes.

Water bath - Heated, capable of temperature control (± 5ºC).

Balance - capable of accurately weighing to the nearest 0.01 g.

Vials - 4 ml, with polytetrafluoroethylene (PTFE)-lined screw caps.

Glass scintillation vials - 20-mL, with PTFE-lined screw caps.

Tongue depressors, disposable.

Beakers - 250ml.

Glass funnel.

Filter paper, coarse grade.

Adhesive labels.

Syringe - 5-mL NIST certified.

250mL Erlenmeyer flasks.

Pipettors.

5.0 REAGENTS

Note: Reagent grade chemicals must be used in all tests. Unless otherwise indicated, it is intended that all reagents must conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades can 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 must be stored in glass to prevent the leaching of contaminants from plastic containers.

Sodium sulfate (granular, anhydrous), Na_2SO_4.

Extraction - All solvents must be pesticide quality or equivalent.

- Methylene Chloride, CH_2Cl_2.
- Nonchromix, used when contamination is detected.

Surrogate and matrix spiking solutions are prepared as listed in Table 2. The detailed list of compounds for each stock mixture is given in Table 1.

Deionized (DI) Water.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

All soil samples for the analysis of BNAs/PNAs/DRO are stored in non-preserved glass containers only. Approximately 0.5 to 30 g (depending on the matrix) of sample is needed for extraction. Oils are weighed out to 0.5 ml. Refrigerate at 4º±2°C. Holding Time for solid samples is 14 days from collection to extraction and 40 days after extraction until analysis.

7.0 PROCEDURE

1. All glassware must be kept immaculate. Glassware must be cleaned as soon as possible after extraction. Glassware washing procedures are found in SOP # GEN-002.

2. The extraction device has a minimum of 300 watts of power and is equipped with ¾" size disrupter horns.

   - 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.

   - Samples are prepared by thorough mixing with sodium sulfate so that it forms a free-flowing solid prior to the addition of the solvent.

   - Three extractions are performed with 60ml of Methylene Chloride solvent for 3 minutes each.

   - 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.

   - 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 ensure that the placement of the horn is correct.

3. Sample handling.

   - 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.

   - 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.

   - Solid waste samples amenable to grinding - Drill or hammer until uniform matrix is achieved.

- 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.

4. Extraction method

- Weigh approximately 0.5-30 g of sample (depending on the matrix) into a 250-ml beaker. Record the weight to the nearest 0.1 g.
  - The default weight used is 30g for a soil sample.
  - If the sample is a solvent or an oil matrix, approximately 0.5 ml of neat sample is weight out and brought up to 2 ml with solvent 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 SOP: ORL-004). The relative response of this base dilution may result in a final analysis of the sample at a higher or lower net dilution.

- Nonporous or wet samples (gummy or clay type) that do not have a free-flowing sandy texture must be mixed with a maximum 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.

- 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 2).

  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 2).

  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 2).

- 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, or DRO, as appropriate, see Table 2).

- 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.

- 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).

- Decant through a conical gravity filter (Whatman No. 41 filter paper or equivalent) and sodium sulfate to catch any excess water into an evaporation tube.

- Repeat the extraction with an additional 60 ml portion 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.

5. Evaporation method

- Place the concentrator tube in the TurboVap Evaporation Station, that has the water bath at 47+/2°C, 21 psi, until the extract reaches a 0.5 ml final volume.

- Transfer the sample extract to a 4 ml pre-calibrated vial. Adjust to 1 ml final volume with methylene chloride.

- Final 1 ml adjustment: if the transfer is greater than 1 ml, use compressed air 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 than 1 ml, add final extract solvent to the meniscus.

8.0 QUALITY CONTROL

Samples are extracted in batches of 20 samples or less. For every batch, there must be a Blank, LCS, MS, and MSD/DUP depending on the clients' request. All the reagent blanks, matrix spikes, or replicate samples must 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.

The Base/Neutral surrogate standard must contain the compounds listed in Table 1. The Acid surrogate standard must contain the compounds listed in Table 1. 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 2.

The Base/Neutral MS/MSD and LCS spikes must contain the compounds listed in Table 1. The Acid MS/MSD and LCS spikes must contain the compounds listed in Table 1. 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 2.

The PNA MS/MSD and LCS spikes must contain the compounds listed in Table 1. The concentrations listed are those in the stock spiking solutions. MS/MSD spike must 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 2.

The DRO MS/MSD and LCS spikes contain 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 2.

For DoD projects, the MS/MSD and LCS spike solution must contain ALL target compounds.

New lot blanks are analyzed to ensure 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.

All pertinent information is entered into an extraction bench sheets (Figure 1 and 2).

9.0 METHOD PERFORMANCE

Laboratory specific data are provided in SOP # ORL-004. The MDLs and PQLs can be found in Merit's LIMS system are from the most recent detection limit studies.

10.0 EQUIPMENT MAINTENANCE AND TROUBLESHOOTING

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. When cavities are observed horns are cleaned and/or replaced.

Each instrument is assigned a maintenance logbook. All maintenance performed on the instrument must be recorded. Additionally, any modifications to the instrument settings shall be noted in the specific instrument logbook. Maintenance procedures provided in the equipment manual shall be followed.

11.0 SAFETY

Eye protection and gloves must be worn while performing the analyses. Every laboratory area has eyewash, emergency shower, and fire extinguisher. The metals lab also has dust masks available for use with dust samples. The air system throughout 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. A reference file of material safety data sheets (MSDSs) is available to all personnel.

Specific attention be paid (but not limited) to:

- Sodium sulfate is mildly toxic by ingestion, not considered an explosion hazard, and oxides of sulfur and sodium may form when heated to decomposition.. Keep in a tightly closed container, stored in a cool, dry, ventilated area. Protect against physical damage. Isolate from incompatible substances. Containers of this material may be hazardous when empty since they retain product residues (dust, solids); observe all warnings and precautions listed for the product.

- Methylene chloride is harmful if swallowed, inhaled or absorbed through skin. Methylene chloride affects central nervous system, liver, cardiovascular system, and blood. Also, it can cause irritation to skin, eyes, and respiratory tract. Risk of cancer depends on level and duration of exposure. Vapor may form flammable mixture in atmosphere that contains a high percentage of oxygen. Sealed containers may rupture when heated. Emits highly toxic fumes of phosgene when heated to decomposition. Decomposes in a flame or hot surface to form toxic gas phosgene and corrosive mists of hydrochloric acid. Carbon dioxide and carbon monoxide may form when heated to decomposition.

12.0 WASTE DISPOSAL AND POLLUTION PREVENTION

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

13.0 DEFINITIONS

Sample Batch: samples of the same or similar matrix; for this method, a sample batch consists of 20 samples or less.

Method Blank: an analyte-free matrix to which all reagents are added in the same volumes or proportions as used in the sample processing. The method blank is carried through the complete sample preparation and analytical procedure. The method blank is used to document contamination resulting from the analytical process.

Laboratory Control Sample (also known as Laboratory Fortified Blank, Spiked Blank, or QC Check Sample): a sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes. It is generally used to establish intra-laboratory or analyst-specific precision and bias or to assess the performance of all or a portion of the measurement system.

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

Matrix Spike Duplicate (also known as Spiked Sample or Fortified Sample Duplicate): a second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

Surrogate: an organic compound which is similar to the target analytes in chemical composition and behavior in the analytical process, but which is not normally found in environmental samples. Its use is to monitor the performance of the extraction, cleanup (as needed), the analytical system, and the effectiveness of the method.

14.0 REFERENCES

Department of Defense, Quality Systems Manual for Environmental Laboratories (DoD QSM), DoD Environmental Data Quality Workgroup, Department of Navy, Lead Service, Based on NELAC Voted Revision 5 June 2003, Version 4.1, April 22, 2009.

US EPA, SW-846. Revision 3; Method 3550B

Table 1: Surrogate/LCS/MS Compounds

Standard Type	Compound	CAS #	Concentration	Supplier
Base/Neutral Surrogate	Nitrobenzene-d5	4165-60-0	5000 ug/ml	RESTEK
	2-Fluorobiphenyl	321-60-8	5000 ug/ml	RESTEK
	p-Terphenyl-d14	1718-51-0	5000 ug/ml	RESTEK
Acid Surrogate	2-Fluorophenol	367-12-4	10000 ug/ml	RESTEK
	Phenol-d6	13127-88-3	10000 ug/ml	RESTEK
	2,4,6-Tribromophenol	118-79-6	10000 ug/ml	RESTEK
Base/Neutral MS/MSD/LCS Spike	Acenaphthene	83-32-9	5000 ug/ml	RESTEK
	1,4-Dichlorobenzene	106-46-7	5000 ug/ml	RESTEK
	2,4-Dinitrotoluene	121-14-2	5000 ug/ml	RESTEK
	N-nitroso-di-n-propylamine	621-64-7	5000 ug/ml	RESTEK
	Pyrene	129-00-0	5000 ug/ml	RESTEK
	1,2,4-Trichlorobenzene	120-82-1	5000 ug/ml	RESTEK
Acid MS/MSD/LCS Spike	4-Chloro-3-methylphenol	59-50-7	10000 ug/ml	RESTEK
	2-Chlorophenol	95-57-8	10000 ug/ml	RESTEK
	4-Nitrophenol	100-02-7	10000 ug/ml	RESTEK
	Pentachlorophenol	87-86-5	10000 ug/ml	RESTEK
	Phenol	108-95-2	10000 ug/ml	RESTEK
PNA MS/MSD/LCS Spike	Naphthalene	91-20-3	2000 ug/ml	RESTEK
	2-Methylnaphthalene	91-57-6	2250 ug/ml	RESTEK
	Acenaphthylene	208-96-8	2000 ug/ml	RESTEK
	Acenaphthene	83-32-9	2000 ug/ml	RESTEK
	Fluorene	86-73-7	2000 ug/ml	RESTEK
	Phenanthrene	85-01-8	2000 ug/ml	RESTEK
	Anthracene	120-12-7	2000 ug/ml	RESTEK
	Fluoranthene	206-44-0	2000 ug/ml	RESTEK
	Pyrene	129-00-0	2000 ug/ml	RESTEK
	Benzo(a)anthracene	56-55-3	2000 ug/ml	RESTEK
	Chrysene	218-01-9	2000 ug/ml	RESTEK
	Benzo(b)fluoranthene	205-99-2	2000 ug/ml	RESTEK
	Benzo(k)fluoranthene	207-08-9	2000 ug/ml	RESTEK
	Benzo(a)pyrene	50-32-8	2000 ug/ml	RESTEK
	Indeno(1,2,3-cd)pyrene	193-39-5	2000 ug/ml	RESTEK
	Dibenzo(ah)anthracene	53-70-3	2000 ug/ml	RESTEK
	Benzo(ghi)perylene	191-24-2	2000 ug/ml	RESTEK

Table 2. 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/MSD/LCS 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/MSD/LCS 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/MSD/LCS Spike:

For 20 ml total solution at 1000 mg/L;
- 20.0 ml of Acetone
- 20.0 mg of neat Diesel Fuel (gravimetric preparation)

Figure 1: SVOC Extraction Bench Sheet

Solvent Lot #: _____									Date: _____	
Na_2SO_4 Lot #: _____			**SVOC Solid Extraction Log**						Time Started: _____	
SSD #: _____			**Method 3550 B**						Time Ended: _____	
MS/LCS #: _____									Batch ID#: _____	

#	Merit #	Matrix	Sample Weight (g)	Solvent	Solvent Vol (ml)	Final Vol (ml)	SSD Vol (ml)	MS Vol (ml)	Analyst	Notes / Date	
Initial Q.C.	BLANK	Sand	30.0 g	CH_2Cl_2	180	1	1	---			
	LCS	Sand	30.0 g					1			
	LCSD	Sand	30.0 g					1			[ ]
	MS							1			[ ]
	MSD							1			
1											
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3											
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Reviewed by: _____ On: _____ Prepared by: Merit Laboratories, Inc.

Figure 2: PNA/DRO Extraction Bench Sheet

Solvent Lot #: _____										Date: _____	
Na_2SO_4 Lot #: _____			**PNA/DRO Solid Extraction Log**							Time Started: _____	
SSD #: _____			**Method 3550 B**							Time Ended: _____	
MS/LCS #: _____										Batch ID#: _____	

#	Merit #	Matrix	Sample Weight (g)	Solvent	Solvent Vol (ml)	Final Vol (ml)	SSD Vol (ml)	MS Vol (ml)	Analyst	Notes / Date	
Initial Q.C.	BLANK	Sand	30.0 g	CH_2Cl_2	180	1	1	---			
	LCS	Sand	30.0 g					1			
	LCSD	Sand	30.0 g					1			[ ]
	MS							1			[ ]
	MSD							1			
1											
2											
3											
4											
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Reviewed by: _____ On: _____ Prepared by: Merit Laboratories, Inc.

STANDARD OPERATING PROCEDURE

SEPARATORY FUNNEL EXTRACTION FOR BNAS/PNAS/TCLP/DRO EPA METHOD 3510C

APPROVALS:

6/3/11

QA Officer — Date

6/3/11

Technical Director — Date

Number	Description of Change	Date
001-006	Previous changes were not documented	
007	Updated to comply with DoD QSM and ISO 17025 standards.	6/3/11
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1.0 SCOPE AND APPLICATION

This SOP is used for extracting nonvolatile and semivolatile base/neutral/acid (BNA) polynuclear aromatic hydrocarbon (PNA), and diesel range organics (DRO) organic compounds from aqueous samples. This SOP is applicable to the isolation and concentration of water-insoluble and slightly water-soluble organics in preparation for a variety of chromatographic procedures. The following BNA method is congruent with Toxicity Characteristic Leaching Procedure (TCLP) and Total Toxic Organics (TTO) procedures in their entirety and can also be used with PNA (with the omission or addition of appropriate steps). 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.

This SOP is not applicable for OHIO VAP samples.

2.0 SUMMARY OF METHOD

A measured volume of sample, up to 1 liter, at a specific pH is extracted with methylene chloride using a separatory funnel. The extract is concentrated. Clean glassware is used to obtain the optimum analytical chromatograms.

3.0 INTERFERENCES

The decomposition of some analytes has been demonstrated under basic extraction conditions. Organochlorine pesticides can de-chlorinate, phthalate esters can exchange, and phenols can react to form tannates.

4.0 APPARATUS AND MATERIALS

Separatory funnel - 2-liter, with polytetrafluoroethylene (PTFE) stopcock.

Evaporation tubes, 250-ml volume, Zymark with end point of 0.5-ml.

Zymark Turbo Vap II Concentration Station with temperature control water bath.

Vials – 4-ml, glass with PTFE-lined screw caps.

pH indicator paper - pH range including the desired extraction pH.

Glass beakers, 250-ml.

Glass funnel.

Filter paper, coarse grade.

Adhesive labels.

Syringe - 5-mL NIST certified.

Graduated cylinder - 1-liter.

250 mL Erlenmeyer flasks.

Pipettors.

Automated Shakers.

5.0 REAGENTS

Note: Reagent grade chemicals musl be used in all tests. Unless otherwise indicated, it is intended that all reagents must conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades can 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 must be stored in glass to prevent the leaching of contaminants from plastic containers.

Deionized (DI) water.

Sodium sulfate (granular, anhydrous), Na_2SO_4.

Sulfuric acid, concentrated, as well as solution (1:1 v/v), H_2SO_4. Slowly add 500 ml of H_2SO_4 to 500 m of DI water.

Sodium Hydroxide solution (10 N), NaOH. Slowly add 1 Liter of DI water to 400 g of NaOH crystals.

Extraction/exchange solvents. All solvents must be of pesticide quality or equivalent.

- Methylene chloride, CH_2Cl_2, boiling point 49°C.
- Acetone, C_3H_6O.

Surrogate and matrix spiking solutions are prepared as listed in Table 2. The detailed list of compounds for each stock mixture is given in §9 and Table 1.

Nonchromix, used when contamination is detected.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

All aqueous samples for the analysis of BNAs, PNAs, and DRO must be stored in Amber glass containers only. Approximately 1-L volume of sample is needed for extraction. Refrigerate at 4º ± 2° C. The holding time for samples is 7 days until extraction and 40 days thereafter for analyses.

Note: If samples contain significantly less volume then 1L, Quality Assurance Manager & client need to be notified. Higher detection limits will be applied to low volume extracts.

7.0 PROCEDURE

1. All glassware must be kept immaculate. Glassware must be cleaned as soon as possible after extraction. Glassware washing procedures are found in SOP #GEN-002.

2. Mark the level of sample on the outside of the bottle. After step 6, pour the sample into the 2-liter separatory funnel. 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.

3. 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. Do not place pH paper directly into sample container.

4. For all samples, spikes, and blanks, pipette 1.0-ml of the appropriate surrogate spiking solution (see Table 2 and §9.2) into the funnel and swirl. For matrix spike samples (including the LCS), add 1ml surrogate and 1-ml matrix spike standard (see Table 2 and §9.3).

5. Add 10-ml of Acetone into the separatory funnel and swirl the sample (applicable for BNAs).

6. Add 35-ml (for PNAs, DRO and phenols), or 30 ml (for BNA/TCLP) of methylene chloride into the sample bottle to rinse it and transfer this rinse solvent to the separatory funnel.

7. Venting prior to the 3 minute shake: Place cap on funnel, tip up/down 5 to 10 times, release and vent into paper towel (to prevent cross contamination). Initial venting must be done immediately after the separatory funnel has been sealed and shaken once. Seal the separatory funnel and shake vigorously for 3 minutes on a horizontal placement at a motor speed 70 in accordance with Table 3 shake program. The separatory funnel must 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.

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 can include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods.

8. Drain the extract through a filter filled with approximately 10g of Na_2SO_4 into a 250-ml glass Zymark evaporation tube.

9. Repeat step 6 three more times with 35 ml (PNA/DRO) or 30 ml (BNA) methylene chloride each in accordance with Table 3 shake program [PNA and DRO samples are done after 4 shakes].
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.

10. Check the pH of the sample with wide-range pH paper and adjust the pH, if necessary, to a pH > 12 using NaOH [BNA only].

11. Repeat step 6 two times at three minutes each in accordance with Table 3 shake program [BNA only].

12. Rinse the funnel and Na_2SO_4 with a squirt of Methylene chloride into the collected sample in between shakes.

13. 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 47°C ± 2°C and 21 psi. Allow the sample to evaporate down to 0.5ml methylene chloride or until the evaporation station signals completion.

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 compressed air to evaporate to the 1-ml mark.

15. Final 1 ml adjustment: if the transfer is greater than 1 ml, use compressed air 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 than 1 ml, add final extract solvent to the meniscus.

8.0 QUALITY CONTROL

Samples are extracted in batches of 20 samples or less. For every batch there must be a Blank, LCS, MS, and MSD/DUP depending on the client's request. All the reagent blanks, matrix spikes, or replicate samples must 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.

The Base/Neutral surrogate standard must contain the compounds listed in Table 1. The Acid surrogate standard must contain the compounds listed in Table 1. 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 2.

The Base/Neutral MS/MSD and LCS spikes must contain the compounds listed in Table 1. The Acid MS/MSD and LCS spikes must contain the compounds listed in Table 1. The concentrations listed are those in the stock spiking solutions. MS/MSD spike must 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 2.

The PNA MS/MSD and LCS spikes must contain the compounds listed in Table 1. The concentrations listed are those in the stock spiking solutions. MS/MSD spike must 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 2.

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 2.

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.*

For DoD projects the MS/MSD and LCS spike solution must contain ALL target compounds.

All pertinent information is entered into an extraction bench sheets (Figure 1, 2, and 3).

9.0 METHOD PERFORMANCE

Laboratory specific data are provided in SOP #ORL-004. The MDLs and PQLs can be found in Merit's LIMS system are from the most recent detection limit studies.

10.0 EQUIPMENT MAINTENANCE AND TROUBLESHOOTING

Each instrument is assigned a maintenance logbook. All maintenance performed on the instrument must be recorded. Additionally, any modifications to the instrument settings shall be noted in the specific instrument logbook. Maintenance procedures provided in the equipment manual shall be followed.

11.0 SAFETY

Eye protection and gloves must be worn while performing the analyses. Every laboratory area has eyewash, emergency shower, and fire extinguisher. The metals lab also has dust masks available for use with dust samples. The air system throughout 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. A reference file of material safety data sheets (MSDSs) is available to all personnel.

Specific attention be paid (but not limited) to:

- Sodium sulfate is mildly toxic by ingestion, not considered an explosion hazard, and oxides of sulfur and sodium may form when heated to decomposition. Keep in a tightly closed container, stored in a cool, dry, ventilated area. Protect against physical damage. Isolate from incompatible substances. Containers of this material may be hazardous when empty since they retain product residues (dust, solids); observe all warnings and precautions listed for the product.

- Methylene chloride is harmful if swallowed, inhaled or absorbed through skin. Methylene chloride affects central nervous system, liver, cardiovascular system, and blood. Also, it can cause irritation to skin, eyes, and respiratory tract. Risk of cancer depends on level and duration of exposure. Vapor may form flammable mixture in atmosphere that contains a high percentage of oxygen. Sealed containers may rupture when heated. Emits highly toxic fumes of phosgene when heated to decomposition. Decomposes in a flame or hot surface to form toxic gas phosgene and corrosive mists of hydrochloric acid. Carbon dioxide and carbon monoxide may form when heated to decomposition.

- 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.

- 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.

- Acetone is an extremely flammable liquid and vapor, vapor may cause flash fire. Hexane is harmful or fatal if swallowed or inhaled, causes irritation to skin, eyes and respiratory tract, and can affect the central nervous system. May cause coughing, dizziness, dullness, and headache. Higher concentrations can produce central nervous system depression, narcosis, and unconsciousness. Carbon dioxide and carbon monoxide may form when heated to decomposition.

12.0 WASTE DISPOSAL AND POLLUTION PREVENTION

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

13.0 DEFINITIONS

Sample Batch: samples of the same or similar matrix; for this method, a sample batch consists of 20 samples or less.

Method Blank: an analyte-free matrix to which all reagents are added in the same volumes or proportions as used in the sample processing. The method blank is carried through the complete sample preparation and analytical procedure. The method blank is used to document contamination resulting from the analytical process.

Laboratory Control Sample (LCS) (also known as Laboratory Fortified Blank, Spiked Blank, or QC Check Sample): a sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes. It is generally used to establish intra-laboratory or analyst-specific precision and bias or to assess the performance of all or a portion of the measurement system.

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

Matrix Spike Duplicate (also known as Spiked Sample or Fortified Sample Duplicate): a second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

Surrogate: an organic compound which is similar to the target analytes in chemical composition and behavior in the analytical process, but which is not normally found in environmental samples. Its use is to monitor the performance of the extraction, cleanup (as needed), the analytical system, and the effectiveness of the method.

14.0 REFERENCES

Department of Defense, *Quality Systems Manual for Environmental Laboratories* (DoD QSM), DoD Environmental Data Quality Workgroup, Department of Navy, Lead Service, Based on NELAC Voted Revision 5 June 2003, Version 4.1, April 22,2009.

USEPA, SW-846, Revision 3; Method 3510C.

Table 1: Surrogate/LCS/MS Compounds

Standard Type	Compound	CAS #	Concentration	Supplier
Base/Neutral Surrogate	Nitrobenzene-d5	4165-60-0	5000 ug/ml	RESTEK
	2-Fluorobiphenyl	321-60-8	5000 ug/ml	RESTEK

	p-Terphenyl-d14	1718-51-0	5000 ug/ml	RESTEK
Acid Surrogate	2-Fluorophenol	367-12-4	10000 ug/ml	RESTEK
	Phenol-d6	13127-88-3	10000 ug/ml	RESTEK
	2,4,6-Tribromophenol	118-79-6	10000 ug/ml	RESTEK
Base/Neutral MS/MSD/LCS Spike	Acenaphthene	83-32-9	5000 ug/ml	RESTEK
	1,4-Dichlorobenzene	106-46-7	5000 ug/ml	RESTEK
	2,4-Dinitrotoluene	121-14-2	5000 ug/ml	RESTEK
	N-nitroso-di-n-propylamine	621-64-7	5000 ug/ml	RESTEK
	Pyrene	129-00-0	5000 ug/ml	RESTEK
	1,2,4-Trichlorobenzene	120-82-1	5000 ug/ml	RESTEK
Acid MS/MSD/LCS Spike	4-Chloro-3-methylphenol	59-50-7	10000 ug/ml	RESTEK
	2-Chlorophenol	95-57-8	10000 ug/ml	RESTEK
	4-Nitrophenol	100-02-7	10000 ug/ml	RESTEK
	Pentachlorophenol	87-86-5	10000 ug/ml	RESTEK
	Phenol	108-95-2	10000 ug/ml	RESTEK
PNA MS/MSD/LCS Spike	Naphthalene	91-20-3	2000 ug/ml	RESTEK
	2-Methylnaphthalene	91-57-6	2250 ug/ml	RESTEK
	Acenaphthylene	208-96-8	2000 ug/ml	RESTEK
	Acenaphthene	83-32-9	2000 ug/ml	RESTEK
	Fluorene	86-73-7	2000 ug/ml	RESTEK
	Phenanthrene	85-01-8	2000 ug/ml	RESTEK
	Anthracene	120-12-7	2000 ug/ml	RESTEK
	Fluoranthene	206-44-0	2000 ug/ml	RESTEK
	Pyrene	129-00-0	2000 ug/ml	RESTEK
	Benzo(a)anthracene	56-55-3	2000 ug/ml	RESTEK
	Chrysene	218-01-9	2000 ug/ml	RESTEK
	Benzo(b)fluoranthene	205-99-2	2000 ug/ml	RESTEK
	Benzo(k)fluoranthene	207-08-9	2000 ug/ml	RESTEK
	Benzo(a)pyrene	50-32-8	2000 ug/ml	RESTEK
	Indeno(1,2,3-cd)pyrene	193-39-5	2000 ug/ml	RESTEK
	Dibenzo(ah)anthracene	53-70-3	2000 ug/ml	RESTEK
	Benzo(ghi)perylene	191-24-2	2000 ug/ml	RESTEK

Table 2: 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 3: Automated Extraction Funnel Shaking Procedure.

Stage	Solvent Volume (BNA/PNA DRO)	pH	Funnel Position	Shaker Time	Shaker Intensity	BNA Extraction	PNA/DRO Extraction
1a	30 ml/ 35 ml	<2	vertical/open	5 to 10 times	to vent	☑	☑
1b			horizontal/closed	3 min.	70		
2	30 ml/ 35 ml	<2	horizontal/closed	3 min.	70	☑	☑
3	30 ml/ 35 ml	<2	horizontal/closed	3 min.	70	☑	☑
4	30 ml/35 ml	<2	horizontal/closed	3 min.	70	☑	☑
5	30 ml	>12	horizontal/closed	3 min.	70	☑	☐
6	30 ml	>12	horizontal/closed	3 min.	70	☑	☐

Notes: (1) Solvent – Methylene Chloride

(2) Funnel Position indicates whether the funnel is horizontally or vertically situated in the automatic shaker and whether the stopcock is open or closed.

(3) *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).

(4) Shaker Intensity is the dial setting on the automatic shaker unit. A higher number indicates a more vigorous shake.

(5) BNA/PNA/DRO Extraction indicates whether the extraction stage is appropriate for the given class of analytes.

Figure 1: SVOC Extraction Bench Sheet

Solvent Lot #: _____

Na_2SO_4 Lot #: _____

MS/LCS #: _____

SSD #: _____

Acid #: _____ Base #: _____

SVOC Liquid Extraction Log

Method 3510 C

Date: _____

Time Started: _____

Time Ended: _____

Batch ID#: _____

#	Merit #	Matrix	Sample Weight (g)	Solvent	Solvent Vol (ml)	Final Vol (ml)	SSD Vol (ml)	MS Vol (ml)	Analyst	Notes / Date
Initial Q.C.	BLANK	D.I.	1000 ml	CH_2Cl_2	180	1	1	---		
	LCS	D.I.	1000 ml					1		
	LCSD	D.I.	1000 ml					1		[ ]
	MS							1		[ ]
	MSD							1		[ ]
1										
2										
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Figure 2: PNA/DRO Extraction Bench Sheet

Solvent Lot #: _____

Na_2SO_4 Lot #: _____

MS/LCS #: _____

SSD #: _____

Acid #: _____ Base #: _____

PNA/DRO Liquid Extraction Log

Method 3510 C

Date: _____

Time Started: _____

Time Ended: _____

Batch ID#: _____

#	Merit #	Matrix	Sample Weight (g)	Solvent	Solvent Vol (ml)	Final Vol (ml)	SSD Vol (ml)	MS Vol (ml)	Analyst	Notes / Date
Initial Q.C.	BLANK	D.I.	1000 ml	CH_2Cl_2	140	1	1	---		
	LCS	D.I.	1000 ml					1		
	LCSD	D.I.	1000 ml					1		[ ]
	MS							1		[ ]
	MSD							1		[ ]
1										
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Figure 3: TCLP Extraction Bench Sheet

Solvent Lot #: _____

Na_2SO_4 Lot #: _____

MS/LCS #: _____

SSD #: _____

Acid #: _____ Base #: _____

TCLP Extraction Log

Method 3510 C

Date: _____

Time Started: _____

Time Ended: _____

Batch ID#: _____

#	Merit #	Matrix	Sample Weight (g)	Solvent	Solvent Vol (ml)	Final Vol (ml)	SSD Vol (ml)	MS Vol (ml)	Analyst	Notes / Date
Initial Q.C.	BLANK	Sol	1000 ml	CH_2Cl_2	180	1	1	---		
	LCS	Sol	1000 ml					1		
	LCSD	Sol	1000 ml					1		
	TCLP MS							1		
	TCLP BLK							1		
	Daily BLK	Sol	1000 ml							
1										
2										
3										
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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, domestic and industrial wastes.

1.2 The SOP 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 Total, Bicarbonate, and Carbonate Alkalinity in liquid samples. Alkalinity is run by Method 2320B.

3.0 INTERFERENCES

3.1 Matrix interferences are due to sample color, samples may need to be diluted.

4.0 APPARATUS AND MATERIALS

4.1 Digital titrator
4.2 Stir plate
4.3 Magnetic Stir bar
4.4 Clear plastic cups
4.5 Pipettors

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 Phenolpthalein Indicator Powder Pillow
5.5 25,000 mg/L alkalinity standard, 10 mL of standard brought to 100 mL with DI Water

6.0 SAMPLE HANDLING AND PRESERVATION

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

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

7.0 PROCEDURE

7.1 Samples must be brought to room temperature before analysis.

7.2 COLOR DEVELOPMENT AND MEASUREMENT (TOTAL ALKALINITY ONLY)

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

7.2.2 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.

7.2.3 Pour one Bromcresol Green-Methyl Red indicator powder pillow in the cup.

7.2.4 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.

7.2.5 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.

7.2.6 Rinse off magnetic stir bar.

7.2.7 Run all quality control samples (i.e. control, blank spike, LCS) by following Sections 7.2.2 to 7.2.4.

7.2.8 Place 100 mL of a sample in another cup. Repeat Sections 7.2.2 to 7.2.4 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.

7.3 CARBONATE AND BICARBONATE MEASUREMENT

7.3.1 Place 100 mL of sample in cup, add the contents of a Phenolpthalein Indicator Powder pillow and swirl to mix.
- 7.3.1.1 If there is no color change, dilute and titrate following Section 7.2.
- 7.3.1.2 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 following Section 7.2. 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 Phenolphthalein 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

8.3 See Table 2 Alkalinity Relationship for how to calculate Bicarbonate and Carbonate Alkalinity

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/ Level 3)
- Method Blank
- Blank Spike (every 10 samples)

10.0 DOCUMENTATION

10.1 Alkalinity 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 TS %
- 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.

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 One each set	85%-115%	Rerun	Notify client. Flag data.
Control	Yes One each set	85%-115%	Rerun	Notify client. Flag data.
Blank Spike	Yes One every 10 samples	85%-115%	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	85%-115%	Analyze by Method of Standard Additions	Notify client. Flag data.
Matrix Spike Duplicate	Yes One every 20 samples Level 3	85%-115%	Analyze by Method of Standard Additions	Notify client. Flag data.

Table 2. Alkalinity Relationship

Row	Result of Titration	Carbonate Alkalinity is equal to:	Bicarbonate Alkalinity is equal to:
1	Phenolphthalein Alkalinity = 0	0	Total Alkalinity
2	Phenolphthalein Alkalinity equal to Total Alkalinity	0	0
3	Phenolphthalein Alkalinity less than one half of Total Alkalinity	2 times the Phenolphthalein Alkalinity	Total Alkalinity minus two times Phenolphthalein Alkalinity
4	Phenolphthalein Alkalinity equal to one half of Total Alkalinity	Total Alkalinity	0
5	Phenolphthalein Alkalinity greater than one half of Total Alkalinity	2 time the difference between Total and Phenolphthalein Alkalinity	0

To use the Table 2 follow these steps;
a) Does the phenolphthalein alkalinity equal zero? If yes, use Row 1.
b) Does the phenolphthalein alkalinity equal total alkalinity? If yes, use Row 2.
c) Multiply the phenolphthalein alkalinity by 2.

d) Select Row 3, 4, or 5 based on comparing the result of Step c with the total alkalinity.
e) Perform the required calculations in the appropriate row.

12.0 REFERENCES

12.1 *Standard Methods*, twentieth edition, Method 2320B, Alkalinity.
12.2 Hach Digital Titrator Model 16900-01 Manual. Alkalinity.

13.0 SAFETY

13.1 Eye protection and gloves must be worn while performing alkalinity analyses.
13.2 Every Laboratory area has eyewash, emergency shower, and fire extinguisher. The metals lab also has dust masks available for use with dust samples.
13.3 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.
13.4 A reference file of material safety data sheets (MSDSs) is available to all personnel.

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.

_____

Analyst Date

_____

Andy Ball, QA Officer Date

_____

Maya V. Murshak, Technical Director Date

SOP #033503: NITROGEN, AMMONIA (NH_3)
POTENTIOMETRIC, ION SELECTIVE ELECTRODE
STANDARD METHOD 4500 NH_3 D

Revision: 9
Date: 04/08/11

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, and soils. Reporting limit for 0.02 mg/l for liquids and 1 mg/kg for soils.

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 is unnecessary.

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. Standard Method 4500 NH_3 D is used.

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 INTERFERENCES

3.1 Volatile amines act as a positive interference.

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

4.0 APPARATUS AND MATERIALS

4.1 Electrometer (pH meter) with expanded mV scale

4.2 Ammonia selective electrode

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

4.4 Plastic cups

5.0 REAGENTS

5.1 Deionized water: Special precautions must be taken to ensure 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.

5.2 Sodium hydroxide (NaOH), 10N

5.3 Environmental Resource Associates quality control nutrients standards

5.4 Ammonium chloride, standard: Hach solutions 1000mg/l

5.5 Concentrated Sulfuric Acid (H_2SO_4)

6.0 SAMPLE HANDLING AND PRESERVATION

6.1 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.

6.2 The holding time for water and soil ammonia samples is 28 days from sampling.

7.0 PROCEDURE

7.1 Samples need to be brought to room temperature before being analyzed.

7.2 Probe is rinsed with 100 mL deionized water containing 1 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 1 mL 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 can 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 liquid sample or 0.1 g to 5 g of soil with 100 ml of deionized water 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 Calculations:

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

Where:

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

8.0 QUALITY CONTROL

8.1 Quality Control Samples for up to twenty samples per batch include:

- 8.1.1 1 method blank (Deionized water)
- 8.1.2 2 standards (1 ppm and 10 ppm) to establish a curve.
- 8.1.3 Calibration Check (5ppm)
- 8.1.4 Laboratory Control Sample (LCS) (2.5 ppm) at a mid-point concentration
- 8.1.5 Control, ERA, from a different source than the calibration curve
- 8.1.6 Matrix Spike (MS) per 20 samples
- 8.1.7 Matrix Spike Duplicate (MSD) (required Level 3)
- 8.1.8 Sample duplicate (DUP) per 20 samples
- 8.1.9 Extra standards to include concentrations of sample set (0.02ppm, 0.1 ppm, 10 – 15 ppm)

8.2 See Table 1 for all quality control items, frequency, limits, and corrective actions.

9.0 METHOD PERFORMANCE

Method detection limit studies are performed annually.

10.0 EQUIPMENT MAINTENANCE AND TROUBLESHOOTING

All equipment shall be maintained and calibrated according to manufacturer's procedures. When equipment is not performing as required, the instrument shall not be used until it is recalibrated or replaced.

11.0 SAFETY

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

11.2 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.

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

11.4 Specific attention be paid (but not limited) to

- 11.4.1 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.
- 11.4.2 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.

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

13.0 DEFINITIONS

13.1 Sample Batch: Samples of the same or similar matrix; for this method, a sample batch consists of 20 samples or less.
13.2 Method Blank: An analyte-free matrix to which all reagents are added in the same volumes or proportions as used in the sample processing. The method blank is carried through the complete sample preparation and analytical procedure. The method blank is used to document contamination resulting from the analytical process.
13.3 Laboratory Control Sample (also known as Laboratory Fortified Blank, Spiked Blank, or QC Check Sample): A Sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes. It is generally used to establish intra-laboratory or analyst-specific precision and bias or to assess the performance of all or a portion of the measurement system.
13.4 Matrix Spike (also known as Spiked Sample or Fortified Sample): A sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available. Matrix spikes are used, for example, to determine the effect of the matrix on a method's recovery efficiency.
13.5 Matrix Spike Duplicate (also known as Spiked Sample or Fortified Sample Duplicate): A second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.
13.6 Laboratory Duplicate: Aliquots of sample taken from the same container under the same laboratory conditions and processed and analyzed under the same conditions but independently.

14.0 REFERENCES

14.1 *Standard Methods*, twentieth edition, Method 4500NH_3 D, Nitrogen (Ammonia).

15.0 APPROVAL & ISSUE:

15.1 This section indicates which personnel have read, accepted and approved the SOP.

_____

Analyst Date

_____

QA Officer Date

_____

Technical Director Date

16.0 TABLES AND FIGURES

16.1 Table 1 Quality Control
16.2 Figure 1: Ammonia Bench Sheet

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	<RL or 1/10 Regulatory limit	Remove contamination and rerun	Notify client. Flag data.
Calibration Standards (1 ppm and 10 ppm)	Yes One each set	90%-110%	Rerun	Notify client. Flag data.
Calibration Check (5 ppm)	Yes One each set	90%-110%	Rerun	Notify client. Flag data.
Laboratory Control Sample (LCS)	Yes One each set	90%-110%	Rerun	Notify client. Flag data.
Control (ERA)	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 (MS)	Yes One each set	80%-120%	Rerun	Notify client. Flag data.
Matrix Spike (MSD)	Level 3	RPD<20%	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.

Figure 1: Ammonia Bench Sheet

Analysis:Ammonia-N

Analyst:_____ **Method #**____4500-NH3 D___

Date Run:_____ **Detection Limit:**____0.02 mg/l____

(mg/l) (mg/l) (mg/l)

Merit #	Dilution (ml)	Conc.	%S	Mv	Time	Result	Spike	%Rec	Notes
Blank	100/100				:				
Cal Set	100/0.1 of 1000 ppm				:		1.0		
Cal Set	100/1.0 of 1000 ppm				:		10.0		
Cal Chk	100/0.5 of 1000 ppm				:		5.0		
LCS	100/0.25 of 1000 ppm				:		2.5		
Control	100/ Era Simple Nutrients				:				
					:				
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Notes:_____

☐ Ammonia 1000ppm Std: Exp: ☐ MDL Study: Exp:
☐ ERA Nutrient Simple Std: Exp: ☐ Sodium Hydroxide: Exp:

QC Batch:_____

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

1.0 SCOPE

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

1.2 This SOP is suitable for all concentration ranges of chloride content. Chloride is run by Method 325.3.

2.0 SUMMARY OF THE METHOD

2.1 This SOP is a procedure for evaluating Chloride in liquid or soil samples.

2.2 A sample is titrated with mercuric nitrate in the presence of diphenylcarbazone indicator. The end point of the titration is the formation of the violet mercury diphenylcarbazone complex.

3.0 INTERFERENCES

3.1 Anions and cations at concentrations normally found in surface waters do not interfere.

4.0 APPARATUS AND MATERIALS

4.1 Digital titrator
4.2 Stir plate
4.3 Clear plastic cups
4.4 Stir Bar
4.5 Analytical balance
4.6 Tongue Depressors
4.7 Graduated Cylinder
4.8 Pipettes
4.9 Centrifuge
4.10 Centrifuge tubes

5.0 REAGENTS

5.1 Deionized (DI) water
5.2 0.2256 mercuric nitrate cartridge
5.3 diphenylcarbazone pillow packets
5.4 1,000 mg/L chloride reference standard solution (2 separate lots)

6.0 SAMPLE HANDLING AND PRESERVATION

6.1 Hold time for chloride is 28 days and samples are refrigerated at 4^{o} C ± 2^{o}C.

6.2 Liquid samples are collected in unpreserved, clear plastic bottles. Soil samples are collected in unpreserved glass containers.

7.0 PROCEDURE

7.1 SOIL PREP

7.1.1 Weigh out at least 2.00-g of the sample in a centrifuge tube.
7.1.2 Fill the tube with 40 –mL of DI Water.
7.1.3 Stir well
7.1.4 Let samples sit covered overnight. If samples do not settle, samples must be centrifuged.

7.2 COLOR DEVELOPMENT AND MEASUREMENT (BOTH SOILS AND LIQUIDS)

7.2.1 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.
7.2.2 Pour one powder pillow in the cup.
7.2.3 Using a digital titrator set up with a 0.2256 mercuric nitrate 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 a purple/pink color.

7.2.4 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.

7.2.5 Rinse off magnetic stir bar and cartridge tip between each sample.

7.2.6 Prepare QC samples (i.e. Blank Spike, Control, LCS, MS, Duplicate) required for each batch.

7.2.6.1 Blank spike (10 ppm) is prepared with 1 mL of 1,000 mg/L chloride reference standard solution and 99 mL of DI Water.

7.2.6.2 Control (50 ppm) is prepared with 5 mL of 1,000 mg/L chloride reference standard solution, different lot than blank spike, and 95 mL of DI Water.

7.2.6.3 Laboratory Control Sample (LCS) (25 ppm) is prepared with 2.5 mL 1,000 mg/L chloride reference standard solution, same lot as blank spike, and 97.5 mL of DI Water.

7.2.6.4 Matrix Spike (MS) (1 ppm) is prepared by adding 1 mL of 1,000 mg/L chloride reference standard solution to pre-determined matrix spike sample.

7.2.6.5 A matrix duplicate prepared the same way as a sample.

7.2.7 Place 10 mL of a sample in plastic cup and add 90.0-mL DI water. For soil samples, take 10 mL of liquid from the centrifuge tube and place into plastic cup and add 90.0 mL of DI Water. 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.

7.2.7.1 Brine samples and sample history may encourage use of higher concentration titration cartridge.

8.0 CALCULATIONS

8.1 Liquids:

$$\text{mg Chloride/L} = \frac{D*100mL*M}{S}$$

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 Soils:

$$\text{mg Chloride/kg} = \left[\frac{D*100mL*M}{10mL} \times \frac{40mL}{S}\right] / TS$$

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

9.0 QUALITY CONTROL

9.1 See Table 1.

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

- Control
- MS
- LCS
- DUP
- MSD (Level III only)
- Method Blank
- Blank Spike

10.0 DOCUMENTATION

10.1 Chloride 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.

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 every 20 samples	<MDL or 1/10 Regulatory limit	Remove contamination and rerun	Notify client. Flag data.
Blank Spike	Yes One every 20 samples	90%-110%	Rerun	Notify client. Flag data.
Control	Yes One every 20 samples	90%-110%	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 every 20 samples	RPD<20%	Rerun entire set	Notify client. Flag data.
Matrix Spike	Yes One every 20 samples	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.

12.0 REFERENCES

12.1 EPA Water NPDES, Method 325.3, EPA Test Methods, Revision 1982, Chloride (mg/L, Titrimetric, Mercuric Nitrate).

12.2 Standard Methods, 20th Edition.

12.3 SW-846, Method 9252, EPA Test Methods, Revision 1982, Chloride (mg/L, Titrimetric, Mercuric Nitrate).

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.

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.

_____

Analyst Date

_____

Andy Ball, QA Officer Date

_____

Maya V. Murshak, Technical Director Date

STANDARD OPERATING PROCEDURE

PYRIDINE-PYRAZALONE COLORIMETRIC METHOD FOR ANALYZING CYANIDE USING THE DR/4000 HACH SPECTROPHOTOMETER METHOD EPA 335.4 AND STANDARD METHOD 4500-CN-E

APPROVALS:

6/3/11

QA Officer — Date

6/3/11

Technical Director — Date

Number	Description of Change	Date
001-009	Previous changes were not documented	
010	Updated to comply with DoD QSM and ISO 17025 standards.	6/3/11
011		
012		
013		
014		
015		
016		
017		
018		
019		
020		

1.0 SCOPE AND APPLICATION

This SOP determines cyanide in drinking, surface, ground, and sea water; domestic and industrial wastes and solids using a colorimetric method after full distillation using the Lachat micro-dist system. The reporting limit for water samples using a double distillation is 0.005 mg/l and 0.5 mg/kg for solids.

2.0 SUMMARY OF METHOD

Cyanide is analyzed after distillation using the DR-4000 Hach spectrophotometer, Method Code 8027. Three separate reagents are added to a distilled neutralized sample. The pyridine-pyrazolone indicator that is used gives an intense blue color if cyanide is present (starts out as pink then goes blue). Reaction time after adding reagents is 30 minutes.

3.0 INTERFERENCES

If the display flashes 0.200, the upper limit of the pre-calibrated range has been exceeded and a sample dilution is needed. A flashing value of –0.020 indicates the sample has a negative absorbance value relative to the blank. This negative value indicates a possible interference in the water sample or a procedure error by the user. Small negative values probably are due to small variations between sample cells or amounts of reagent added and should be treated as a concentration value of zero. Delaying the addition of the CyaniVer 5 Reagent Pillow for more than 0.5minutes after addition of CyaniVer 4 will give lower test results. It is not essential that the entire CyaniVer 4 reagent be dissolved before proceeding with the addition of CyaniVer 5. Too much chlorine will cause a milky white precipitate after addition of CyaniVer 5. See CN- Lachat Distillation SOP IRL-013 for pre-distillation treatment of samples.

4.0 APPARATUS AND MATERIALS

DR/4000 Hach Spectrophotometer (wavelength knob to 612 nm)
10 mL sample cells
10 mL sample cells adapter
25 mL clear glass vials

5.0 REAGENTS

CyaniVer 3 powder pillows for 10 mL sample. (Contains: Sodium Phosphate Dibasic, Halane, & Potassium Phosphate, Monobasic). Shelf life for CyaniVer 3, 4 & 5 is 5 years at 10-30 degrees C.

CyaniVer 4 powder pillows for 10 ml sample. (Contains: Ascorbic Acid, Pyridine-3-nitrophthalic acid, & Sodium Sulfate).

CyaniVer 5 powder pillows for 10ml sample. (Contains: Potassium Phosphate, Monobasic, Sodium Sulfate, 3-Methyl-1-phenyl-2pyrazolin-5-one, & Sodium Phosphate Dibasic).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

Water samples are collected in plastic containers and preserved with NaOH to a pH ≥ 12 and cooled to 4 ±2 °C. Soil samples are collected in a non preserved glass container and cooled to 4 ±2 °C. Holding time for cyanide is 14 days from the time of sampling.

7.0 PROCEDURE

1. Allow for DR/4000 warm-up (approximately 15 min).

2. All samples including QC samples having been distilled, neutralized, and brought to final volume (10 mL) in the 15ml glass vials are now ready to be analyzed. It is possible to do two samples at a time. Start with method blank, which is used to zero instrument.

3. Add the contents of one CyaniVer 3 reagent pillow to each sample vial, stopper and shake for 0.5 minutes—press: 0.5 timer. When timer goes off, reset timer for 0.5 and allow samples to stand undisturbed.

4. After the timer sounds, add the contents of a CyaniVer 4 reagent pillow to each sample re-stopper and shake for 0.1 minute--press timer. When timer sounds, immediately add CyaniVer 5 reagent pillow and shake vigorously to dissolve. Set timer for 30 minutes. Repeat procedure for all the samples. *See 3.0*.

5. The cyanide calibration curve needs to be entered in the DR/4000.

6. Select user program **175**; calibration curve & wavelength 612 nm are then auto selected. Place the 10 mL vial adapters into cell compartment making sure openings are aligned with light path in compartment.

7. When 30-minute reaction period is over pour method blank into 10ml sample cell, cap the cell and place into cell compartment with letter on cell facing the front.

8. Press: **Zero** Absorbance so displays reads 0.000. Enter the entire calibration curve.

9. Press 0.000 Std 1, which is Absorbance, then Press 0.000 Std 2, which is the corresponding concentration to that Absorbance.

10. Repeat this procedure with the 6 calibration distillates of the curve. Once the curve is entered, press: **Best Fit Calculate** and then press: **Conc**. The Cyanide Calibration curve is now ready. A calibration coefficient of 0.999 or greater is required for the working standard curve. If less than 0.999; rerun standards.

11. Pour samples into 10ml cell and place into cell compartment and read samples mg CN-/L directly from display. Record reading in Cyanide bench book.

12. Calculations :

Calculate cyanide in sample as follows:

$$mg\ CN^{-} = \frac{mg}{L}\ from\ display\ x \frac{Final\ Volume(ml)}{Sample\ Volume\ or\ Weight(ml\ /\ g)}$$

Example = spectro reading 0.041 mg/L x 10 mL/5 mL = 0.082 mg/L

Relative Percent Difference: $RPD = \frac{(S-D)}{\left[\frac{S+D}{2}\right]} \times 100$

Where: S = Initial sample result
D = Duplicate sample result

Spike Recovery Percent Recovery: $\frac{SSR-SR}{SA} \times 100$

Where: SSR = Spike sample result
SR = Sample (unspiked) result
SA = Spike added

8.0 QUALITY CONTROL

All of the quality control items employed and evaluated are provided in Table 1. In addition, the table indicates the frequency of each QC item along with appropriate courses of corrective action. The analyst will follow SOP # QA-007 and complete the appropriate review form upon completion of the analysis.

9.0 METHOD PERFORMANCE

Precision and accuracy studies are performed on as needed basis. (Ex. new instrument, etc.). Method Detection Limit studies are performed every six months.

10.0 EQUIPMENT MAINTENANCE AND TROUBLESHOOTING

All equipment shall be maintained and calibrated according to manufacturer's procedures. When equipment is not performing as required, the instrument shall not be used until it is recalibrated or replaced.

11.0 SAFETY

Eye protection and gloves must be worn while performing the analyses. Every laboratory area has eyewash, emergency shower, and fire extinguisher. The metals lab also has dust masks available for use with dust samples. The air system throughout 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. A reference file of material safety data sheets (MSDSs) is available to all personnel.

Specific attention be paid (but not limited) to:

- 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.

- 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.

12.0 WASTE DISPOSAL AND POLLUTION PREVENTION

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

13.0 DEFINITIONS

Sample Batch: samples of the same or similar matrix; for this method, a sample batch consists of 20 samples or less.

Method Blank: an analyte-free matrix to which all reagents are added in the same volumes or proportions as used in the sample processing. The method blank is carried through the complete sample preparation and analytical procedure. The method blank is used to document contamination resulting from the analytical process.

Laboratory Control Sample (also known as Laboratory Fortified Blank, Spiked Blank, or QC Check Sample): a sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes. It is generally used to establish intra-laboratory or analyst-specific precision and bias or to assess the performance of all or a portion of the measurement system.

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

Matrix Spike Duplicate (also known as Spiked Sample or Fortified Sample Duplicate): a second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

Initial Calibration (ICAL): set of operations that establish, under specific conditions, the relationship between values of quantities indicating by a measuring instrument, or values represented by a material measure or a reference material, and the corresponding values realized by standards. An analytical instrument is said to be calibrated when an instrumental response can be related to the concentration of the target anions. This relationship is depicted graphically, and referred to as a "calibration curve". Initial calibration curves must be established based upon the requisite number of standards identified within the method for each target analyte.

Laboratory Duplicate: aliquots of sample taken from the same container under the same laboratory conditions and processed and analyzed under the same conditions but independently.

Initial Calibration Verification (ICV): the initial calibration verification standard (different lot # or manufacturer from the initial calibration standard) shall verify the initial calibration curve. The initial calibration verification standard involves the analysis of all target analytes each time the initial calibration is performed.

Continuing Calibration Verification Standard (CCV): a standard solution that is used to check the validity of a calibration curve on a daily basis. It also provides information on satisfactory maintenance and adjustment of the instrument during sample analysis.

14.0 REFERENCES

Department of Defense, *Quality Systems Manual for Environmental Laboratories* (DoD QSM), DoD Environmental Data Quality Workgroup, Department of Navy, Lead Service, Based on NELAC Voted Revision 5 June 2003, Version 4.1, April 22,2009.

Lachat Instrument Micro-Dist Distillation System Reference and Methods Manual.

USEPA, Method for the Chemical Analysis of Water and Wastes; Method 335.4.

Table 1. Quality Control Items, Frequency, and Corrective Action

QC Items	Frequency	Acceptance Criteria	Corrective Action	Corrective Action after Reanalyzing
Method (preparation) Blank	One per batch	<MDL or 1/10 Regulatory limit	Remove contamination and re-digest samples.	Notify client. Flag data.
Laboratory Control Sample (LCS)	One for every 10 samples	90%-110%	Re-digest the sample set.	Notify client. Flag data.
Continuing Calibration Verification (CCV)	One for every 10 samples	90% - 110%	All samples bracketed by CCV outside the acceptable control limits must be re-digested and re-analyzed.	Notify client. Flag data.
Matrix Duplicate	1/ 20 samples 1/10 samples for drinking water samples	RPD<20%	Re-digest samples and QC.	Notify client. Flag data.
Matrix Spike	1/ 20 samples 1/10 samples for drinking water samples	80%-120%	Analyze by Method of Standard Additions	Notify client. Flag data.
Matrix Spike Duplicate	One for every 20 samples for Level 3 and DoD	80%-120%	Analyze by Method of Standard Additions	Notify client. Flag data.
Dilution & Rerun	If result indicates suppressive interference	Does interference persist?	Yes. Rerun with Method of Standard Additions	Notify client. Flag data.

Table 2. Quality Control Items, Frequency, and Corrective Action for DoD Projects

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Initial calibration (ICAL) (six standards and a calibration blank)	Daily ICAL prior to sample analysis.	$r \geq 0.995$.	Correct problem, then repeat ICAL.	Flagging criteria are not appropriate.	Problem must be corrected. No samples may be run until calibration has passed. All calibration standards must be distilled if samples expected to contain sulfides.
Distilled standards (one high and one low)	Once per multipoint calibration.	Within ± 15% of true value.	Correct problem, then repeat distilled standards.	Flagging criteria are not appropriate.	Problem must be corrected. No samples may be run until distilled standards have passed.
Second source calibration verification (ICV)	Once after each ICAL, prior to beginning a sample run.	Within ± 15% of true value.	Correct problem, then and verify second source standard. If that fails, correct problem and repeat ICAL.	Flagging criteria are not appropriate.	Problem must be corrected. No samples may be run until calibration has been verified.
Method blank	One per preparatory batch.	No analytes detected > ½ RL and > 1/10 the amount measured in any sample of 1/10 the regulatory limit (whichever is greater). Blank result must not otherwise affect sample results.	Correct problem. If required, reprep and reanalyze method blank and all samples processed with contaminated blank.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply flag to all results for the specific analyte(s) in all samples in the associated preparatory batch.	Problem must be corrected. Results may not be reported without a valid method blank. Flagging is only appropriate in cases where the samples cannot be reanalyzed.
LCS	One per preparatory batch.	QC acceptance criteria specified by DoD, if available.	Correct problem, then reprep and reanalyze the LCS and all samples in the associated preparatory batch for failed analytes, if sufficient sample material is available.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply flag to specific analyte(s) in all samples in the associated preparatory batch.	Problem must be corrected. Results may not be reported without a valid LCS. Flagging is only appropriate in cases where the samples cannot be reanalyzed.
Matrix spike (MS)	One per preparatory batch.	For matrix evaluation, use QC acceptance criteria specified by DoD for	Examine the project-specific DQOs. If the matrix spike	For specific analyte in the parent sample. Apply flag if acceptance	If MS results are outside the LCS limits, the data shall be evaluated to determine the source of difference and to

		LCS.	falls outside the DoD criteria, the method of standard additions shall be used for the analysis.	criteria are not met.	determine if there is a matrix effect or analytical error.

QC Check	**Minimum Frequency**	**Acceptance Criteria**	**Corrective Action**	**Flagging Criteria**	**Comments**
Matrix spike duplicate (MSD) or sample duplicate (replicate)	One per preparatory batch.	MSD: For matrix evaluation use QC acceptance criteria specified by DoD for LCS. MSD or sample duplicate: RPD ≤ 20% (between MS and MSD or sample and sample duplicate).	Correct problem and reanalyze sample and duplicate.	Apply flag if sample cannot be rerun or reanalysis does not correct problem.	The data shall be evaluated to determine the source of difference.
Results reported between DL and LOQ	NA	NA	NA	Apply flag to all results between DL and LOQ.	

Figure 1:

Analysis: ***Total Cyanide*** ***CAL ID#*** _____

Analyst: ___ **Method #**335.4/ 8027(Hach) **Program #**175 HACH DR/4000 Spec.

Date Run: **Detection Limit:** 0.005 mg/l **Wavelength** 612 nm

ID STD ID/TAG	MERIT # TIME	DILUTION	(mg/l) CONC.	ABS	(mg/l) %S	RESULT	SPIKE	(Run) %REC
	Blank	10/10						
	Blank Spike	10/.05ml 10ppm			0.050			
	Control	10 / 1ml			0.920		ERA P180-502	
	LCS	10/0.1ml 10ppm			0.100			

Notes: **Lachat micro-distillation / sample prep. ; double distillation for lower detection limit / Dist. Tubes**

User fill ID# _____

Releasing Solution ID _____**CyaniVer3 lot** ___**;** **CyaniVer4 lot** ____ **;** **CyaniVer5 lot**_____

Peer Review: _____**CN- Stock ID** _____**QC Batch ID** _____ **Chlorine chk** _____

Distillation block temp: _____ **Distillation (start/end) time:** _____

STANDARD OPERATING PROCEDURE

LACHATCN SOP FOR TOTAL CYANIDE DISTILLATION (LACHAT MICRO-DIST)
METHOD EPA 335.4 AND STANDARD METHOD 4500-CN-E

APPROVALS:

5/27/11

Barbara Richardson, QA Officer — Date

5/27/11

Maya V. Murshak, Technical Director — Date

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Number	Description of Change	Date
001-004	Previous changes were not documented	
005	Updated to comply with DoD QSM and ISO 17025 standards.	5/27/11
006		
007		
008		
009		
010		
011		
012		
013		
014		
015		

1.0 SCOPE AND APPLICATION

This method is applicable to drinking, surface, groundwaters, treated mixed wastewater, soils, sludges, and some industrial process waters. The method is suitable for distilling samples containing from 0.002 to 5.0 mg Free and Combined Cyanide / L with the Micro-Dist distillation apparatus.

2.0 SUMMARY OF THE METHOD

This SOP is a procedure for cleanup of liquid and soil samples for the determination of total cyanide. The Micro-Dist system was developed for the analytical distillation of samples which are largely aqueous. The system strips analytical distillation down to its bare essentials. The sample is pipetted into a sample tube and sealed to a collector tube. This assembly is placed in a special heating block which fits very tightly, allowing the poorly-conducting polypropylene to be heated rapidly yet locally. As the sample boils, its vapors rise within the tube and pass through a hydrophobic, porous membrane. The vapors condense above the membrane to form droplets, which pool over the membrane, but cannot pass back through it. The short, vertical path of distillation is possible because of the physical separation of distilling sample and distillate by the hydrophobic membrane. See SOP for Total Cyanide Pyridine-Pyrazalone Colorimetric for testing the distillate for Total Cyanide.

3.0 INTERFERENCES

Oxidizing agents can destroy cyanides during storage.
Sulfide can complex with cyanide in sample or distillate.
Fatty acids cause interference during distillation.
Carbonate causes interference during distillation.
Aldehydes cause interference during distillation.
Glucose/sugars cause interference during distillation.
Sulfur-containing compound causes interference during distillation by forming free sulfide that is captured in distillate.

4.0 APPARATUS AND MATERIALS

Micro-Dist Heating Block, 120 VAC transformer.
Blue sample tube rack, 72 tube capacity.
White Collector tube rack, 40 tube capacity.
A pair of heat-resistant gloves.
50 ml polyethylene centrifuge tubes.
Red Micro-Dist assembly press.

Pipettor.

100 ml Pyrex beaker.

Cyanide-1 Collector tubes with sample tubes (0.25 M NaOH) Shelf life / 1 yr.

Volumetric flasks

Thermometer

15 ml glass vials for colorimetric analysis.

5.0 REAGENTS

Deionized (DI) water.

CN- Releasing Solution, $MgCl_2$ / H_2SO_4: **Make up in hood.** In 100 ml Pyrex beaker, Dissolve 8.05 g of $MgCl_2$ in 27.7 ml of DI water and add slowly while mixing 19 ml of Concentrated H_2SO_4. Let cool. Pour into 125 ml amber glass container. *See CN- Releasing Solution Prep Log*. Shelf life is 2 months. $MgCl_2$ / Hach H_2SO_4 / VWRBrand.

Sulfamic Acid, NH_2SO_3H. / Hach Shelf life 5 years.

2.5 N HCl (250/52 ml concentrated HCl) *See Wet Chem Reagent Prep Log*. Shelf life 1 year.

1.0 N NaOH (200/8 g NaOH pellets). *See Wet Chem Reagent Prep Log*. Shelf life 1 year.

Phenolphthalein - Weigh 0.125 g of phenolphthalein into a 25 ml volumetric flask, pipette 12.5 ml DI & 12.5 ml Isopropyl alcohol into flask and dissolve. *See Wet Chem Reagent Prep Log*. Shelf life 1 year.

Potassium iodide – starch test paper. Hach.

Acetate buffer solution, pH 4.6; Hach shelf life 1 year.

Sodium Thiosulfate Pentahydrate ACS grade Hach Shelf life 5 years.

Zinc Acetate 2 N. Hach Shelf life 2 years.

Lead acetate test paper. Hach.

6.0 SAMPLE HANDLING AND PRESERVATION

Liquid samples must be collected in polyethylene containers preserved with NaOH (pH >12) and refrigerated at 4 ± 2ºC. Soil samples are collected in non-preserved glass containers and refrigerated at 4 ± 2ºC. Samples must be run within 14 days of collection.

7.0 PROCEDURE

1. Preliminary Treatment of Sample
   I. Oxidizing agents, like chlorine, decompose most cyanide. Test sample by placing a drop on a strip of potassium iodide paper previously moistened with acetate buffer

solution, pH 4.6. If paper turns blue, add sodium thiosulfate, adding less than 0.1g $Na_2S_2O_3$/L.

II. Oxidized products of sulfide convert CN- to SCN- rapidly, especially at high pH. Test for sulfide by placing a drop of sample on lead acetate test paper previously moistened with acetate buffer solution, pH 4.6. Darkening of the paper indicates presence of sulfide. Add 3 drops of zinc acetate 2N per 100ml sample to settle out sulfide, let settle for 30min. Pour off supernatant into another bottle leaving sulfide precipitate behind. Run supernatant for total cyanide.

III. Sulfamic acid is added in the distillation process to avoid nitrite (NO_2-) interference.

2. Standard & QC Preparation

I. Blanks: Method blank follows the entire procedure including digestion. 5 ml of DI water. Then follow steps 7.5-7.18.

II. LCS (0.1 ppm): Laboratory control sample follows entire procedure including digestion. 5 ml of DI water plus 0.1 ml of 10 ppm of working standard (Working standard: 49.5 ml DI water plus 0.5 ml of stock standards @ 1000 ppm) Then follow steps 7.5-7.18.

III. MS/MSD (0.1 ppm): matrix spike/matrix spike duplicate follows entire procedure including digestion. 5 ml of sample plus 0.1 ml of 10 ppm of working standard (Working standard: 49.5 ml DI water plus 0.5 ml of stock standards @ 1000 ppm) Then follow steps 7.5-7.18.

IV. Prepare a set of six standards ranging from 0.005 – 0.200 mg/l.

i. Prepare Stock Cyanide solution as follows: Dissolve 0.2 g NaOH and 0.251 g KCN in 100 ml DI = 1,000 ppm.

ii. Prepare a 1 ppm working standard: Pipet 0.1 ml into a 100 ml volumetric flask and bring to volume. *See Cyanide Standards Prep Log*.

iii. Prepare a Blank, 0.005, 0.01, 0.02, 0.05, 0.100 & 0.200 mg/l standard solutions for 10 ml final volume.

iv. Distill standards in the same manner as the samples following steps 7.5-7.19.

3. Set dial of distillation block to 120 degrees C. Allow the heater block to warm up. This will take about 40 minutes.

4. Put as many collector tubes into the white rack as you have samples; up to 21 maximum for block. Number tubes from 1 – 21 with a marker. Re-seal the foil pack after removing the tubes if there are any left to avoid evaporation of NaOH solution in tubes.

5. Put as many sample tubes into the blue rack as you have samples, matching up with the number of collector tubes.

6. With sample numbers corresponding to tube numbers recorded on bench sheet begin pipetting 5 ml of liquids into sample tubes. (When distilling solids use 0.1-0.5 g of sample and 3 ml DI water)

7. When all sample tubes are filled with sample for each set, add 2 small crystals of Sulfamic acid into each sample tube. Add, 0.7 ml of releasing solution using an automatic pipettor to sample tube (1 at a time then cap). **Do this in a hood.**

8. Immediately push the uncapped bottom end of corresponding collector tube over the end of the sample tube to start seal. Then place the assembly in the press, putting the sample tube through the hole in the white base. Press down on the handle until the stop ring on the sample tube hits the bottom of the collector tube.

9. Push each tube all the way into the heater block pre-heated to 120 degrees C so that the collector stop ring touches the block.

10. For water samples, set timer and leave in block for 30 minutes. For solids or sludges, set timer and leave in block for 30 minutes.

11. When time is up, put on heat resistant gloves. Remove the first tube from the block and immediately pull off its sample tube by twisting it back-and-forth while pulling down. Dispose of sample tube and hot solution left in it by dropping it into the sink or waste bucket. Place each collector tube into the white rack.

12. Allow tubes to cool for about 10 minutes at least.

13. For each collector tube, hold the tube horizontally and rinse its walls with the distillate in order to homogenize it. Then, slowly roll the distillate around in the tube to gather all droplets clinging to the tube walls into the bulk of the distillate. Slowly return collector tube to an upright position and lightly tap tube to get all distillate to bottom of tube.

14. Break away the top section of the collector tube by pulling hard towards yourself to break, then twisting and tearing off the top.

15. Gently pour distillate into 15ml glass vial. Keep sample below 10ml, so sample can be neutralized before analysis.

16. Add 1 drop of Phenolpthlalein, sample should turn pink (pH > 8.3)

17. Add 2.5N HCl drop wise to sample until it just goes clear. A 0.5N HCl solution may be used when color change is close to keep from going too acidic. Sample pH should around 7 before reagents are added.

18. Bring all samples to 10 ml final volume using calibrated 15ml glass vial.

19. Samples are now ready for cyanide analysis using Merit's SOP #033354.

8.0 QUALITY CONTROL

All of the quality control items employed and evaluated are provided in Table 1. In addition, the table indicates the frequency of each QC item along with appropriate courses of corrective action. The analyst will follow SOP #_____ and complete the appropriate review form upon completion of the analysis.

9.0 METHOD PERFORMANCE

This method is evaluated by testing a laboratory control sample and duplicate samples.

10.0 EQUIPMENT MAINTENANCE AND TROUBLESHOOTING

All equipment shall be maintained and calibrated according to manufacturer's procedures. When equipment is not performing as required, the instrument shall not be used until it is recalibrated or replaced.

11.0 SAFETY

Eye protection and gloves must be worn while performing the analyses. Every laboratory area has eyewash, emergency shower, and fire extinguisher. The metals lab also has dust masks available for use with dust samples. The air system throughout 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.

A reference file of material safety data sheets (MSDSs) is available to all personnel. Specific attention be paid (but not limited) to:

a. 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.
b. 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.

12.0 WASTE DISPOSAL AND POLLUTION PREVENTION

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

13.0 DEFINITIONS

Sample Batch: Samples of the same or similar matrix; for this method, a sample batch consists of 20 samples or less.

Method Blank: An analyte-free matrix to which all reagents are added in the same volumes or proportions as used in the sample processing. The method blank is carried through the complete sample preparation and analytical procedure. The method blank is used to document contamination resulting from the analytical process.

Laboratory Control Sample (also known as Laboratory Fortified Blank, Spiked Blank, or QC Check Sample): A Sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes. It is generally used to establish intra-laboratory or analyst-specific precision and bias or to assess the performance of all or a portion of the measurement system.

Matrix Spike (also known as Spiked Sample or Fortified Sample): A sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent

estimate of target analyte concentration is available. Matrix spikes are used, for example, to determine the effect of the matrix on a method's recovery efficiency.

Matrix Spike Duplicate (also known as Spiked Sample or Fortified Sample Duplicate): A second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

Laboratory Duplicate: Aliquots of sample taken from the same container under the same laboratory conditions and processed and analyzed under the same conditions but independently.

Initial Calibration (ICAL): Set of operations that establish, under specific conditions, the relationship between values of quantities indicating by a measuring instrument, or values represented by a material measure or a reference material, and the corresponding values realized by standards. An analytical instrument is said to be calibrated when an instrumental response can be related to the concentration of the target anions. This relationship is depicted graphically, and referred to as a "calibration curve". Initial calibration curves must be established based upon the requisite number of standards identified within the method for each target analyte.

14.0 REFERENCES

Department of Defense, *Quality Systems Manual for Environmental* Laboratories (DoD QSM), DoD Environmental Data Quality Workgroup, Department of Navy, Lead Service, Based on NELAC Voted Revision 5 June 2003, Version 4.1, April 22,2009.

Lachat Instrument Micro-Dist Distillation System Reference and Methods Manual.

USEPA, Method for the Chemical Analysis of Water and Wastes; Method 335.4.

USEPA, *SW-846*, Revision 3; Method 9010B.

USEPA, *Standard Methods for the Examination of Water and Wastewater*, 20th Edition, Method 4500-CN-E, Cyanide, Residual, for Cyanides Amenable to Chlorination after Distillation, Colorimetric.

Table 1. Quality Control Items Frequency, and Corrective Action

QC Items	**Frequency**	**Acceptance Criteria**	**Corrective Action**	**Corrective Action after Reanalyzing**
Method (preparation) Blank	One per batch	<MDL or 1/10 Regulatory limit	Remove contamination and rerun	Notify client. Flag data.
Laboratory Control Sample (LCS)	One for every 10 samples	90%-110%	Rerun	Notify client. Flag data.
Matrix Duplicate	1/ 20 samples 1/10 samples for drinking water samples	RPD<20%	Rerun entire set	Notify client. Flag data.
Matrix Spike	1/ 20 samples 1/10 samples for drinking water samples	80%-120%	Analyze by Method of Standard Additions	Notify client. Flag data.
Matrix Spike Duplicate	One for every 20 samples for Level 3 and DoD	80%-120%	Analyze by Method of Standard Additions	Notify client. Flag data.
Dilution & Rerun	If result indicates suppressive interference	Does interference persist?	Yes. Rerun with Method of Standard Additions	Notify client. Flag data.

Table 2. Quality Control Items, Frequency and Corrective Action for DoD Projects

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Initial calibration (ICAL) (six standards and a calibration blank)	Daily ICAL prior to sample analysis.	$r \geq 0.995$.	Correct problem, then repeat ICAL.	Flagging criteria are not appropriate.	Problem must be corrected. No samples may be run until calibration has passed. All calibration standards must be distilled if samples expected to contain sulfides.
Distilled standards (one high and one low)	Once per multipoint calibration.	Within ± 15% of true value.	Correct problem, then repeat distilled standards.	Flagging criteria are not appropriate.	Problem must be corrected. No samples may be run until distilled standards have passed.
Method blank	One per preparatory batch.	No analytes detected > ½ RL and > 1/10 the amount measured in any sample of 1/10 the regulatory limit (whichever is greater). Blank result must not otherwise affect sample results.	Correct problem. If required, re-prep and reanalyze method blank and all samples processed with contaminated blank.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply flag to all results for the specific analyte(s) in all samples in the associated preparatory batch.	Problem must be corrected. Results may not be reported without a valid method blank. Flagging is only appropriate in cases where the samples cannot be reanalyzed.
LCS	One per preparatory batch.	QC acceptance criteria specified by DoD, if available.	Correct problem, then re-prep and reanalyze the LCS and all samples in the associated preparatory batch for failed analytes, if sufficient sample material is available.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply flag to specific analyte(s) in all samples in the associated preparatory batch.	Problem must be corrected. Results may not be reported without a valid LCS. Flagging is only appropriate in cases where the samples cannot be reanalyzed.
Matrix spike (MS)	One per preparatory batch.	For matrix evaluation, use QC acceptance criteria specified by DoD for LCS.	Examine the project-specific DQOs. If the matrix spike falls outside the DoD criteria, the method of standard additions shall be used for the analysis.	For specific analyte in the parent sample. Apply flag if acceptance criteria are not met.	If MS results are outside the LCS limits, the data shall be evaluated to determine the source of difference and to determine if there is a matrix effect or analytical error.
Matrix spike duplicate (MSD) or sample duplicate (replicate)	One per preparatory batch.	MSD: For matrix evaluation use QC acceptance criteria specified by DoD for LCS. MSD or sample duplicate: RPD ≤ 20% (between MS and MSD or sample and sample duplicate).	Correct problem and reanalyze sample and duplicate.	Apply flag if sample cannot be rerun or reanalysis does not correct problem.	The data shall be evaluated to determine the source of difference.

Figure 1: Cyanide Distillation Bench Sheet

Analysis: ***Total Cyanide*** **CAL ID#** _____

Analyst:_____ **Method #**335.4/ 8027(Hach) **Program #**175 HACH DR/4000 Spec.

Date Run:_____ **Detection Limit:** 0.005 mg/l **Wavelength:** 612 nm

			(mg/l)			(mg/l)	(mg/l)			(Run)
ID	**Merit #**	**Dilution**	**Conc.**	**ABS**	**%S**	**Result**	**Spike**	**%Rec**		
STD ID/Tag	**Time**									
	Blank	10/10								
	Blank Spike	10/.05ml of 10ppm					0.050			
	Control	10 / 1ml					0.920		Era P180-502	
	LCS	10/0.1ml of 10ppm					0.100			

Notes:Lachat micro-distillation / sample prep. ; double distillation for lower detection limit / Dist. Tubes

Releasing Solution ID _____ CyaniVer3 lot _____; CyaniVer4 lot _____; CyaniVer5 lot_____

Peer Review (Analyst/Date):_____ CN- Stock ID _____ QC Batch ID
Chlorine chk _____

Distillation block temp: _____ Distillation (start/end) time: _____

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.

_____

Analyst Date

_____

Andy Ball, QA Officer Date

_____

Maya V. Murshak, Technical Director Date

STANDARD OPERATING PROCEDURE

ION CHROMATOGRAPHY FOR ANALYZING ANIONS (CHLORIDE, FLUORIDE, NITRATE, NITRITE, BROMIDE & SULFATE) USING THE DX-100 DIONEX ION CHROMATOGRAPH EPA METHOD 300.0

APPROVALS:

5/27/11

QA Officer — Date

5/27/11

Technical Director — Date

Number	Description of Change	Date
001-006	Previous changes were not documented	
007	Updated to comply with DoD QSM and ISO 17025 standards.	5/27/11
008		
009		
010		
011		
012		
013		
014		
015		
016		
017		

1.0 SCOPE AND APPLICATION

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

The anion reporting limits are as follows:
Bromide – 1 mg/l
Chloride – 1 mg/l
Fluoride – 0.2 mg/l
Nitrate-N – 0.1 mg/l
Nitrite-N – 0.1 mg/l
Sulfate – 1 mg/l.

2.0 SUMMARY OF THE METHOD

This SOP is a procedure for evaluating Anions (Chloride, Sulfate, Nitrate-N, Nitrite-N, Fluoride & Bromide) in liquid samples. A water sample is injected into a stream of carbonate-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

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. The acetate anion elutes early during the chromatographic run. The retention times of the anions also seem to differ when large amounts of acetate are present. Therefore, this method is not recommended for leachates of solid samples when acetic acid is used for pH adjustment.

4.0 APPARATUS & MATERIALS

Ion Chromatograph (DX-100 Dionex).

Anion separator column, resolves Br-; Cl-; SO_4; NO_3-; NO_2-; F- and PO_4 (not run with this method).

Guard column, protects separator column.

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

5 ml polyvials with filtercaps.

50 ml centrifuge tubes with screw caps.

Filtering apparatus & 0.5 micron filters (Metrigard, Glass Fiber Filter, 47mm /GE Water & Process Technologies).

Auto-pipettors (.05 – 1 mL).

5.0 REAGENTS

Deionized (DI) water.

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

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.

Control ERA.

Standard Anion solutions:

- Chloride (Hach Std) 1,000ppm. Expiration listed on standard bottle.
- Sulfate (Hach Std) 1,000ppm Expiration listed on standard bottle.
- Fluoride (Hach Std) 100ppm Expiration listed on standard bottle.
- Nitrate-N (Hach Std) 100ppm Expiration listed on standard bottle.
- Bromide (KBr) (Hach) 1,000ppm 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.
- Nitrite-N ($NaNO_2$) (Hach) 100ppm Dissolve: 0.0498g $NaNO_2$ in water and dilute to 100ml, *See stock solutions prep log.* Prepared fresh every 48 hours as need. $NaNO_2$ shelf life is 5 years.

6.0 SAMPLE HANDLING AND PRESERVATION

Samples must be collected in unpreserved high-density polyethylene containers. All bottles purchased by Merit are pre-cleaned certified. 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

1. System Startup and Test

   I. 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.

   II. Confirm system air is working and pressure is between 50 and 60 psi.

   III. Confirm that the eluent container is at least half full before a run. If not, make up working eluent: Add new working eluent as follows.

      a. Turn eluent pressure switch to off (should be set at 5psi).

      b. Take cap off eluent container and slowly add working eluent, replace cap and swirl to mix.

      c. Re-pressurize eluent container by turning eluent switch to on.

      d. Open valve below Pulse Damper and allow to bleed for 1 minute.

   IV. Ensure pump flow rate adjustment is correct (180 = 1.8 ml/min).

   V. Make sure detector range is set to operating range 30 uS.

   VI. Check waste container, if close to full empty before startup.

   VII. 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).

   VIII. Let system equilibrate for at least 45 minutes before running samples (Conductivity reading should be between 15 and 17).

   IX. Set Low Limit pressure switch to on.

2. Running the Analysis

I. All samples must be filtered through 0.5 micron filters prior to being analyzed.

II. All Anion runs begin with a Blank, Blank Spike, ERA Control and LCS.

III. Fill polyvial with 5ml of sample to be tested.

IV. Place filtercap on polyvial and push to top of vial with filtercap tool.

V. The sample can now be placed in autosampler tray.

VI. Open schedule program; Double-click to setup IC run.

VII. Type in sample ID under **Sample Name**; Norm.met under **Method**; the date of run under **Data File**, ex.(090501); & dilution factor under **Dil**.

VIII. Click on **File; Save As** (type in date); click **ok.**

IX. Go to Run program, click on **Load**; **Schedule,** scroll through to find schedule just set and click **ok.**

X. Push **Run** button on autosampler the 1st tray will then load.

XI. Push green **Run** button on Computer Interface. The scheduled run will now begin.

3. Calibration

I. 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.

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

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

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

V. 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**.

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

VII. 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.

4. Calculations

I. Calculate sample results using the following equation:

C = H x F x 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.

II. Relative Percent Difference: $$RPD = \frac{(S - D)}{\left[\frac{S + D}{2}\right]} \times 100$$

Where: S = Initial sample result

D = Duplicate sample result

III. Spike Recovery Percent Recovery: $$\frac{SSR - SR}{SA} \times 100$$

Where: SSR = Spike sample result

SR = Sample (unspiked) result

SA = Spike added

8.0 QUALITY CONTROL

All of the quality control items employed and evaluated are provided in Table 1and 2. In addition, the table indicates the frequency of each QC item along with appropriate courses of corrective action. The analyst will follow SOP # _____ and complete the appropriate review form upon completion of the analysis.

9.0 METHOD PERFORMANCE

Precision and accuracy studies are performed on as needed basis.

Method Detection Limit studies are performed every 6 months.

10.0 EQUIPMENT MAINTENANCE AND TROUBLESHOOTING

All equipment shall be maintained and calibrated according to manufacturer's procedures. Each instrument is assigned a maintenance logbook. All maintenance performed on the instrument must be recorded. Additionally, any modifications to the instrument settings shall be noted in the specific instrument logbook. Maintenance procedures provided in the equipment manual shall be followed. When equipment is not performing as required, the instrument shall not be used until it is recalibrated or replaced.

11.0 SAFETY

Every laboratory area has eyewash, emergency shower, and fire extinguisher. The metals lab also has dust masks available for use with dust samples. The air system throughout 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. A reference file of material safety data sheets (MSDSs) is available to all personnel.

12.0 WASTE DISPOSAL AND POLLUTION PREVENTION

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

13.0 DEFINITIONS

Sample Batch: samples of the same or similar matrix; for this method, a sample batch consists of 20 samples or less.

Method Blank: an analyte-free matrix to which all reagents are added in the same volumes or proportions as used in the sample processing. The method blank is carried through the complete sample preparation and analytical procedure. The method blank is used to document contamination resulting from the analytical process.

Laboratory Control Sample (also known as Laboratory Fortified Blank, Spiked Blank, or QC Check Sample): a sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes. It is generally used to establish intra-laboratory or analyst-specific precision and bias or to assess the performance of all or a portion of the measurement system.

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

Matrix Spike Duplicate (also known as Spiked Sample or Fortified Sample Duplicate): a second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

Laboratory Duplicate: aliquots of sample taken from the same container under the same laboratory conditions and processed and analyzed under the same conditions but independently.

Blank Spike: a sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes at a concentration in the bottom half of the calibration.

Control Standard: the control standard (different lot # or manufacturer from the initial calibration standard) shall verify the initial calibration curve. The control standard involves the analysis of all target analytes each time the initial calibration is performed.

Initial Calibration (ICAL): set of operations that establish, under specific conditions, the relationship between values of quantities indicating by a measuring instrument, or values represented by a material measure or a reference material, and the corresponding values realized by standards. An analytical

instrument is said to be calibrated when an instrumental response can be related to the concentration of the target anions. This relationship is depicted graphically, and referred to as a "calibration curve". Initial calibration curves must be established based upon the requisite number of standards identified within the method for each target analyte.

Initial Calibration Verification (ICV): the initial calibration verification standard (different lot # or manufacture from the initial calibration standard) shall verify the initial calibration curve. The initial calibration verification standard involves the analysis of all target analytes each time the initial calibration is performed.

Continuing Calibration Verification Standard (CCV): a standard solution that is used to check the validity of a calibration curve on a daily basis. It also provides information on satisfactory maintenance and adjustment of the instrument during sample analysis.

14.0 REFFERENCES

Department of Defense, *Quality Systems Manual for Environmental Laboratories* (DoD QSM), DoD Environmental Data Quality Workgroup, Department of Navy, Lead Service, Based on NELAC Voted Revision 5 June 2003, Version 4.1, April 22,2009.

Dionex DX-100 Ion Chromatograph Instrument Manual.

US EPA *Determination of Inorganic Anions by Ion Chromatography*, Method 300.0, Revision 2.2, 1999.

Table 1. Quality Control Items, Frequency and Corrective Action

QC Item	**Frequency**	**Acceptance Criteria**	**Corrective Action**	**Corrective Action after Reanalyzing**
Method (preparation) Blank	One per batch	<MDL or 1/10 Regulatory limit	Remove contamination and rerun	Notify client. Flag data.
Blank Spike	One every 10 for drinking Water and DoD/ One every 20 for solids and wastewaters	90%-110%	Re-prep blank spike and rerun	Re-calibration and reanalyze
Control Standard (mid range check standard)	One every 20 sample	90%-110%	Reanalyze	Discontinue sample analysis, determine cause and/or in case of drift, recalibrate. Reanalyze all samples following last acceptable control.
Laboratory Control Sample (LCS) Soluble or insoluble	One every 10 for drinking Water / One per batch	90%-110%	Rerun	Notify client. Flag data.
Matrix Duplicate	Every 10 drinking Water / One per batch	RPD<15%	Rerun entire set	Notify client. Flag data.
Matrix Spike	Every 10 drinking Water / One per batch	80%-120%	Analyze by Method of Standard Additions	Notify client. Flag data.
Matrix Spike Duplicate	Level 3 One every 10 samples	80%-120% RPD<15%		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.

Table 2: Quality Control Items, Frequency, and Corrective Action for DoD Projects

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Retention time (RT) window width calculated for each analyte	After method set-up and major maintenance (e.g., column change)	RT width is ± 3 times standard deviation for each analyte RT over a 24-hour period.	NA	NA	
Initial calibration (ICAL) for all analytes (minimum three standards and one calibration blank)	ICAL prior to sample analyses.	$r \geq 0.995$	Correct problem, then repeat ICAL.	Flagging criteria not appropriate.	Problem must be corrected. No sample may be run until ICAL has passed.
Initial calibration verification (ICV) (second source)	Once after each ICAL, prior to beginning a sample run	All analytes within ± 10% of true value and retention times within appropriate windows.	Correct problem and verify second source standard. Rerun second source verification. If that fails, correct problem and repeat ICAL.	Flagging criteria not appropriate.	Problem must be corrected. No sample may be run until calibration has been verified.
Retention time window position establishment for each analyte	Once per multipoint calibration.	Position shall be set using the midpoint standard of the ICAL curve when ICAL is performed On days when ICAL is not performed, the initial CCV is used.	NA	NA	
Midrange continuing calibration verification (CCV)	After every 10 field samples and at the end of the analysis sequence.	All project analytes within established retention time windows. Within ± 10% of true value.	Correct problem, then rerun calibration verification. If that fails, then repeat ICAL. Reanalyze all samples since the last successful calibration verification.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply flag to all results for the specific analytes in all samples since the last acceptable calibration verification.	Problem must be corrected. Results may not be reported without a valid CCV. Flagging is only appropriate in cases where the samples cannot be reanalyzed. Retention time windows are updated per the method.

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Method blank	One per preparatory batch.	No analytes detected > ½ RL and > 1/10 the amount measured in any sample of 1/10 the regulatory limit (whichever is greater). Blank result must not otherwise affect sample results.	Correct problem. If required, reprep and reanalyze method blank and all samples processed with contaminated blank.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply flag to all results for the specific analyte(s) in all samples in the associated preparatory batch.	Problem must be corrected. Results may not be reported without a valid method blank. Flagging is only appropriate in cases where the samples cannot be reanalyzed.
LCS containing all analytes to be reported	One per preparatory batch.	Laboratory in-house limits not to exceed ± 20%. Control limits may not be greater than ± 3 times the standard deviation of the mean LCS recovery.	Correct problem, then reprep and reanalyze the LCS and all samples in the associated preparatory batch for failed analytes, if sufficient sample material is available.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply flag to specific analyte(s) in all samples in the associated preparatory batch.	Problem must be corrected. Results may not be reported without a valid LCS. Flagging is only appropriate in cases where the samples cannot be reanalyzed.
Matrix spike (MS)	One per preparatory batch.	For matrix evaluation use laboratory in house LCS limits (not to exceed ± 20%).	Examine the project-specific DQOs. Contact the client as to additional measures to be taken.	For the specific analyte(s) in the parent sample, apply flag if acceptance criteria are not met.	For matrix evaluation only. If MS results are outside the LCS limits, the data shall be evaluated to determine the source of difference and to determine if there is a matrix effect or analytical error.
Matrix spike duplicate	One per preparatory batch.	For matrix evaluation use laboratory in house LCS limits (not to exceed ± 20%). RPD ≤ 15% (between MS and MSD).	Examine the project specific DQOs. Contact the client as to additional measures to be taken.	For the specific analyte(s) in the parent sample, apply flag if acceptance criteria are not met.	The data shall be evaluated to determine the source of difference.
Sample duplicate (replicate)	One per every 10 samples.	%D ≤ 10%(between sample and sample duplicate).	Correct problem and reanalyze sample and duplicate.	Apply flag if sample cannot be rerun or reanalysis does not correct	The data shall be evaluated to determine the source of difference.

				problem.	
Results reported between DL and LOQ	NA	NA	NA	Apply flag to all results between DL and LOQ.	

STANDARD OPERATING PROCEDURE

TOTAL DISSOLVED SOLIDS (TDS) (ALSO CALLED: TOTAL FILTERABLE RESIDUE)
STANDARD METHOD #: 2540C

APPROVALS:

5/27/11

Barbara Richardson, QA Officer — Date

5/27/11

Maya V. Murshak, Technical Director — Date

Number	Description of Change	Date
001-005	Previous changes were not documented	
006	Updated to comply with DoD QSM and ISO 17025 standards.	5/27/11
007		
008		
009		
010		
011		
012		
013		
014		
015		
016		

1.0 SCOPE AND APPLICATION

This SOP determines filterable residue (TDS) in drinking, surface, and saline waters and domestic and industrial wastes. The reporting limit is 1 mg/l for TDS.

2.0 SUMMARY OF METHOD

An aliquot of sample is taken from a stirring sample and filtered through a filter 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^{o} C in the oven. The dish + solids is moved to a 180^{o} C oven (usually a muffle oven) and dried to a constant weight (usually at least 1 hour). The weight of solids in the dish represents the TDS.

3.0 INTERFERENCES

Poor shaking or stirring can lead to incorrect results.

Improper drying of the solids (not to constant weight) will give higher results than the true value.

Highly mineralized waters containing significant concentrations of calcium, magnesium, chloride, and/or sulfate can be hygroscopic and will require prolonged drying, desiccation, and rapid weighing.

Samples containing high concentrations of bicarbonate will require careful and possibly prolonged drying at 180 ^{o}C to ensure that all the bicarbonate is converted to carbonate.

Too much residue in the evaporating dish will crust over and entrap water that will not be driven off during drying. Total residue must be limited to about 200 mg.

4.0 APPARATUS AND MATERIALS

Un-weighed glass fiber filters.

Vacuum filtering apparatus compatible with 47 mm glass fiber filters.

25 mL large mouth pipettes.

Graduated cylinders: 50 mL, 100 mL.

150 mL aluminum or ceramic evaporating dishes.

Oven, 103 ^{o}C ± 2 ^{o}C.

Oven, 180 ^{o}C ± 2 ^{o}C.

Muffle Furnace.

Magnetic stir bar

Magnetic stir plate

Beakers

Thermometer.

Desiccators.

Analytical Balance, capable of weighing to 0.1 mg.

Vacuum pump.

Tweezers.

5.0 REAGENTS

Deionized (DI) Water.
Laboratory Control Sample (LCS) from ERA.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

The sample is usually a composite sample collected in a plastic or glass liter bottle with no preservation other than refrigeration at 4 ± 2^{o}C. The holding time is 7 days from sample collection.

7.0 PROCEDURE

1. Record the date and time of analysis, as well as your initials as the analyst on the bench sheet (Figure 1) and in the appropriate batch for TDS. A batch is defined as 10 samples of the same or similar matrix.

2. Record the evaporating dish weight on the TDS bench sheet. Using tweezers, place the filter in the filter holder with the wrinkled side up.

3. Place the filter holder assembly in the clean 150 mL side arm flask with the vacuum hose attached to the side arm.

4. Turn on the vacuum and filter 100 ml of DI water through the filter until all of the water is drawn through. This is the Blank.

5. Record the 100 ml volume on the bench sheet(s) for the Blank.

6. Record on the bench sheet the tin number and the evaporating dish weight and place the filter in the filter holder assembly with the wrinkled side up, apply vacuum, and wet the filter with a little DI water to ensure adhesion to the holder.

7. 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 beaker.

8. Place a Teflon-covered, magnetic stirring bar in the beaker and place the beaker on top of a magnetic stirrer. Stir for 1 minute or more.

9. Using a 25 ml serological pipette with a wide opening, remove 25.0 ml of well mixed sample from halfway into the cup and halfway between the mixing vortex and the side of the cup. Then drain the pipette onto and through the filter.

10. Repeat pipetting (step 9) 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).

11. 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 onto the filter from the cylinder.

12. Record the volume you filtered on the bench sheet.

13. 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.

14. 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.

15. Record the weight on the bench sheet.

16. 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 four percent or 0.5 mg, whichever is less.

17. Record the weight on the bench sheet.

18. Be sure to perform the quality control (QC) analyses summarized in Section 8.0.

19. Repeat Steps 6 through 17 for each sample.

20. Calculate TDS as follows:

TDS mg/l = [[(Grams of dish + residue) – (Grams dish)]/ml sample filtered] X 1000 ml/L X 1000 mg/Gram

Relative Percent Difference $RPD = \frac{(S - D)}{\left[\frac{S + D}{2}\right]} \times 100$

Where: S = Initial sample result
D = Duplicate sample result

Spike Recovery Percent Recovery $\frac{SSR - SR}{SA} \times 100$

Where: SSR = Spike sample result
SR = Sample (unspiked) result
SA = Spike added

8.0 QUALITY CONTROL

All of the QC items employed and evaluated are provided in Table 1. In addition, the table indicates the frequency of each QC item along with appropriate courses of corrective action. The analyst will follow SOP # and complete the appropriate review form upon completion of the analysis.

9.0 METHOD PERFORMANCE

This method is evaluated by testing a LCS and duplicate samples.

10.0 EQUIPMENT MAINTENANCE AND TROUBLESHOOTING

All equipment must be maintained and calibrated according to manufacturer's procedures. When equipment is not performing as required, the instrument must not be used until it is recalibrated or replaced.

11.0 SAFETY

Eye protection and gloves must be worn while performing TDS analyses. Every Laboratory area has eyewash, emergency shower, and fire extinguisher. The metals lab also has dust masks available for use with dust samples. The air system throughout the laboratory area is on a 100 percent fresh air exchange system. This system exchanges 100 percent the air in the laboratory area with air from outside six times per hour and 30 times per hour when the emergency purge button is hit. A reference file of material safety data sheets (MSDSs) is available to all personnel.

12.0 WASTE DISPOSAL AND POLLUTION PREVENTION

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

13.0 DEFINITIONS

Filterable residue: solids capable of passing through a glass fiber filter and dried to constant weight at 180 ^{o}C

Sample Batch: samples of the same or similar matrix; a sample batch consists of 10 samples or less

Method Blank: an analyte-free matrix to which all reagents are added in the same volumes or proportions as used in the sample processing. The method blank is carried through the complete sample preparation and analytical procedure. The method blank is used to document contamination resulting from the analytical process.

Laboratory Duplicate: aliquots of sample taken from the same container under the same laboratory conditions and processed and analyzed under the same conditions but independently.

Laboratory Control Spike: Milli-Q water (for water) and Organic-Free Soil (for soil) is spiked with the target analytes and carried through the complete sample preparation and analytical procedure. The control spike is used to document the ability to generate acceptable precision and bias, to verify the analytical system's performance, and to document method accuracy for each matrix.

14.0 REFERENCES

Standard Methods for Examination of Water and Wastewater, Twentieth Edition, Method 2540C, *Total Dissolved Solids Dried at 180 ^{o}C.*

Table 1: Quality Control Items, Frequency, and Corrective Action

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	± 5 % of average	Reset sample duplicates	Footnote non-homogeneity
Analytical Balance Check with "S" Weights	1/day	± 0.1% or ± 0.5mg, whichever is greater	Recalibrate Balance and Reweigh	Call for Service
Constant Weight Verification	1/10 samples	4 % or 0.5 mg whichever is less	Dry longer and reweigh.	Dry longer and reweigh.

Figure 1: TDS Bench Sheet

Total Dissolved Solids

TSS: VLIMS Code: 4615; EPA Method: 2540C

Date Started:_____ Date Finished:_____
Time Started:_____ Time Finished:_____

Analyst:_____ Reviewed By:_____

Batch ID:_____ Reviewed Date:_____

Temperature:_____

Merit #	TSS Y/N	Tin #	sample (mls)	Tin (grams)	dry solids + tin 180°C (grams)	reweigh 15 min. 180°C (grams)	Cond.	TDS (mg/L)
Blank								
LCS Lot								
Dup								

LCS value = _____

% Rec = _____ Acceptance criteria: _____

% RPD = _____ Acceptance criteria: ± 20%

STANDARD OPERATING PROCEDURE

PERSULFATE –WET OXIDATION METHOD FOR ANALYZING TOTAL ORGANIC CARBON (TOC)
EPA METHOD 415.1

APPROVALS:

8/3/11

QA Officer Date

8/3/11

Technical Director Date

Number	Description of Change	Date
001-005	Previous changes were not documented	
006	2011 Internal Audit Findings	08/03/11
007		
008		
009		
010		
011		
012		
013		
014		
015		
016		

1.0 SCOPE AND APPLICATION

This SOP is for the Persulfate-Wet Oxidation Method for analyzing Total Organic Carbon. This method is applicable to drinking, surface, ground waters & treated mixed wastewater. Reporting limit 1.0 mg/L for water samples. TOC is run by EPA Method 415.1.

2.0 SUMMARY OF METHOD

This SOP is a procedure for evaluating Total Organic Carbon in liquid samples. To remove TIC (total inorganic carbon), the instrument transfers a specified sample volume to the reaction chamber with a preprogrammed volume of H_3PO_4. The acidified sample (sample must be equal to or less than a pH of 2) is sparged with a stream of inert gas as bicarbonates in the sample dissociated to CO_2. The resulting gas flow is vented for the pre-programmed sparge time (nominal time: 2 minutes). NOTE: During this process, any POC (purgeable organic carbon) in the sample is removed and goes undetected. The system determines TOC by measuring carbon dioxide released by chemical oxidation of the organic carbon in the sample. After TIC removal, sodium persulfate ($Na_2S_2O_8$), a strong oxidizer, is added. This oxidant quickly reacts with organic carbon in the sample at 100°C to form carbon dioxide. When the oxidation reaction is complete, the carbon doxide is purged from the solution and routed to the NDIR detector that is sensitive to the specific absorption for the wavelength of carbon dioxide. When the TOC in the sample has been calculated, sample results are reported as ppm or ppb TOC.

3.0 INTERFERENCES

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) can 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 can 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 APPARATUS AND MATERIALS

Wet Oxidation TOC Carbon Analyzer with autosampler

40 ml VOA vials with septum

125 ml amber glass / 2,000 stock standard

100 ml volumetric flasks

1 L volumetric flask

Calibrated analytical scale

Calibrated 0.1 - 1 ml micro-pipettor with tips

5.0 REAGENTS

Deionized (DI) water

Potassium Acid Phthalate (PAP) ($C_8H_5O_4K$) / TOC Standard: Weigh 0.425 g (dried) PAP into 100 ml volumetric flask, add 60 or 70 ml DI water, add 0.1 ml concentrated phosphoric acid, bring to volume = 2,000 ppm TOC (Store this solution in dark glass under refrigeration and replace monthly).

100 ppm Working TOC Standard: Dilute 5 ml of 2,000 ppm TOC into a 100 ml volumetric flask and bring to volume (Store this solution in dark glass under refrigeration and prepare fresh weekly).

Phosphoric Acid Solution 5%(H_3PO_4): Add 59.0 ml of 85% H_3PO_4 concentrated to reagent water for a total volume of 1 L in a 1 L volumetric flask. (Shelf life is 3 weeks un-refrigerated).

Sodium Persulfate Solution 10%: weigh 100 g $Na_2S_2O_8$ into 500 ml beaker, add 400 ml DI water, dissolve. Pour into 500 ml volumetric flask and bring to volume. Purge with gas several hours after connecting bottle with solution to instrument. (Shelf life is 3 weeks un-refrigerated).

Nitrogen tank

Control ERA / TOC

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

Samples must be collected in glass or plastic bottles with TFE-lined cap (40 ml VOA vials are preferable) and acidified to a pH < 2 with H_2SO_4. Holding time for preserved samples are 28 days from collection when stored in refrigeration at 4 ± 2° C. Holding time for unpreserved samples are 7 days from collection when stored in refrigeration at 4 ± 2° C.

7.0 PROCEDURE

1 DAILY STARTUP

- Open valve on nitrogen tank and verify that instrument input pressure is 60 psi.
- Make sure there is enough persulfate reagent in supply bottle to last through at least a day's operation.
- Check to see that waste container is empty.
- Make sure the acid bottle has sufficient acid.

- Make sure that container with DI water is full.

2 SYSTEM ON

- Turn on computer first (do not log in into Launchpad).
- Turn on power on autosampler.
- Turn on power on main instrument unit and and log in (default log in user name is TOC, default password is TOC).
- Log into Launchpad in computer (default user name is TOC, default password is TOC).
- From Launchpad choose PC Applications and double-click on DGS icon. Verify that the right bottom icon on Status Monitor Screen is green color, which indicates that Data Gathering Service (DGC) is operational.

3 CONFIGURE THE METHOD AND ESTABLISH PROPER CALIBRATION PARAMETERS FOR MID-LEVEL METHOD

- Press Editor –Method-New button to configure a new method.
- Enter an appropriate method name, which is the date when the new method is created.
- Under sample Introduction, set the following values:
  - Select NPOC Only from the Mode dropdown list.
  - Press OK on the dialog box.
- Set (verify) the new method parameters as follows:
  - Sample volume 2 ml
  - Acid volume 0.5 ml
  - Persulfate volume 1 ml
  - EPC (psi) 20
- Press the Calibration button to access the Calibration screen and set the new parameters for the mid-level applications:
  - Calibration Standard 1.00 ppm
  - Calibration Standard 2.00 ppm
  - Calibration Standard 5.00 ppm
  - Calibration Standard 10.0 ppm
  - Calibration Standard 50.0 ppm
  - Calibration Standard 100 ppm
- Press OK to exit the Calibration screen
- Press the Times button and verify that the correct time for TOC/TC react time is entered

for the mid-level method, (2:30 min/sec)

- Press OK and Save to save the configured method.
- The instrument can run a low-level, mid-level, and high-level methods. The mid-level method (1 – 100 ppm) is used to analyze TOC.

4 CREATING THE SEQUENCE

- Press Editor →Sequence →New button.
- Enter an appropriate sequence Name (date of the sequence), for example 041211.
- Press the Add/Insert Sample button near the bottom of the screen to access the Add /Insert dialog box.
  - Under Sample Type, select Clean Up from the dropdown list.
  - Verify the value for # Reps is 2.
  - Verify the value for # of Samples is 1.
  - Press OK to exit the Add/Insert Sample screen.
- Press the Add/Insert Sample button to access the Add/Insert dialog box.
- Under Sample Type select Cal from the dropdown list.
- In the Methods section Primary dropdown list, select the method configured in the previous “Configuring a Method” section (date the method was created) for example 041211.
- Press OK to exit the Add/Insert Samples screen.
- Press Save; a message appears stating that the “Sequence has been saved”. Press OK.
  - Note: Sequence of samples, check standards, and quality control samples (QC) are created by following the same steps described in “Creating a Sequence”.

5 LOADIND AND STARTING THE SEQUENCE

- Press Monitor →Sequence →Load Active Sequence button to access the Load Active Sequence dialog box.
- Highlight the sequence created in the previous “Creating a Sequence” section (date the sequence was created, for example 041211).
- Press the Load button.
- Press Start (►) to begin the sequence.

6 REPORTING

- Start TOC Reporter by double-clicking Reporter from the Launchpad PC Applications tab.
- The TOC Reporter Login dialog box appears. The default username is “toc”. The default

password is "toc". Select an Instrument ID – C 519731232 Wet Chemistry. Click OK.

- To include samples in report, select the checkbox next to each sample in the data tree view. Create the report by right-clicking the sequence in the tree view and choosing Generate New Report.
- Before the report can be saved, it must be previewed, by clicking Preview Report, then click Save Report.
- To print a report, open the Report Viewer by previewing the report contents. Press the print icon at the top of the Report Viewer.

8.0 QUALITY CONTROL

A sample batch consists of 20 samples or less. The QC samples that are analyzed per batch are:

- QC Blank
- ICV
- CCV
- LCS
- Matrix Spike

See Table 1 for quality control items, frequency, and corrective actions..

9.0 METHOD PERFORMANCE

Precision and accuracy studies are performed annually. Method Detection Limit (MDL) studies are performed annually. Based on current method restrictions, Limit of Detection (LOD) evaluation is not required. Results will be reported only inside working range of instrument calibration. Limit of Quantitation (LOQ) is analyzed annually.

10.0 EQUIPMENT MAINTENANCE AND TROUBLESHOOTING

All equipment shall be maintained and calibrated according to manufacturer's procedures. When equipment is not performing as required, the instrument shall not be used until it is recalibrated or replaced. All maintenance must be entered in the maintenance logbook.

11.0 SAFETY

Eye protection and gloves must be worn when preparing available cyanide samples. Specific attention be paid (but not limited) to

- Phosphoric acid is corrosive, causes severe irritation and burns on contact, contact with most metals can cause the formation of flammable and explosive hydrogen gas, when diluting the acid must always be added slowly to water in small amounts, and never use hot water and never add water to the acid.

12.0 WASTE DISPOSAL AND POLLUTION PREVENTION

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

13.0 DEFINITIONS

Sample Batch: Samples of the same or similar matrix; for this method, a sample batch consists of 10 samples or less.

Method Blank or Laboratory Reagent Blank: An analyte-free matrix to which all reagents are added in the same volumes or proportions as used in the sample processing. The method blank is carried through the complete sample preparation and analytical procedure. The method blank is used to document contamination resulting from the analytical process.

Laboratory Control Sample (also known as Laboratory Fortified Blank, Spiked Blank, or QC Check Sample): A Sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes. It is generally used to establish intra-laboratory or analyst-specific precision and bias or to assess the performance of all or a portion of the measurement system.

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

Initial Calibration (ICAL): Set of operations that establish, under specific conditions, the relationship between values of quantities indicating by a measuring instrument, or values represented by a material measure or a

reference material, and the corresponding values realized by standards. An analytical instrument is said to be calibrated when an instrumental response can be related to the concentration of the target anions. This relationship is depicted graphically, and referred to as a "calibration curve". Initial calibration curves must be established based upon the requisite number of standards identified within the method for each target analyte.

Laboratory Duplicate: Aliquots of sample taken from the same container under the same laboratory conditions and processed and analyzed under the same conditions but independently.

Initial Calibration Verification (ICV): The initial calibration verification standard (different lot # or manufacturer from the initial calibration standard) shall verify the initial calibration curve. The initial calibration verification standard involves the analysis of all target analytes each time the initial calibration is performed.

Continuing Calibration Verification Standard (CCV): A standard solution that is used to check the validity of a calibration curve on a daily basis. It also provides information on satisfactory maintenance and adjustment of the instrument during sample analysis.

14.0 REFERENCES

Total Organic Carbon in Water, EPA Method 415.1, revision 11/16/1999.

Aurora 1030 Wet Oxidation TOC analyzer Operators Manual, Rev. 1.5 – May 2009.

Atoc Software Version 1.4.2 Operators Manual, Rev 1.2 - August 2010

Table 1. Quality Control Items, Frequency, and Corrective Action

QC Items	Frequency	Acceptance Criteria	Corrective Action
Initial Calibration (minimum blank + 5 points) (ICAL)	When needed or daily when required by project	R = 0.995	Terminate analysis, recalibrate and verify before sample analysis
Initial Calibration Verification (ICV) (separate source from ICAL standards)	Immediately following ICAL and at the beginning of each batch.	± 10% from expected concentration	Reprep ICV and reanalyze Identify and document problem Recalibrate and reanalyze ICV
Continuing Calibration Verification (CCV)	After every 10 samples and at the end of the run	± 10% from expected concentration	Recalibrate and verify Reanalyze samples back to last good CCV
QC Blank	After CCVs One per Batch	< 10 x RL (reporting limit)	Terminate analysis Identify and document the problem Reanalyze all associated samples
Replicate Samples	All samples must be run in replicate. Report average value and RPD.	RPD < 20%	Rerun sample. Flag associated data.
Matrix Spike (MS)	MS to be run in replicate. One MS per batch. Report average value and RPD.	± 25% from expected value	Rerun sample. Flag associated data.
Laboratory Control Sample (LCS)	LCS to be run in replicate. One LCS per batch. Report average value and RPD.	± 20% from expected concentration	Terminate analysis Identify and document the problem Reanalyze all associated samples

STANDARD OPERATING PROCEDURE

MICROWAVE ASSISTED ACID DIGESTION OF SOLID SAMPLES USEPA METHOD 3050B

APPROVALS:

6/3/11

QA Officer Date

6/3/11

Technical Director Date

Number	Description of Change	Date
001-008	Previous changes were not documented	
009	Updated to comply with DoD QSM and ISO 17025 standards.	6/3/11
010		
011		
012		
013		
014		
015		
016		
017		
018		
019		

1.0 SCOPE AND APPLICATION

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.

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. 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 (Tl)	7440-28-0
*Tin (Sn)	7440-31-5
*Titanium (Ti)	7440-32-6
Vanadium (V)	7440-62-2
Zinc (Zn)	7440-66-6

* Not approved for DoD work

2.0 SUMMARY OF METHOD

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

3.0 INTERFERENCES

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 Section 8.0. Samples that are highly reactive or contaminated may require dilution before analysis. If samples are diluted, then any dilutions must be accounted for in all subsequent calculations. Highly reactive samples may also require pre-digestion in a hood to minimize the danger of thermal runaway and excessively vigorous reactions.

4.0 APPARATUS AND MATERIALS

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

- 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

- 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.

- 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

Glass Fiber Filter paper, 0.45 µm.

Membrane Filter paper, 0.45 µm.

Analytical balances, 510 g capacity, minimum accuracy ± 0.001 g, and 250g capacity, minimum accuracy ±0.0001g.

Filter funnel, glass, or disposable polypropylene.

Digital bottle top dispenser capable of dispensing volumes of 0-5 ml in 0.02 ml increments.

Disposable Polypropylene vessels, 50 ml, compatible with centrifuge.

Plastic containers to support minimum of 200 ml.

Disposable tongue depressors for sample handling.

Disposable Pasteur pipettes.

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.

Centrifuge (IEC Centra GP8).

5.0 REAGENTS

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.

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

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

Standards added to digestion:

- Spiking Solutions:
  - Multi-element standard solution **WS1** (Figure 1), contains 10 µg/ml (ppm) each of Al, Sb, As, Ba, Be, B, Cd, Cr, Co, Cu, Fe, Pb, Li, Mo, Mn, Ni, Se, Sr, Sn, Ag, Tl, Ti, V, and Zn. The spiking solution is made by diluting the WS1, 2 to 1 (5 µg/ml). The 5 µg/ml spiking solution is added to the QC samples accordingly, 1.0 ml is added to MS/MSD samples and 0.5 ml is added to the laboratory control sample (LCS), using the Eppendorf automatic pipette.
  - Multi-element standard solution **HM** (Figure 1) contains 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.
  - Spiking solutions are prepared according to the Standard Prep Log (Figure 1). 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 are recorded in the standard prep log.

- All standards are NIST traceable.

♦ Internal Standards (after digestion):

- Lithium 6, 1000 µg/ml stock solution.
- Scandium, 1000 µg/ml stock solution.
- Yttrium, 1000 µg/ml stock solution.
- Rhodium, 1000 µg/ml stock solution.
- Rhenium, 1000 µg/ml stock solution.

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

- 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 bottle 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.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

Soil samples are collected without preservation, usually in glass containers with Teflon lined caps. Non-aqueous samples must be refrigerated at 4 ± 2° Celsius. 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. The Microwave Accelerated Reaction Systems are equipped with a temperature feedback control system. Microwaves are calibrated once a year according to the manufacturer's operation manual.

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

3. Sample Digestion.

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 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.*

- Homogenize sample by chopping and mixing sample with a tongue depressor or spatula. Remove any foreign object such as sticks, leaves, or rocks. Transfer 0.2 to 0.3 grams sample (wet weight) for a soil matrix or 0.05 to 2 grams sample (wet weight) for liquidly sludges and other various solid matrices to a digestion vessel, and record the weight on the digestion log (Figure 2), to a minimum of 0.001 g.

- For every sample batch, prepare a Laboratory Reagent Blank (LRB) and Laboratory Control Sample (LCS) by transferring 0.25 grams sand to the digestion vessel. Record the weight on the digestion log (Figure 2) to a minimum of 0.001 g. Additionally, designate a Matrix Spike (MS) and Matrix Spike Duplicate (MSD) or Duplicate (Dp) prepared as per 7.3.1.

- 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 0.5 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.

- Add 1 ± 0.1 mL of concentrated nitric acid to each conical vessel in the fume hood. Mix the slurry, then wait 5-10 minutes for any reaction to occur.

- Loosely cap the vessel and place into the carousel.

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

- Allow samples to set for 5 minutes then repeat previous step.

- 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. When the vessels have cooled to near room temperature, determine if the microwave vessels and caps are intact. If the sample vessel look compromised (i.e. cap is not on, sides of the vessel are wet), then the sample is considered compromised and the sample must be re-digested.

- Add 1 ml of the Internal Standard working solution to each sample and QC sample using an Eppendorf automatic pipettor. Dilute to the 50 ml mark with DI Water, into a calibrated (per lot) digestion vessel.

- 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 0.5 ml of the **HM** solution.

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

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

  - 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.

  - 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.

- Calculations

Dilution factor(DF:

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

Relative Percent Difference: $RPD = \frac{(S - D)}{\left[\frac{S + D}{2}\right]} \times 100$

Where: S = Initial sample result
D = Duplicate sample result

Spike Recovery Percent Recovery: $\frac{SSR - SR}{SA} \times 100$

Where: SSR = Spike sample result
SR = Sample (unspiked) result
SA = Spike added

- Record pertinent information onto the digestion log (Figure 2). The following information must be included: Date, start time, end time, analyst initials, method reference, sample IDs, sample weight or volume, MS/MSD/LCS spiking concentration and lot#, acid lot #, dilution factor, final volume and any pertinent remarks.

8.0 QUALITY CONTROL

All of the quality control items employed and evaluated are provided in Table 1 & 2. In addition, the table indicates the frequency of each QC item along with appropriate courses of corrective action.

The analyst will follow SOP # QA-007 and complete the appropriate review form upon completion of the analysis.

9.0 METHOD PERFORMANCE

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

10.0 EQUIPMENT MAINTENANCE AND TROUBLESHOOTING

Each instrument is assigned a maintenance logbook. All maintenance performed on the instrument must be recorded. Additionally, any modifications to the instrument settings shall be noted in the specific instrument logbook. Maintenance procedures provided in the equipment manual shall be followed.

11.0 SAFETY

Every Laboratory area has eyewash, emergency shower, and fire extinguisher. The metals lab also has dust masks available for use with dust samples. The air system throughout 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. A reference file of material safety data sheets (MSDSs) is available to all personnel.

Specific attention be paid (but not limited) to:

- 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.

- 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.

- 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.

12.0 WASTE DISPOSAL

Samples.

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

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

Acid bottles.

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

13.0 DEFINITIONS

Sample Batch: samples of the same or similar matrix; for metals a sample batch consists of 20 samples or less.

Method Blank (Laboratory Reagent Blank) (LRB): an analyte-free matrix to which all reagents are added in the same volumes or proportions as used in the sample processing. The method blank is carried through the complete sample preparation and analytical procedure. The method blank is used to document contamination resulting from the analytical process.

Laboratory Control Sample (LCS) (also known as Laboratory Fortified Blank, Spiked Blank, or QC Check Sample): a sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes carried through the complete sample prep and analytical procedure. It is generally used to establish intra-laboratory or analyst-specific precision and bias or to assess the performance of all or a portion of the measurement system.

Matrix Spike (MS) (also known as Spiked Sample or Fortified Sample): a sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target

analyte concentration is available. matrix spikes are used, for example, to determine the effect of the matrix on a method's recovery efficiency.

Matrix Spike Duplicate (MSD) (also known as Spiked Sample or Fortified Sample Duplicate): a second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

Laboratory Duplicate: aliquots of sample taken from the same container under the same laboratory conditions and processed and analyzed under the same conditions but independently.

14.0 REFERENCES

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TABLE 1 Quality Control Items, Frequency and Corrective Action

QA Items	Frequency	Acceptance Criteria	Corrective Action
Laboratory Reagent Blank (Method Blank)	One per sample batch	<RL/dilution	Remove contamination and re-digest sample set
Laboratory Control Sample	One per sample batch	85%-115%	Re-digest the sample set

Matrix Spike	One per every 20 samples	75%-125%	Analyze by Method of Standard Additions (MSA)
Matrix Spike Duplicate	One per ever 20 samples	75%-125% RPD <20%	Analyze by Method of Standard Additions (MSA)
Matrix Duplicate	One per every 20 samples	RPD <20%	Re-digest the sample set and QC.

TABLE 2 Quality Control Items, Frequency and Corrective Action for DoD Projects

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Method blank	One per preparatory batch.	No analytes detected > ½ RL and greater than 1/10 the regulatory limit (whichever is greater). Blank result must not otherwise affect sample results. For common laboratory contaminants, no analytes detected > RL.	Correct problem. If required, reprep and reanalyze method blank and all samples processed with the contaminated blank.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply flag to all results for the specific analyte(s) in all samples in the associated preparatory batch.	Problem must be corrected. Results may not be reported without a valid method blank. Flagging is only appropriate in cases where the samples cannot be reanalyzed.
LCS containing all analytes to be reported	One per preparatory batch.	80 – 120%	Correct problem, then prep and reanalyze the LCS and all samples in the associated preparatory batch for failed analytes, if sufficient sample material is available.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply flag to specific analyte(s) in all samples in the associated preparatory batch.	Problem must be corrected. Results may not be reported without a valid LCS. Flagging is only appropriate in cases where the samples cannot be reanalyzed.
Matrix Spike (MS)	One per preparatory batch.	For matrix evaluation, use QC acceptance criteria specified by DoD for LCS.	Examine the project-specific DQOs. If the matrix Spike falls outside of DoD criteria, additional quality control tests (dilution test and post-digestion spike addition) are required to evaluate matrix effects.	For the specific analyte(s) in the parent sample, apply flag if acceptance criteria are not met.	For matrix evaluation only. If MS results are outside the LCS limits, the data shall be evaluated to determine the source of difference and to determine if there is a matrix effect or analytical error.
Matrix spike duplicate (MSD) or sample duplicate	One per preparatory batch.	MSD: For matrix evaluation use QC acceptance criteria specified by DoD for LCS. MSD or sample duplicate: RPD < 20% (between MS and MSD or sample and sample duplicate).	Examine the project-specific DQOs. Contact the client as to additional measures to be taken.	For the specific analyte(s) in the parent sample, apply flag if acceptance criteria are not met.	The data shall be evaluated to determine the source of difference.

FIGURE 1: STANDARD PREP LOG

Standard Preparation

Inorganic Stock Solution IV-7 + IV-19 (100 ppm) + CGSN1-1 + CGLI1-1 + CGSR1-1 (1000 ppm)

I. Working Stock Solution 1 (WS1)

10 mls IV-7 + 10 mls IV-19+ 1 ml CGSN1-1 + 1 ml CGLI1-1 + 1 ml CGSR1-1 + 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. Spiking Solution

50 mls of WS1 to a final volume of 100 mls = 5.0ppm

IV. STANDARDS

Standards	Volume Working Stock Solution	Internal Standard 2.5 ppm	HNO_3	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
0.001 ppm	1.00 mls WS2	2 mls	2 mls	100 mls
0.0005 ppm	0.50 mls WS2	2 mls	2 mls	100 mls
0.0001 ppm	0.10 mls WS2	2 mls	2 mls	100 mls
0.00 ppm	0.00 mls	2 mls	2 mls	100 mls

ICP/MS MINERALS PREP LOG

Date	IS ID	Exp. Date	Analyst

Standards **ppm**	**Volume of Working Stock**	**Source and Lot # of Working Stock (100ppm)**	**Internal Standard 5.0 ppm**	**HNO_3**	Final Volume
0.0	**0.0**		**2 mls**	**2 mls**	**100 mls**
0.50	**0.5**		**2 mls**	**2 mls**	**100 mls**
1.0	**1.0**		**2 mls**	**2 mls**	**100 mls**
2.0	**2.0**		**2 mls**	**2 mls**	**100 mls**
5.0	**5.0**		**2 mls**	**2 mls**	**100 mls**
10.0	**10.0**		**2 mls**	**2 mls**	**100 mls**
ICV – 5.0	**5.0**		**2 mls**	**2 mls**	**100 mls**

FIGURE 2: METALS DIGESTION LOG

Metals Digestion

3015A \ 3050B DATE _____

TIME START _____ ANALYST _____

TIME FINISH _____ PREP BATCH MTD-_____

15.0 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 / 0.50 mls of 5ppm Spiking Solution

Samples: Water = 0.05 ppm = 50 mls / 0.50 mls of 5ppm Spiking Solution

Soil = 0.10 ppm = 50 mls / 1.0 mls of 5ppm Spiking Solution

Spiking Solution - Lot #_____

2) Spike values for minerals (Ca-Mg-K-Na)

LCS = 1.0 ppm = 50 mls / 0.50 mls HM Stock Solution

Samples (Water or Soil) = 2.0 ppm = 50 mls / 1.0 mls HM Stock Solution

High Purity Stock Solution (HM)- Lot #_____

3) HNO_3 Lot #_____ 4) Centrifuge Tube Lot #_____

STANDARD OPERATING PROCEDURE

MICROWAVE ASSISTED ACID DIGESTION OF LIQUID SAMPLES AND EXTRACTS US EPA METHOD 3015A

APPROVALS:

06/03/11

QA Officer Date

06/03/11

Technical Director Date

Number	Description of Change	Date
001-007	Previous changes were not documented	
008	Updated to comply with DoD QSM and ISO 17025 standards.	6/3/11
009		
010		
011		
012		
013		
014		
015		
016		
017		
018		

1.0 SCOPE AND APPLICATION

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.

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 (Tl)	7440-28-0
*Tin (Sn)	7440-31-5
*Titanium (Ti)	7440-32-6
Vanadium (V)	7440-62-2
Zinc (Zn)	7440-66-6

* Not approved for DoD work

2.0 SUMMARY OF METHOD

A representative 0.5 to 25 g/ml aqueous sample is digested in 1 ml of concentrated nitric acid in a polypropylene digestion vessel heated using microwave heating and brought 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.

3.0 INTERFERENCES

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

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

- 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.

- 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.

- 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

Analytical balances, 510g capacity, minimum accuracy ± 0.001g and 250g capacity, minimum accuracy ±0.0001g.

Filter funnel, glass or disposable polypropylene.

Glass-fiber filter paper, 0.45 µm.

Membrane filters, 0.45 µm.

Digital bottle top dispenser capable of dispensing volumes of 0-5 ml in 0.02 ml increments.

Disposable polypropylene vessels, 50 ml, compatible with centrifuge.

Plastic containers to support minimum of 200 ml.

Disposable Pasteur pipettes.

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.

Centrifuge (IEC Centra GP8).

5.0 REAGENTS

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.

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

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

Standards added to digestion:

- Spiking Solutions
  - Spiking solutions are prepared according to the Standard Prep Log (Figure 1). 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.
  - All standards are NIST traceable.
  - Multi-element standard solution **WS1** (Figure 1), contains 10 µg/ml (ppm) each of Al, Sb, As, Ba, Be, B, Cd, Cr, Co, Cu, Fe, Pb, Li, Mo, Mn, Ni, Se, Sr, Sn, Ag, Tl, Ti, V, and Zn. The spiking solution is made by diluting the WS1, 2 to 1 (5 µg/ml). The 5 µg/ml spiking solution is added to the QC samples accordingly, 0.5 ml is added to MS/MSD samples and 0.5 ml is added to the laboratory control sample (LCS), using the Eppendorf automatic pipette.
  - Multi-element standard solution High Purity Mineral (**HM)** (Figure 1) contains 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), by weighing the amounts (1.0 g, 0.50 g) on the scale.
- Internal Standards (After digestion):
  - Lithium 6, 1000 µg/ml stock solution.
  - Scandium, 1000 µg/ml stock solution.
  - Yttrium, 1000 µg/ml stock solution.
  - Rhodium, 1000 µg/ml stock solution.

- Rhenium, 1000 µg/ml stock solution.

- 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 bottle 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

Water samples are collected in HNO_3 pre-preserved plastic containers and are acidified to pH of <2. (Approximately 125 ml volume). 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

1. The Microwave Accelerated Reaction Systems are equipped with a temperature feedback control system. Microwaves are calibrated once a year according to the manufacturer's operation manual.

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.*

3. Digestion using industrial Microwave.

   - 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 digestion log (Figure 2).

- With every batch of 20 analytical samples measure a volume of reagent water equal to the sample volume as described at above 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.

- With every batch of samples measure a volume of reagent water equal to the sample volume as described at above 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.

- 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 (Dup).

- For analysis of all metals except Ca, Mg, K and Na, add 0.5 ml of the QC Spiking Solution (WSI) to the QC samples (LCS, MS/MSD). For Ca, Mg, K and Na, add 0.5 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 digestion log (Figure 2).

- Add 1 $\pm$ 0.1 ml of concentrated nitric acid to each vessel, by using the bottle top dispensers in the fume hood.

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.

- Loosely cap the vessel and place into the carousel.
- Samples are slowly ramped in the microwave to 95 ± 5 degrees Celsius over the course of a few minutes and maintained at this temperature for 30 minutes.

- 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.

- When the vessels have cooled to near room temperature, determine if the microwave vessels and caps are intact. If the sample vessel look compromised (i.e. cap is not on, sides of the

vessel are wet), then the sample is considered compromised and the sample must be re-digested.

- 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).

- 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.

    - 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.

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

    - 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.

4. Calculations:

Dilution factor (DF:

$$DF = \frac{Final\ Volume\ (50)}{Sample\ amount}$$

Relative Percent Difference:

$$RPD = \frac{(S - D)}{\left[\frac{S + D}{2}\right]} \times 100$$

Where: S = Initial sample result
D = Duplicate sample result

Spike Recovery Percent Recovery:

$$\frac{SSR - SR}{SA} \times 100$$

Where: SSR = Spike sample result
SR = Sample (unspiked) result
SA = Spike added

- Record pertinent information onto the digestion log (Figure 2). The following information must be included: Date, start time, end time, analyst initials, method reference, sample IDs,

sample weight or volume, MS/MSD/LCS spiking concentration and lot #, acid lot #, dilution factor, final volume and any pertinent remarks.

8.0 QUALITY CONTROL

All of the quality control items employed and evaluated are provided in Table 1 and 2. In addition, the table indicates the frequency of each QC item along with appropriate courses of corrective action. A dilution test is performed once per every 20 samples. The dilution test is performed by taking 10 mls of a parent sample after digestion and adding 0.8 mls acid and 0.8 mls internal standard and bringing to a final volume of 50 mls with DI water. The dilution test is used to identify matrix interference and is not applicable if the measured concentration is less than 100 times the MDL for each measured analyte.

The analyst will follow SOP #QA-007 and complete the appropriate review form upon completion of the analysis.

9.0 METHOD PERFORMANCE

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

10.0 EQUIPMENT MAINTENANCE AND TROUBLESHOOTING

Each instrument is assigned a maintenance logbook. All maintenance performed on the instrument must be recorded. Additionally, any modifications to the instrument settings shall be noted in the specific instrument logbook. Maintenance procedures provided in the equipment manual shall be followed.

11.0 SAFETY

Every Laboratory area has eyewash, emergency shower, and fire extinguisher. The metals lab also has dust masks available for use with dust samples. The air system throughout 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. A reference file of material safety data sheets (MSDSs) is available to all personnel.

Specific attention be paid (but not limited) to:

- 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.

- 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.

- 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.

12.0 WASTE DISPOSAL

Samples.

- All digested samples are neutralized with baking soda and diluted before being disposed of with the normal laboratory wastewater.

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

Acid bottles.

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

13.0 DEFINITIONS

Sample Batch: samples of the same or similar matrix; for metals a sample batch consists of 20 samples or less.

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Laboratory Control Sample (LCS) (also known as Laboratory Fortified Blank, Spiked Blank, or QC Check Sample): a sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes carried through the complete sample prep and analytical procedure. It is generally used to establish intra-laboratory or analyst-specific precision and bias or to assess the performance of all or a portion of the measurement system.

Matrix Spike (MS) (also known as Spiked Sample or Fortified Sample): a sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target

analyte concentration is available. Matrix spikes are used, for example, to determine the effect of the matrix on a method's recovery efficiency.

Matrix Spike Duplicate (MSD) (also known as Spiked Sample or Fortified Sample Duplicate): a second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

Laboratory Duplicate: aliquots of sample taken from the same container under the same laboratory conditions and processed and analyzed under the same conditions but independently.

Dilution Test: a digested sample is diluted five-fold and analyzed to determine if matrix interference is present.

14.0 REFERENCES

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Laboratory Reagent Blank (Method Blank)	One per sample batch	<RL/dilution	Remove contamination and re-digest sample set
Laboratory Control Sample	One per sample batch	85%-115%	Re-digest the sample set
Matrix Spike	One per every 10 samples	75%-125%	Analyze by Method of Standard Additions (MSA)
Matrix Spike Duplicate	One per ever 10 samples	75%-125% RPD <20%	Analyze by Method of Standard Additions (MSA)
Matrix Duplicate	One per every 10 samples	RPD <20%	Re-digest the sample set and QC.
Dilution Test	When result indicates suppressive interference	$\pm$ 10% of the original measurement	If interferences exist; rerun with MSA

TABLE 2 Quality Control Items, Frequency and Corrective Action for DoD Projects

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Method blank	One per preparatory batch.	No analytes detected > ½ RL and greater than 1/10 the regulatory limit (whichever is greater). Blank result must not otherwise affect sample results. For common laboratory contaminants, no analytes detected > RL.	Correct problem. If required, reprep and reanalyze method blank and all samples processed with the contaminated blank.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply flag to all results for the specific analyte(s) in all samples in the associated preparatory batch.	Problem must be corrected. Results may not be reported without a valid method blank. Flagging is only appropriate in cases where the samples cannot be reanalyzed.
LCS containing all analytes to be reported	One per preparatory batch.	80 – 120%	Correct problem, then prep and reanalyze the LCS and all samples in the associated preparatory batch for failed analytes, if sufficient sample material is available.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply flag to specific analyte(s) in all samples in the associated preparatory batch.	Problem must be corrected. Results may not be reported without a valid LCS. Flagging is only appropriate in cases where the samples cannot be reanalyzed.
Matrix Spike (MS)	One per preparatory batch.	For matrix evaluation, use QC acceptance criteria specified by DoD for LCS.	Examine the project-specific DQOs. If the matrix Spike falls outside of DoD criteria, additional quality control tests (dilution test and post-digestion spike addition) are required to evaluate matrix effects.	For the specific analyte(s) in the parent sample, apply flag if acceptance criteria are not met.	For matrix evaluation only. If MS results are outside the LCS limits, the data shall be evaluated to determine the source of difference and to determine if there is a matrix effect or analytical error.
Matrix spike duplicate (MSD) or sample duplicate	One per preparatory batch.	MSD: For matrix evaluation use QC acceptance criteria specified by DoD for LCS. MSD or sample duplicate: RPD < 20% (between MS and MSD or sample and sample duplicate).	Examine the project-specific DQOs. Contact the client as to additional measures to be taken.	For the specific analyte(s) in the parent sample, apply flag if acceptance criteria are not met.	The data shall be evaluated to determine the source of difference.

FIGURE 1: STANDARD PREP LOG

Standard Preparation

Inorganic Stock Solution IV-7 + IV-19 (100 ppm) + CGSN1-1 + CGLI1-1 + CGSR1-1 (1000 ppm)

I. Working Stock Solution 1 (WS1)

10 mls IV-7 + 10 mls IV-19+ 1 ml CGSN1-1 + 1 ml CGLI1-1 + 1 ml CGSR1-1 + 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. Spiking Solution

50 mls of WS1 to a final volume of 100 mls = 5.0ppm

IV. STANDARDS

Standards	Volume Working Stock Solution	Internal Standard 2.5 ppm	HNO_3	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
0.001 ppm	1.00 mls WS2	2 mls	2 mls	100 mls
0.0005 ppm	0.50 mls WS2	2 mls	2 mls	100 mls
0.0001 ppm	0.10 mls WS2	2 mls	2 mls	100 mls
0.00 ppm	0.00 mls	2 mls	2 mls	100 mls

ICP/MS MINERALS PREP LOG

Date	IS ID	Exp. Date	Analyst

Standards **ppm**	**Volume of Working Stock**	**Source and Lot # of Working Stock (100ppm)**	**Internal Standard 5.0 ppm**	**HNO_3**	Final Volume
0.0	**0.0**		**2 mls**	**2 mls**	**100 mls**
0.50	**0.5**		**2 mls**	**2 mls**	**100 mls**
1.0	**1.0**		**2 mls**	**2 mls**	**100 mls**
2.0	**2.0**		**2 mls**	**2 mls**	**100 mls**
5.0	**5.0**		**2 mls**	**2 mls**	**100 mls**
10.0	**10.0**		**2 mls**	**2 mls**	**100 mls**
ICV – 5.0	**5.0**		**2 mls**	**2 mls**	**100 mls**

FIGURE 2: METALS DIGESTION LOG

Metals Digestion

3015A \ 3050B DATE _____

TIME START _____ START TEMP _____ ANALYST _____

TIME FINISH _____ FINISH TEMP _____ PREP BATCH MTD-_____

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 / 0.50 mls of 5ppm Spiking Solution

Samples: Water = 0.05 ppm = 50 mls / 0.50 mls of 5ppm Spiking Solution

Soil = 0.10 ppm = 50 mls / 1.0 mls of 5ppm Spiking Solution

Spiking Solution - Lot # _____

2) Spike values for minerals (Ca-Mg-K-Na)

LCS = 1.0 ppm = 50 mls / 0.50 mls HM Stock Solution

Samples (Water or Soil) = 2.0 ppm = 50 mls / 1.0 mls HM Stock Solution

High Purity Stock Solution (HM) - Lot # _____

3) HNO_3 Lot #_____

4) Centrifuge Tube Lot #_____

STANDARD OPERATING PROCEDURE

METALS BY INDUCTIVELY COUPLED PLASMA - MASS SPECTROMETRY METHODS 6020, 6020A, 200.8

APPROVALS:

6/3/11

QA Officer Date

6/3/11

Technical Director Date

Number	Description of Change	Date
001	Updated to comply with DoD QSM and ISO 17025 standards.	6/3/11
002		
003		
004		
005		
006		
007		
008		
009		
010		
011		
012		

1.0 SCOPE AND APPLICATION

Inductively coupled plasma-mass spectrometry (ICP-MS) is applicable for the determination of sub-µg/L concentrations of a large number of elements in water samples and in waste extracts or digestions. 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 water samples with turbidity <1 NTU. This SOP follows the guidelines of the EPA Methods 200.8, 6020, and 6020A. The metals that are determined by using this SOP are listed in Table 1 with associated reporting limits (RL) and quantitation limits (QL) and which methods can be used for each element.

If this SOP is followed to determine any analyte not listed in Table 1, it is the responsibility of the analyst to demonstrate the accuracy and precision of the method as well as method detection limit (MDL) and multi-point calibration. The analyst is always required to monitor potential sources of interferences and take appropriate action to ensure data of known quality. Use of this SOP is restricted to analysts who are knowledgeable in the recognition and in the correction of spectral, chemical and physical interferences in ICP-MS. This SOP is for use on all samples that do not require Ohio VAP certification.

2.0 SUMMARY OF METHOD

Prior to analysis, samples which require total ("acid-leachable") values are digested using appropriate sample digestion procedures (Document #'s MET-003 and MET-001). 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 interferences, and memory interferences.

- **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 of the analyte elements). They can be isobaric elemental and isobaric molecular interferences (polyatomic, refractory oxide, and doubly charged ions).

  - 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 are 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.

  - 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 is determined from the ratio of the net isotope signals observed for a standard solution at a concentration providing suitable (<1%) counting statistics.

    - 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 is 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]).

- 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 are 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 is corrected, upon the evaluation of data. It is suggested that the <u>elemental</u> isobaric interference equations be <u>included</u> in all methods (parameters) from the beginning, but potential <u>polyatomic</u> species (masses) that could interfere be <u>only monitored</u> (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 (See Table 6a & 6b for summary of QC requirements).

- Abundance sensitivity is a property defining the degree to which the wings of a mass peak contribute to adjacent masses. Wing overlap interference can occur when a small ion peak is being measured adjacent to a large one. The potential for these interferences must 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.

- **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 can result in differences between instrument responses for the samples and calibration standards. Physical interferences can 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 must 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 is effectively used to compensate for many physical interference effects. Internal standards must ideally display similar analytical behavior to the elements being determined. Generally, an internal standard must 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.

- **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 can occur is dependent on the sample and needs 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 must be recognized and suitable rinse times must 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 memory interference is suspected, the sample must be reanalyzed after analysis of a blank indicates that the carryover has been eliminated.

4.0 APPARATUS AND MATERIALS

Inductively coupled plasma-mass spectrometers:

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

- **Hewlett-Packard (HP) 4500 ICP-MS**:
  - Windows 95 Operating system.
  - Chem Station Software.
  - Cetac ASX150 Autosampler.
- **Agilent 7500Ce ICP MS:**
  - Windows XP Operating system.
  - Chem Station Software.
  - Agilent ASX 500 Series autosampler .

Argon gas supply: liquid argon cylinders

Analytical balance, 510 g capacity, minimum accuracy ± 0.001 g.

Digital bottle top dispenser capable of dispensing volumes of 0-5 ml in 0.02 ml increments.

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.

Note: dispensers are calibrated quarterly according to SOP #010010.

Disposable Pasteur pipettes.

Polypropylene vessels, 50 mL.

Plastic cups to support minimum of 200 ml.

Plastic bottles.

5.0 REAGENTS & STANDARDS

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.

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.

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

Internal Standard stock solutions:

- Lithium 6, 1000 µg/ml stock solution.
- Scandium, 1000 µg/ml stock solution.
- Yttrium, 1000 µg/ml stock solution.
- Rhodium, 1000 µg/ml stock solution.
- Rhenium, 1000 µg/ml stock solution.
- Internal Standard Working Solution (IS-WS): From the above stock solution, 2.5 ml 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), which corresponds to 2.5 µg/ml. This represents the internal standard working solution from which 1 ml (for a 50 ml final volume) must be added to all calibration standards and blanks. This provides a 0.05 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. See Appendix 1 for blank page of standard preparation log book page.

Multi-element standard stock solution from three of four different vendors:

- Inorganic Venture (IV), 100 mg/L each of Ag, Al, B, Ba, As, Be, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sb, Se, Sr, Sn, Ti, Tl, V, and Zn. This solution is used for the preparation of standards.
- High Purity Standards (HM), 100 µg/ml each of Ca, Mg, K, and Na. This solution is used for the preparation of the calibration standards and for the minerals standard.
- 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, and Zn. This solution is used for the preparation of the initial calibration verification (ICV) standards.
- Environmental Resource 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, and S.

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 Prep Log and Appendix 2 for ICV prep log.

Multi-element 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 more frequent if needed. They must be verified using a quality control standard (ICV). Table 2 (metals) and Table 3 (minerals) are used as guidance, when preparing standards.

Blanks: Three types of blanks are required for the analysis. The calibration blank (std-0.00) is used in establishing the calibration curve. The Laboratory Reagent Blank (LRB) also known as method blank 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.

- The calibration blank (std-0.00), the initial calibration blank (ICB), 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. The preparation of these blanks can be found in the standards prep-log. The calibration blank is used in the calibration process, the ICB is used to check the instrument before analyzing samples, and the CCB is used to verify the instrument in the middle and end of analytical runs.

- The Laboratory Reagent Blank (LRB) also known as method blank must be carried through the complete preparation procedure and contain the same volumes of reagents as the sample solutions.

- The rinse blank consists of 2% HNO_3 (v/v) in reagent water. Prepare a sufficient quantity to flush the system between all standards, quality control samples, and analytical samples. Rinse blank is prepared by adding 20 ml of concentrated HNO_3 to 1000 ml of DI water in a large plastic container.

The interference check solution (ICS) is prepared to contain known concentrations of interfering elements that 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.

- Interference check stock solution A, containing 1000 µg/ml each of Al, Ca, Fe, Mg, Na, P, K, and 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, 2 ml HNO_3, and dilution to 100 g on the scale with reagent water.

- 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, 2 ml HNO_3, and dilution to 100 g on the scale with reagent water.

- The final concentration of the elements in ICS-A and ICS-AB is listed in Table 4. These solutions are prepared fresh every 2 weeks or as needed.

The initial calibration verification solution (ICV) is used to verify the calibration before samples are analyzed. The ICV 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 (known as a second source) is defined as a standard from a source different from those used in the standards for instrument calibration.

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 Number 5, Section 7.0). This solution is also used to verify that the instrument has reached thermal stability (See See Number 4, Section 7.0).

- Tuning solution for HP 4500 ICP-MS: 10 µg/ml each of Li, Y, Ce, and Tl is used to tune the instrument according to the manufacturer instructions.

- Tuning solution for PE Elan 9000 and Agilent 7500Ce ICP-MS: 10µg/ml each of Li 7, Be 9, Mg 25, Co 59, In 115, Tl 205, and Pb 208.

Working standards and solutions are prepared every two weeks according to recipes in the standards prep log. The logbook is available in the metals lab. Concentrations of the LCS can be found on the laboratory bench sheet.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

All samples are collected in appropriate plastic or glass containers.

- Water samples are collected in HNO_3 pre-preserved plastic containers (approximately 125 ml volume), and are acidified to pH of <2.
- Soil samples are collected without preservation, usually in glass containers with Teflon lined caps. Non-aqueous samples must be refrigerated at 4 ±2 C° upon receipt.

Holding times for metals are 6 months from the date of sampling to analysis. For TCLP samples the holding time is 6 months from sampling to TCLP extraction then 6 months from TCLP extraction to analysis.

7.0 PROCEDURE

1. Solubilization and digestion procedures are presented in the Sample Preparation Document #'s (MET-003 and/or MET-001). A sample digestion log sheet is found in Figure 3.

2. Initiate appropriate operating configuration of the instrument's computer according to the instrument manufacturer's instructions.

3. Set up the instrument with the proper operating parameters according to the instrument manufacturer's instructions.

4. Operating conditions: The analyst must follow the instructions provided by the instrument manufacturer. Allow at least 30 minutes for the instrument to equilibrate before analyzing any samples. The thermal stability must be verified by analyzing a tuning solution described in Section 5.0.

5. For all analysis tune instrument according to following parameters.

   - The tuning must 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 be verified to be within 0.6-0.9 amu full width at 5 percent peak height (not applicable for HP4500 ICP-MS due to manufacturer presets).

   Note: A peak height of 5 percent is used instead of 10 percent because 5 percent is the tighter restriction and this SOP is written to meet the requirements of methods 200.8, 6020, and 6020A.

- Perform tune after machine is warmed up and every 12 hours following.

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.

6. The instrument is calibrated daily and re-calibrated as needed. Calibrate the instrument for the analytes of interest (recommended isotopes for the elements in Table 1 are provided in Table 5a and Table 5b), using the calibration blank and at least three non-zero calibration standards according to the instrument manufacturer's procedure. A multi-point calibration curve is analyzed and evaluated. For the calibration curve to be acceptable, a correlation coefficient of greater than or equal to 0.998 must be achieved. If the required correlation coefficient is not achieved then the extreme upper and lower calibration points may be removed from the multi-point curve as long as three non-zero points remain such that the linear range is narrowed and the non-linear upper and/or lower portions are removed. If narrowing the linear range does not improve the correlation coefficient to 0.998, then replace the calibration standards and re-calibrate the instrument. The reporting limit (RL) must be greater than or equal to the lowest calibration point or the concentration of low level initial calibration verification (LLICV), whichever is lower.

The principle of calculation for the linear curve fit and the coefficient of determination (COD) is found in SW 846 method 8000C Sections 11.5.2.1 through 11.5.2.3. ICP-MS manufacturer software is preprogrammed for this calculation.

The multi point calibration is verified with a mid level ICV standard with control limits of 90%-110% and a low-level ICV with limits of 70%-130% (80%-120% for DoD projects). Table 2 and Table 3 (Section 5.0) provide information to what calibration standards are used. (More information on limits and corrective actions can be found in Section 8 and Table 6a & 6b). Flush the system with the rinse blank (Section 5.0) between each standard solution. The instrument must be set to use the mean of at least three integrations for both calculation of calibration points and the calculation of sample concentrations.

7. All masses that affect data quality must be monitored to determine potential effects from matrix components on the analyte peaks. Preferred isotopes are referenced in Tables 5a and 5b.

8. Immediately after the calibration has been established, the calibration must be verified and documented for every analyte by the analysis of the initial calibration verification solution (ICV,

Section 5.0) using a second source standard. When measurements exceed ± 10% of the true 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 require re-calibration to correct for instrument drift. A re-calibration must then be followed immediately by a new analysis of an ICV, LLICV, and initial calibration blank (ICB) before any further samples are analyzed. Corrective actions for specific situations are found in Section 8 and summarized in Table 6a & 6b.

9. A low-level initial calibration verification (LLICV) must be analyzed after every calibration to verify the linearity near the lower end of the calibration curve. The LLICV is made from the same source as the calibration standards at a concentration comparable to the reporting limits of elements being reported. When the LLICV measurements exceed ± 30% (± 20% for DoD projects) of the true value, the analyses must be terminated, the problem corrected, the instrument re-calibrated, and the new calibration verified. (limits and corrective action information can be found in Section 8.0 and is summarized in Table 6a & 6b).

10. Flush the system with the rinse blank solution (Section 5.0) 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 (limits and corrective action information can be found in Section 8.0 and is summarized in Table 6a & 6b).

11. Dilute and reanalyze samples that are more concentrated than the linear range (LR) (Section 8.0) for an analyte or measure an alternate less-abundant isotope. The linearity at the alternate mass must be confirmed by appropriate calibration (Numbers 6 through 8, Section 7.0).

12. Interference Check Solutions (ICS) are run to verify the magnitude of elemental and molecular-ion isobaric interferences. This is performed every 12 hours. This is done by analyzing interference check solutions A and AB. (Concentration of elements in solution found in Table 4, other reagent information is in Section 5.0)

Corrective Action: The ICS needs to be within 70-135% (± 20%, of true value, for DoD projects). If the ICS fails, re-evaluate the equations used for the corrections, make the necessary adjustments, recalibrate the instrument and re-analyze the samples associated with the failed ICS. See Table 6a &6b for ICS summary and Section 8.0 for more information.

Note: Precipitation from solution AB can occur with some elements, specifically silver. Rinse the instrument 5 –10 minutes before analyzing any other samples to help improve performance.

13. Calculations: the quantitative values are reported in appropriate units, such as milligrams per liter (mg/L) for aqueous samples and milligrams per kilogram (mg/kg) for solid samples.

♦ The appropriate dilution factor (DF) on water samples resulted from sample preparation (see Document # MET-003) 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, using the following equation

C *x* DF = SC
Where, C = digest concentration
DF = Dilution Factor
SC = Sample Concentration

The ICP/MS software carries out this calculation for the analyst.

♦ 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 is 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.

♦ Calculations performed by the data system include appropriate interference corrections, internal standard normalization, and the summation of signals (for example 206, 207 and 208 m/z for lead) to compensate for any differences in the abundances of these isotopes between samples and standards.

Note: The instrument must be set to use the mean of at least three integrations for both calculation of calibration points and the calculation of sample concentrations.

- Hardness by Calculation

  The preferred method for calculating Hardness Standard Method 2340B. Hardness is calculated from the Calcium and Magnesium results from this procedure using the following equation:

  CaCo3/L = 2.497 [Ca] + 4.118[Mg]
  Where:
  CaCO3 is the total hardness by calculation
  Ca is the total Calcium by 6020A in mg/L
  Mg is the total Magnesium by 6020A in mg/L

  Relative Percent Difference: $$RPD = \frac{(S - D)}{\left[\frac{S + D}{2}\right]} \times 100$$

  Where: S = Initial sample result
  D = Duplicate sample result

  Spike Recovery Percent Recovery: $$\frac{SSR - SR}{SA} \times 100$$

  Where: SSR = Spike sample result
  SR = Sample (unspiked) result
  SA = Spike added

8.0 QUALITY CONTROL

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

Demonstration of Performance.

- The demonstration of performance is used to demonstrate instrument performance and has two parts. The first is initial demonstration of performance this is done by performing method detection limit (MDL) studies, linear range studies, and precision and accuracy studies prior to the analysis of samples. The second is continual demonstration of performance is done by annual MDLs and linear range studies. MDL studies are performed by following SOP #060004 (Determination of Method Detection Limit). Analyst performance is demonstrated by analysis of proficiency test and blind samples multiple times per year.

- Linear calibration ranges: Linear calibration ranges are primarily detector limited. The upper limit of the linear calibration range must be established by determining the signal responses from a minimum of five different concentration standards. Care must be taken to avoid potential damage to the detector during this process. The linear calibration range, which is used for the analysis of samples, must be judged by the analyst from the resulting data. The upper LR 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 LR limit must be diluted and reanalyzed. The LR must

be verified whenever, in the judgment of the analyst, a change in analytical performance caused by either a change in instrument hardware or operating conditions would dictate they be re-determined. See Section 7.6 for curve specific criteria.

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 an interference source is present, and cannot be corrected, the sample elements impacted must be flagged. The ICS is used to verify the correction equations used by the instrument. Requirements are found in Section 8.0 and Table 4 and preparation information is in Section 5.0.

The intensities of all internal standards must be monitored for every analysis. When the intensity of any internal standard falls outside the control limits as compared with the first calibration standard (Calibration Blank or std-0.00), the following procedure is followed. Check for instrument drift, instrument drift is characterized by internal standards outside control limits for QC samples (Section 8.0), recalibrate instrument and reanalyze samples. If matrix interference is suspected, 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. (Summary of control limits and corrective actions can be found in Table 6a & 6b)

- The intensity levels of the internal standards for the ICV/ICB/LLICV, CCV/CCB, LCS/LRB must also be within the specified acceptance limits (refer to Section 8.0 for limits and Section 7.0, Numbers 6-12 for procedure information). If they are not within limits, terminate the analysis, correct the problem, recalibrate, verify the new calibration, and reanalyze the affected samples.

Check the instrument calibration by analyzing appropriate quality control solutions as follows (Summarized in Table 6a & 6b):

- Initial Calibration must include a blank and minimum of three non-zero points. A correlation coefficient of 0.998 must be achieved. Section 7.0 for calibration procedure.

- Immediately after instrument calibration check instrument calibration by analyzing the ICV described in Section 5.0. ICV limits are 90%-110%. The ICB has to be less than the lower limit of quantitation for every target element. The lower limit of the calibration must be checked by analyzing the low-level initial calibration verification (LLICV) with acceptance limits of 70%-130% (± 20% for DoD projects). Summary of limits and corrective actions are found in Table 6a & 6b, the procedure for this is found in Section 7.0, Numbers 6 through 9.

- When running samples verify calibration at a frequency of every 10 analytical samples with the CCV standard with limits of 90-110% and the continuing calibration blank (CCB) with acceptance criteria of less than the lower limit of quantitation for every target element. These solutions must also be analyzed for each analyte at the beginning of the analysis and after the last sample. 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. See Table 6a &6b for summary of acceptance criteria and corrective actions, the procedure for this information for this is found in Section 7.0, Number 10.

- Corrective action for out of compliance ICV, LLICV, and CCV, is to terminate the analysis, correct the problem, and recalibrate the instrument. Control limits and corrective actions are found in Section 8.0 and summarized in Table 6a & 6b.

Laboratory Reagent blank (LRB) also known as Method blank. Method blank (LRB) must be carried throughout the entire sample preparation and analytical process. The LRB is prepared by using a volume or weight of reagent water at the volume or weight specified in the preparation method and then carried through the appropriate analytical process. The LRB has to be below the RL divided by the dilution factor for each target analyte. If the LRB does not contain target analytes at a level that interferes with the project specific requirements, then the LRB is acceptable. Control limits and corrective actions are summarized in Table 6a & 6b.

A Laboratory Control Sample (LCS) must be analyzed for each analyte using the same sample preparations, analytical methods, and QA/QC procedures employed for the test samples. One LCS must be prepared and analyzed for each sample batch at a frequency of one LCS for a least every 20 samples or every 10 samples for drinking waters. The recovery limits for the LCS are 85-115% of the true value (stated in the preparation log). If the LCS is outside of the control limits the entire sample batch must be re-digested and re-analyzed. Control limits and corrective actions are summarized in Table 6a & 6b. (In method 200.8, the LCS is referred to as the Laboratory Fortified Blank, LFB).

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, a concentration of 0.10 mg/kg is added pre-digestion. The acceptable limits for performance are summarized in Section 8.10 and Table 6a & 6b.

- Calculate the percent recovery of each analyte, corrected for background concentrations measured in the unfortified (original) sample. Percent recovery must 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.

Analyze one matrix duplicate (Dp) sample for every 10 water samples or every 20 soil samples. In some cases, a matrix spike duplicate (MSD) is used instead of the matrix duplicate, especially if the analytes in the sample are of low concentration. A control limit of 20% RPD must 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 must 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. Control limits and corrective actions are summarized in Table 6a & 6b.

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).

The Quality Control requirements and limits vary slightly, based upon the method referenced in the analytical report (i.e. 6020A 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 water samples and 20 soil samples. The acceptable limits for performance are summarized in Table 6a & 6b and the procedures can be found in Section 7.0, Numbers 6-12.

- Requirements for all methods:
  - 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.
  - 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, must be recovered to within 75 to 125 percent of the known value. The spike addition must be based on the indigenous concentration of each element of interest in the sample. If the spike is not recovered within the specified limits, the sample is spiked and re-analyzed according to Figure 1. The same recovery limits apply to the spiked dilution.

- 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 8.0.

- When the intensity of any internal standard in the sample to falls outside 70-125% of the intensity of that internal standard in the initial calibration standard (Calibration Blank or std-0.00), follow the procedure described in Section 8.0. The intensity levels of the internal standards for the ICV/LLICV/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.

♦ Method 6020/6020A specific requirements:

- 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.

- 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. This is done by analyzing the interference check solutions ICS-A and ICS-AB. The recovery of the elements of interest in ICS-AB (listed in Table 4 at a concentration of 0.02 ppm) must be between 70-135% (± 20% for DoD projects) (see Section 7.0, Number 12 for procedure information and Table 6a & 6b for a summary).

- The LLICV is used to verify the linearity of the low end of the calibration curve. The LLICV must be analyzed after every new calibration with the measurements not exceeding ± 30% (± 20% for DoD projects) of the true value. If the LLICV is outside of these limits the run must

be stopped and the instrument recalibrated and the new calibration verified (see Section 7.0, Number 9 for procedure information and Table 6a & 6b for a summary).

The analyst will follow SOP #QA-007 and complete the appropriate review form upon completion of the analysis.

9.0 METHOD PERFORMANCE

The precision and accuracy of the method depends upon the overall performance of the sample preparation and analysis. Performance Evaluation samples are analyzed periodically in order to prove the performance of the method. 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, 6020 and 6020A.

10.0 EQUIPMENT MAINTENANCE AND TROUBLESHOOTING

All equipment shall be maintained and calibrated according to manufacturer's procedures. When equipment is not performing as required, the instrument shall not be used until it is recalibrated or replaced.

11.0 SAFETY

Every Laboratory area has eyewash, emergency shower, and fire extinguisher. The metals lab also has dust masks available for use with dust samples. The air system throughout 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. A reference file of material safety data sheets (MSDSs) is available to all personnel.

Specific attention be paid (but not limited) to:

- 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.

- 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.

- 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.

- 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.

12.0 WASTE DISPOSAL

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

13.0 DEFINITIONS

Sample Batch: samples of the same or similar matrix; for this method, a sample batch consists of 20 samples or less.

Method Blank: also referred to as a Laboratory Reagent Blank. an analyte-free matrix to which all reagents are added in the same volumes or proportions as used in the sample processing. The method blank is carried through the complete sample preparation and analytical procedure. The method blank is used to document contamination resulting from the analytical process.

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

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

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

Laboratory Duplicate: aliquots of sample taken from the same container under the same laboratory conditions and processed and analyzed under the same conditions but independently.

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

Method Detection Limit (MDL): the method detection limit is the minimum concentration of a substance that can be measured and reported with 99 percent confidence that the analyte concentration is greater than zero. It is determined from analysis of a sample in a given matrix containing the analyte. An acceptable MDL standard check must produce a signal at least three times the instrument's noise level. Also, a MDL check injection must be made after each major instrument repair or changing of instruments (prior to sample analysis) to determine the performance sensitivity of the analysis.

Calibration Standards: a series of known standard solutions used for calibration of the instrument within the measurable linear range. Calibration standards shall contain, in correct proportion, all reagents required by the method. A minimum of 4 calibration points are used for calibration. Acceptance of the calibration requires a correlation coefficient of 0.997 or better. No samples shall be analyzed without acceptable calibration.

Initial Calibration Verification (ICV): the initial calibration verification standard (different lot # or manufacturer from the initial calibration standard) shall verify the initial calibration curve. The initial calibration verification standard involves the analysis of all target analytes each time the initial calibration is performed.

Continuing Calibration Verification Standard (CCV): a standard solution that is used to check the validity of a calibration curve on a daily basis. It also provides information on satisfactory maintenance and adjustment of the instrument during sample analysis.

Initial calibration blank (ICB): a reagent blank solution, which is analyzed immediately following the ICV. The ICB is analyzed to check for drifts in calibration or possible analyte carry-over.

Continuing Calibration Blank (CCB): a reagent blank solution, which is analyzed immediately following the CCV. The CCB is analyzed to check for drifts in calibration or possible analyte carry-over.

14.0 REFERENCES

Method 200.8, Revision 5.4, 1998.

SW-846, Method 6020A Revision 1, 2007.

SW-846, Method 8000C Revision 3, 2003.

Table 1. List of elements analyzed.

Element	**Symbol**	**CAS#**	**Reporting Limits**		**Method Reference**			DoD Reportable	Quantitaion limit * ug/L	Laboratory performance based
			mg/L	**mg/kg**	**6020**	**200.8**	**6020A**			
Aluminum	Al	7429-90-5	0.05	0.5	X	X	X	X	0.5	
Antimony	Sb	7440-36-0	0.002	0.3	X	X	X	X	2.0	
Arsenic	As	7440-38-2	0.001	0.1	X	X	X	X	0.5	
Barium	Ba	7440-39-3	0.01	1.0	X	X	X	X	0.5	
Beryllium	Be	7440-39-3	0.001	0.50	X	X	X	X	0.5	
Boron	B	7440-42-8	0.01	1.0						X
Cadmium	Cd	7440-43-9	0.0005	0.2	X	X	X	X	0.5	
Calcium	Ca	7440-70-2	0.05	10.0	X		X	X	200	
Chromium	Cr	7440-47-3	0.005	2.0	X	X	X	X	0.5	
Cobalt	Co	7440-48-4	0.01	0.5	X	X	X	X	0.5	
Copper	Cu	7440-50-8	0.004	1.0	X	X	X	X	0.5	
Iron	Fe	7439-89-6	0.1	1.0	X		X	X	2.0	
Lead	Pb	7439-92-1	0.003	1.0	X	X	X	X	0.5	
Lithium	Li	7439-93-2	0.01	1.0						X
Magnesium	Mg	7439-95-4	1.0	4.0	X		X	X	200	
Manganese	Mn	7439-96-5	0.02	1.0	X	X	X	X	2.0	
Molybdenum	Mo	7439-98-7	0.005	0.50		X		X	2.0	
Nickel	Ni	7440-02-0	0.005	1.0	X	X	X	X	0.5	
Potassium	K	7440-09-7	1.0	5.0	X		X	X	200	
Selenium	Se	7782-49-2	0.005	0.2	X	X	X	X	0.5	
Silver	Ag	7440-22-4	0.0002	0.1	X	X	X	X	0.5	
Sodium	Na	7440-23-5	0.05	10.0	X		X	X	200	
Strontium	Sr	7440-24-6	0.005	0.50					1.0	X
Tin	Sn	7440-31-5	0.02	1.0						X
Titanium	Ti	7440-32-6	0.005	1.0					0.5	X
Thallium	Tl	7440-28-0	0.001	0.50	X	X	X	X	0.5	
Vanadium	V	7440-62-2	0.004	1.0	X	X	X	X	0.5	
Zinc	Zn	7440-66-6	0.01	1.0	X	X	X	X	2.0	
* Quantitation limit for individual samples is affected by sample dilutions										

TABLE 2. **STANDARD PREPARATION**

Inorganic Stock Solution IV-7 + IV-19 (100 ppm) + CGSN1-1 + CGLI1-1 + CGSR1-1 (1000 ppm)

I. Working Stock Solution 1 (WS1)

10 mls IV-7 + 10 mls IV-19+ 1 ml CGSN1-1 + 1 ml CGLI1-1 + 1 ml CGSR1-1 + 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. Spiking Solution

50 mls of WS1 to a final volume of 100 mls = 5.0ppm

IV. STANDARDS

Standards	**Volume Working Stock Solution**	**Internal Standard 2.5 ppm**	**HNO_3**	**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
0.001 ppm	1.00 mls WS2	2 mls	2 mls	100 mls
0.0005 ppm	0.50 mls WS2	2 mls	2 mls	100 mls
0.0001 ppm	0.10 mls WS2	2 mls	2 mls	100 mls
0.00 ppm	0.00 mls	2 mls	2 mls	100 mls

Table 3. Standard preparation for Ca, Mg, K, Na (minerals).

Standards ppm	Volume of Working Stock	Source and Lot # of Working Stock (100ppm)	Internal Standard 5.0 ppm	HNO_3	Final Volume
0.0	0.0	High Purity (HM) –	2 mls	2 mls	100 mls
0.20	0.2	High Purity (HM) –	2 ml	2 ml	100 ml
0.50	0.5	High Purity (HM) -	2 ml	2 ml	100 ml
1.0	1.0	High Purity (HM) -	2 ml	2 ml	100 ml
2.0	2.0	High Purity (HM) -	2 ml	2 ml	100 ml
5.0	5.0	High Purity (HM) -	2 ml	2 ml	100 ml
10.0	10.0	High Purity (HM) -	2 ml	2 ml	100 ml
ICV- 5.0	5.0	Spex –	2 ml	2 ml	100 ml

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 must 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 6a. Summary of 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.
Calibration Curve	Once a day and as necessary	R ≥ 0.998 The lowest non-zero calibration point must be at or below reporting limit	Remove allowed points keeping minimum of 3 non-zero points, replace calibration standards if needed and recalibrate instrument.
ICV	After every calibration	90-110%	Verify that method parameters are valid, check calibration tables, replace calibration standards if necessary, and recalibrate the instrument.
ICB	After every ICV	Less than the lower limit of quantitation for every target element.	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.
LLICV	After initial calibration	70-130% Not required for 200.8	Verify that method parameters are valid, check calibration tables, replace calibration standards if necessary, prepare a fresh calibration blank, and recalibrate the instrument.
CCV	After Every 10 sample or less	90-110%	Recalibrate the instrument. Follow method specific requirements (6020, 6020A or 200.8) as to what data prior to the CCV can be used.
CCB	After Every 10 sample or less	Less than the lower limit of quantitation for every target element.	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 or less	85-115%	Re-digest the entire sample batch and reanalyze.
LRB (MB)	Every batch of 20 samples or less	<RL/Dilution factor	Re-digest the entire sample batch and reanalyze.
Dp	Every 10 water samples or every 20 soil samples	0-20%	If all other QC acceptable continue the run; sample result must be flagged; otherwise recalibrate instrument and reanalyze samples.
MS	Every 10 water samples or every 20 soil samples, prior to digestion	75-125%	The sample is spiked and re-analyzed according to Figure 1. .
MSD†	Every 10 water samples or every 20 soil samples, prior to digestion	0-20%	Same as for duplicate.
Dil‡	Once with every batch of 20 samples or less	0-10% Not required for 200.8	If concentration analyzed >100 x MDL, flag data for possible matrix interference.
ICS-A‡	Every 12 hours	<RL for water samples Not required for 200.8	Reevaluate the equations used for corrections, make the necessary adjustments, and recalibrate the instrument. Re-analyze samples associated with the failed ICS.
ICS-AB‡	Every 12 hours	70-135% Not required for 200.8	Reevaluate the equations used for corrections, make the necessary adjustments, and recalibrate the instrument. Re-analyze samples associated with the failed ICS.
IS Samples	With every sample	70-125%	Verify matrix interference by ruling out instrument drift by unacceptable IS recoveries in standards. Dilute 4+1 and reanalyze. Repeat until inside control limits.
IS QC Samples	With every QC Sample	80-120% for ICV/ICB and CCV/CCB	For CCV/CCB's recalibrate the instrument and reanalyze the affected samples.

NOTE:
- *This is a summery table for more information see Sections 8.4 to 8.10
- RL = Reporting Limit.
- Dil = Dilution Test.
- † MSD optional instead of duplicate sample.
- ‡ When Method 6020 & 6020A referenced in the analytical report.
- IS = Internal Standard

Table 6b. Quality Control Items, Frequency, and Corrective Actions for DoD Projects

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Demonstrate acceptable analytical capability	Prior to using any test method and at any time there is a change in instrument type, personnel, test method, or sample matrix.	QC acceptance criteria published by DoD, if available; otherwise method-specified criteria.	Recalculate results; locate and fix problem, then rerun demonstration for those analytes that did not meet criteria.	NA.	This is a demonstration of analytical ability to generate acceptable precision and bias per the procedure in Appendix C. No analysis shall be allowed by analyst until successful demonstration of capability is complete.
Instrument detection limit (IDL) study	At initial set-up and after significant change in instrument type, personnel, test method, or sample matrix.	IDLs shall be ≤ LOD.	NA.	NA.	Samples may not be analyzed without a valid IDL.
Tuning	Prior to ICAL.	Mass calibration ≤ 0.1 amu from the true value; Resolution < 0.9 amu full width at 10% peak height; For stability, RSD ≤ 5% for at least four replicate analyses.	Retune instrument then reanalyze tuning solutions.	Flagging criteria are not appropriate.	No analysis shall be performed without a valid MS tune.
Initial calibration (ICAL) for all analytes (minimum one high standard and a calibration blank)	Daily ICAL prior to sample analysis.	If more than one calibration standard is used, r ≥ 0.995.	Correct problem, then repeat ICAL.	Flagging criteria are not appropriate.	Problem must be corrected. No samples may be run until ICAL has passed.
Second source calibration verification	Once after each ICAL, prior to beginning a sample run.	Value of second source for all analytes within ± 10% of true value.	Verify second source standard. Rerun second source verification. If that fails, correct problem and repeat ICAL.	Flagging criteria are not appropriate.	Problem must be corrected. No samples may be run until calibration has been verified.

Table 6b. Quality Control Items, Frequency, and Corrective Actions for DoD Projects

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Continuing calibration verification (CCV)	After every 10 field samples and at the end of the analysis sequence.	All analytes within ± 10% of true value.	Correct problem, rerun calibration verification. If that fails, then repeat ICAL. Reanalyze all samples since the last successful calibration verification.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply Q-flag to all results for the specific analyte(s) in all samples since the last acceptable calibration verification.	Problem must be corrected. Results may not be reported without a valid CCV. Flagging is only appropriate in cases where the samples cannot be reanalyzed.
Low-level calibration check standard	Daily, after one-point ICAL.	Within ± 20% of true value.	Correct problem, then reanalyze.	Flagging criteria are not appropriate.	No samples may be analyzed without a valid low-level calibration check standard. Low-level calibration check standard should be less than or equal to the reporting limit.
Linear dynamic range or high-level check standard	Every 6 months.	Within ±10% of true value.	NA.	NA.	
Method blank	One per preparatory batch.	No analytes detected > ½ RL and greater than 1/10 the amount measured in any sample or 1/10 the regulatory limit (whichever is greater). Blank result must not otherwise affect sample results. For common laboratory contaminants, no analytes detected > RL.	Correct problem. If required, reprep and reanalyze method blank and all samples processed with the contaminated blank.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply B-flag to all results for the specific analyte(s) in all samples in the associated preparatory batch.	Problem must be corrected. Results may not be reported without a valid method blank. Flagging is only appropriate in cases where the samples cannot be reanalyzed.
Calibration blank	Before beginning a sample run, after every 10 samples, and at end of the analysis sequence.	No analytes detected > LOD.	Correct problem. Re-prep and reanalyze calibration blank. All samples following the last acceptable calibration blank must be reanalyzed.	Apply B-flag to all results for specific analyte(s) in all samples associated with the blank.	
Interference check solutions (ICS-A and ICS-	At the beginning of an analytical run and every 12 hours.	ICS-A: Absolute value of concentration for all non-spiked analytes < LOD (unless they are a	Terminate analysis, locate and correct problem, reanalyze ICS, reanalyze all	If corrective action fails, apply Q-flag to all results for specific analyte(s) in all samples associated with the ICS.	

Table 6b. Quality Control Items, Frequency, and Corrective Actions for DoD Projects

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
AB)		verified trace impurity from one of the spiked analytes ICS-AB: Within ± 20% of true value.	samples.		
LCS containing all analytes to be reported	One per preparatory batch.	80% to 120%	Correct problem, then reprep and reanalyze the LCS and all samples in the associated preparatory batch for failed analytes, if sufficient sample material is available.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply Q-flag to specific analyte(s) in all samples in the associated preparatory batch.	Problem must be corrected. Results may not be reported without a valid LCS. Flagging is only appropriate in cases where the samples cannot be reanalyzed.
Matrix spike (MS)	One per preparatory batch per matrix.	For matrix evaluation, use QC acceptance criteria specified by DoD for LCS.	Examine the project-specific DQOs. If the matrix spike falls outside of DoD criteria, additional quality control tests (dilution test and post-digestion spike addition) are required to evaluate matrix effects.	For the specific analyte(s) in the parent sample, apply J-flag if acceptance criteria are not met.	For matrix evaluation only. If MS results are outside the LCS limits, the data shall be evaluated to determine the source of difference and to determine if there is a matrix effect or analytical error.
Matrix spike duplicate (MSD) or sample duplicate	One per preparatory batch per matrix.	MSD: For matrix evaluation use QC acceptance criteria specified by DoD for LCS MSD or sample duplicate: RPD < 20% (between MS and MSD or sample and sample duplicate).	Examine the project-specific DQOs. Contact the client as to additional measures to be taken.	For the specific analyte(s) in the parent sample, apply J-flag if acceptance criteria are not met.	The data shall be evaluated to determine the source of difference.
Dilution test	One per preparatory batch.	Five-fold dilution must agree within ± 10% of the original measurement.	Perform post-digestion spike addition.	Flagging criteria are not appropriate.	Only applicable for samples with concentrations > 50 x LOQ.
Post digestion spike addition	When dilution test fails or analyte concentration for all samples < 50 x LOD.	Recovery within 75-125%.	Run all associated samples in the preparatory batch by method of standard additions (MSA) or see flagging criteria.	For the specific analyte(s) in the parent sample, apply J-flag if acceptance criteria are not met.	Spike addition should produce a concentration of 10 – 100 x LOQ.
Method of standard	When matrix interference is	NA.	NA.	NA.	Document use of MSA in the case narrative.

Table 6b. Quality Control Items, Frequency, and Corrective Actions for DoD Projects					
QC Check	**Minimum Frequency**	**Acceptance Criteria**	**Corrective Action**	**Flagging Criteria**	**Comments**
additions (MSA)	confirmed.				
Internal standards (IS)	Every sample.	IS intensity within 30-120% of intensity of the IS in the ICAL.	Reanalyze sample at 5-fold dilution with addition of appropriate amounts of internal standards.	Flagging criteria are not appropriate.	
Results reported between DL and LOQ	NA.	NA.	NA.	Apply J-flag to all results between DL and LOQ.	

FIGURE 1.
ICP/MS STANDARDS PREP LOG

DATE	Standards	IS id	Exp. Date	Analyst

Source:_____

Lot #: _____

Exp. Date: _____

FIGURE 2
ICP/MS INITIAL CALIBRATION VERIFICATION (ICV) PREP LOG

DATE	ICV ID	IS id	EXP. DATE	Analyst

Source ID **Lot#** **Expiration Date**

S = SPEX _____ _____

H = High Purity _____ _____

E = ERA _____ _____

FIGURE 2: METALS DIGESTION LOG

METALS DIGESTION

3015A \ 3050B DATE _____

TIME START _____ ANALYST _____

TIME FINISH _____ PREP BATCH MTD-_____

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 / 0.50 mls of 5ppm Spiking Solution

Samples: Water = 0.05 ppm = 50 mls / 0.50 mls of 5ppm Spiking Solution

Soil = 0.10 ppm = 50 mls / 1.0 mls of 5ppm Spiking Solution

Spiking Solution - Lot #_____

2) Spike values for minerals (Ca-Mg-K-Na)

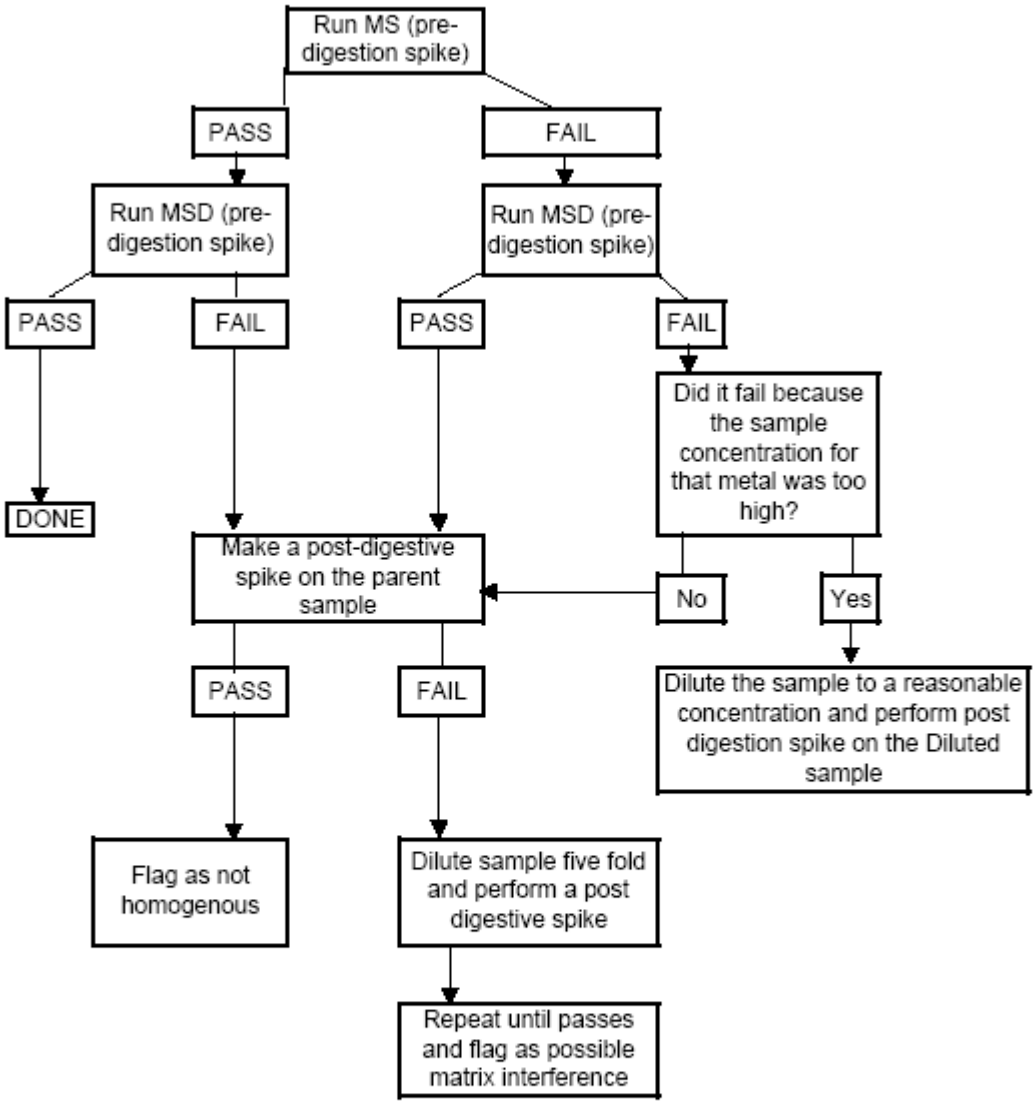
LCS = 1.0 ppm = 50 mls / 0.50 mls HM Stock Solution

Samples (Water or Soil) = 2.0 ppm = 50 mls / 1.0 mls HM Stock Solution

High Purity Stock Solution (HM)- Lot #_____

3) HNO_3 Lot #_____ 4) Centrifuge Tube Lot #_____

FIGURE 4 MS/MSD CORRECTIVE ACTION FLOW CHART



STANDARD OPERATING PROCEDURE

MERCURY IN WATERS, SOLIDS, AND WASTES (COLD-VAPOR TECHNIQUE) USEPA METHOD 245.1 AND SW-846 METHODS 7470A/7471B

APPROVALS:

6/3/11

QA Officer — Date

6/3/11

Technical Director — Date

Number	Description of Change	Date
001-009	Previous changes were not documented	
010	Updated to comply with DoD QSM and ISO 17025 standards.	6/3/11
011		
012		
013		
014		
015		
016		
017		
018		
019		
020		

1.0 SCOPE AND APPLICATION

This 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. This SOP is not applicable for OHIO VAP samples.

2.0 SUMMARY OF METHOD

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 7471B, and 245.1. Typical detection limit for aqueous samples 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 for aqueous samples as low as 0.01 µg/L, with a practical quantitation limit of 0.1 µg/L can be obtained without difficulty. Solid reporting limits range from 0.005 mg/kg to 0.10 mg/kg.

3.0 INTERFERENCES

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

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.

Seawaters, brines, and industrial effluents high in chlorides require additional potassium permanganate (as much as 25 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.

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 minutes more than the retention time of the calibration standards.

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

4.0 APPARATUS AND MATERIALS

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

- Computer-controlled 4-channel high-performance peristaltic pump (12-roller pump head).
- Computerized thermally ozone-free Hg lamp with a thermally controlled Hg lamp housing (for a stabilized Hg vapor lamp).
- 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.
- Integrated ASX-510 Auto Sampler for accommodation of calibration standards and up to 360 samples.

Digestion block.

Polypropylene digestion vessels.

VWR Brand Digital Pipettor dispensing variable volumes from 100 to 1000 µl.

Pipette Dispenser Bottles with adjustable volume 0 - 5 ml in 0.2 ml increments.

Graduated cylinder 100 ml, 1000 ml or equivalent.

Disposable Pasteur pipettes.

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.

Disposable plastic cups.

Analytical balance, 300 g capacity, minimum accuracy ± 0.001 g.

Filter funnel, glass or disposable polypropylene.

Glass-fiber filter paper, 0.45 µm.

Teflon bottles for calibration standards.

Centrifuge.

Tongue Depressors.

Membrane Filters.

Filter flask.

Computer.

5.0 REAGENTS

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

Sulfuric acid (H_2SO_4), concentrated: Trace metal grade, expiration date taken from manufacturer guidelines.

Hydrochloric Acid (HCl), concentrated: Trace metal grade, expiration date taken from manufacturer guidelines.

Nitric 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, shelf life of 1 year from date prepared. End of day rinse.

Nitric acid (HNO_3), concentrated: Trace metal grade, expiration date taken from manufacturer guidelines.

Stannous chloride: 10% stannous chloride in 7% HCl. Prepare as needed, can be stored for 3 days.

Sodium chloride-Hydroxylamine hydrochloride solution, 12%w/v: Dissolve 120 g of sodium chloride and 120 g of Hydroxylamine hydrochloride in 1000 g reagent water. Prepare as needed, shelf life of 1 year from date prepared.

Potassium permanganate ($KMnO_4$), 5% solution (w/v): Dissolve 50 g of potassium permanganate in 1000 g of reagent water. Prepare as needed, shelf life of 1 year from date prepared.

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, shelf life of 1 year from date prepared.

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

The HPS stock solution is used for preparing calibration standards; the SPEX stock solution is used for preparing the initial calibration verification (ICV) standard.

- Mercury working standard: Dilute 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 working solutions must be prepared fresh before making standards. Acidity of the working standard must be maintained at 7% HCl (v/v). This acid (7 ml) must be added immediately after measuring the standard aliquot, and before dilution to final volume (100 g). [According to instrument documentation calibration standards contain 7% HCl].

Instrument rinse solution: 1% HNO_3 and 1% HCl solution.

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

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. Non-aqueous samples should be analyzed as soon as possible. If solid samples are not analyzed immediately, refrigerate samples at 4^0C. Holding time for mercury must not exceed 28 days, from time of collection to time of analysis.

7.0 PROCEDURE

Turn on the Hot Block and allow it to heat to 95^0 C while the samples are being prepared.

1. Sample Preparation:

- Liquids
  - Using a disposable serological pipette, transfer 25 ml/g sample or a smaller amount, if the sample is expected to foam or if it is not aqueous to a polypropylene vessel. The amount of sample used is recorded in the digestion log. Vessels are labeled with sample ID.
  - Repeat this procedure for a batch of 20 samples or less.
  - Each batch needs to include a matrix (spike) duplicate and a matrix spike for every 10 samples, and a Laboratory Control Sample (LCS) and a Laboratory Reagent Blank (LRB) for every 20 samples.
  - To each of the samples, MS-MSD, LCS, standards, and blanks add (under a hood) 1.25 mL conc. H_2SO_4 and 0.66 mL conc. HNO_3 and let set.
  - Dilute to 25 ml (g) with deionized water if needed.
  - The LCS is prepared by adding 0.5 ml of the 100 ppb HPS working standard to 25 ml/g DI water (measured using a disposable serological pipette).

- Prepare MS/MSD by adding 0.5 ml of the 100 ppb HPS working standard solution to the QC samples (measured using a disposable serological pipette).
- Add 3.75 ml Potassium permanganate ($KMnO_4$) solution to all vessels.
- Wait 15 min. The purple permanganate color must remain for at least 15 minutes. If the purple color is gone, add additional $KMnO_4$ in 1 mL aliquots until the purple color remains for at least 15 minutes. Record any extra permanganate added in the sample digestion log (figure 1). The same amount of extra $KMnO_4$ will have to be added to all other samples and standards. (Corrections to the dilution factor will be performed as per 7.1.1.15)
- To all samples, standards, and blanks add 2.0 mL potassium persulfate ($K_2S_2O_8$) solution.
- Place the loosely capped samples in the block digester.
- Heat samples at $95^0C \pm 3^0C$ for 2 hours. Record start and end block digester times on the digestion bench sheet.
- Following digestion, remove the samples and place under a hood to cool.
- When the samples are cool, add 1.5 mL Sodium chloride-hydroxylamine hydrochloride solution to all samples, standards, and blanks. Tightly cap and mix by inverting until samples are clear. Samples are now ready for analysis.
- Calculate the dilution factor (DF) by the formula:

$$DF = \frac{FinalVolume(25)}{Sampleamount} \times \frac{100}{\%Totalsolids} \times CF$$

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 digestion log (Figure 1) and is used in the determination of the mercury result by the CVAA analyzer.

♦ Solids

- Homogenize sample by chopping and mixing sample with a tongue depressor or spatula. Remove any foreign object such as sticks, leaves, or rocks. Weigh

approximately 0.5 g homogenized sample and place into polypropylene vessel. Label vessel with sample ID.

- The amount of sample used is recorded in the preparation log. Repeat this procedure for a batch of 20 samples or less.
- Each batch needs to include a matrix (spike) duplicate, a matrix spike, a Laboratory Control Sample (LCS), and a LRB for every 20 samples.
- LRB and LCS: Weigh out approximately 0.5 grams sand. Record Lot # of sand on digestion log.
- To each of the samples, MS-MSD, LCS, standards, and blanks add (under a hood) 1.25 mL conc. H_2SO_4 and 0.66 mL conc. HNO_3 and let set.
- Dilute to 25 ml (g) with deionized water.
- LCS and MS/MSD: Add 0.5 ml of the 100 ppb HPS working standard solution to the QC sample.
- Add 3.75 mL of potassium permanganate solution to each sample and let stand at least 15 min.
- Add additional portions of potassium permanganate solution, if needed, until the purple color persists for at least 15 min (see 7.1.1.9). Ensure that equal amounts of potassium permanganate are added to standards and blanks.
- Heat for 2 hours min at 95 ± 3 ^{o}C. Record start and end digestion block times on digestion bench sheet.
- Cool and add 1.5 mL of sodium chloride-hydroxylamine hydrochloride to reduce the excess permanganate.
- Calculate the dilution factor (*DF*) by the formula:

$$DF = \frac{FinalVolume(25)}{Sampleamount} \times \frac{100}{\%Totalsolids} \times CF$$

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 digestion log (Figure 1) and is used in the determination of the mercury result by the CVAA analyzer.

2. Calibration Procedure:

- Prepare 7 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, 1.0 ml, 2.0 ml, 6.0 ml and 10 ml in 8 Teflon bottles (125 ml) add 7 ml HCl and bring to 100 ml then add 5 ml H_2SO_4, 2.5 ml HNO_3, 15 ml $KMnO_4$, 8 ml $K_2S_2O_8$, and 6 ml Sodium chloride-Hydroxylamine Hydrochloride. This will provide a calibration curve of 0.0, 0.1, 0.2, 0.5, 1.0, 2.0, 6.0, 10.0 µg/L. The minimum acceptable correlation coefficient is provided in Tables 1 and 2.

- Prepare in a similar manner an Initial Calibration Verification (ICV) standard made from a different source than the calibration standards(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 and dilute to middle of calibration, followed by the steps described in Section 7.0.

- Continuing Calibration Verification (CCV) standard is also prepared as in 7.0 from the HPS working standard, to a concentration of 2.0 µg/L.

- The standard solutions described above must be kept in sealed Teflon bottles, and are to be prepared every 2 weeks or fresh daily for all DoD projects. 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, from the same mercury working standard.

3. Sample Analysis:

- Turn on the Mercury Analyzer and allow it to warm up for a minimum of 1 hour.

- 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).

- Start the Quick Trace program.
  - Click on the instrument button then the analyzer button.
  - Set the pump to 50% and the gas to 100 ml/minute.

- Check to make sure the reagent has a smooth segmented flow. Once this has be established set the pump speed to 100% and the gas flow to 300 ml/minute.
    - Disconnect the GLS exhaust tubing and crimp the waste tubing just before the mixing tee.
    - 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.
    - Wait for the water to drain out of the GLS and then attach the GLS exhaust tubing.
- Place the reagent capillary in the reagent bottle and appropriate tubing into the rinse solution.
- Type in the number of samples that you are running. Then go into method editor and click "read sample" to zero mercury analyzer and pick a standard
- Verify the baseline and peak are correct for the standard.
- Exit method editor and press start to analyze samples

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

5. Shutting down instrument: Rinse 10% Nitric Acid through the instrument for 10 minutes then DI water for 1 minute, drain out, and shut off.

6. Calculations:

Relative Percent Difference: $$RPD = \frac{(S - D)}{\left[\frac{S + D}{2}\right]} \times 100$$

Where: S = Initial sample result
D = Duplicate sample result

Spike Recovery Percent Recovery: $$\frac{SSR - SR}{SA} \times 100$$

Where: SSR = Spike sample result
SR = Sample (unspiked) result
SA = Spike added

8.0 QUALITY CONTROL

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

Initial Demonstration of Performance.

- 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.

- Linear calibration ranges - The upper limit of the linear calibration range must 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 must be determined initially, and whenever a significant change in instrument response is observed.

- A Method Detection Limit (MDL) study is performed annually or whenever a significant change in background or instrument response is expected (e.g. detector change) by following the procedure from SOP #060004.

Assessing Laboratory Performance.

- The laboratory must analyze at least one LRB with each batch of 20 samples of samples or less. 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 (1/2 the reporting limit for DoD projects), 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.

- The laboratory must analyze at least one LCS with each batch of 20 samples or less. Calculate accuracy as percent recovery. If recovery of mercury falls outside control limits (See Table 1 and Table 2), the method is judged out of control. The source of the problem should be identified and resolved and new aliquots of the samples re-digested and reanalyzed.

- Instrument performance:

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

- Check instrument calibration by analyzing the initial calibration verification solution (ICV), made from a source different than the calibration standards (Section 5.0), and the initial calibration blank (ICB). Corrective action listed in Tables 1 and 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 at the beginning of the analysis and after the last sample.

Assessing Analyte Recovery and Data Quality.

- The laboratory must analyze a matrix spike (MS) with every 10 aqueous samples or 20 soil samples. Calculate the percent recovery of each analyte, corrected for background concentrations measured in the unfortified (original) sample. Percent recovery can 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 acceptance limits for MS samples are provided in Tables 1 and 2. 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 must 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 25% of the concentration of mercury in the original sample.

- Analyze one matrix duplicate (Dp) sample for every 10 aqueous samples or 20 soil samples. 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 must 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 re-digested and reanalyzed.

Quality control items employed and evaluated are provided in Table 1 (Table 2 for DoD projects). In addition, the table indicates the frequency of each QC item along with appropriate courses of corrective action.

The analyst will follow SOP QA-007 and complete the appropriate review form upon completion of the analysis.

9.0 METHOD PERFORMANCE

The precision and accuracy of the method will depend upon the overall performance of the sample preparation and analysis. Performance Evaluation samples are analyzed periodically in order to prove the performance of the method.

10.0 EQUIPMENT MAINTENANCE AND TROUBLESHOOTING

Each instrument is assigned a maintenance logbook. All maintenance performed on the instrument must be recorded. Additionally, any modifications to the instrument settings shall be noted in the specific instrument logbook. Maintenance procedures provided in the equipment manual shall be followed. Maintenance may include changing drain line and or waste lines.

11.0 SAFETY

Many mercury compounds are highly toxic if swallowed, inhaled, or absorbed through the skin. Extreme care must be exercised in the handling of concentrated mercury reagents. Concentrated mercury reagents should only be handled by analysts knowledgeable of their risks and of safe handling procedures. Eye protection and gloves must be worn while performing the analyses. Every laboratory area has eyewash, emergency shower, and fire extinguisher. The metals lab also has dust masks available for use with dust samples. The air system throughout 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. A reference file of material safety data sheets (MSDSs) is available to all personnel.

Specific attention be paid (but not limited) to:

- 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.

- 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.

- 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.

- 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.

12.0 WASTE DISPOSAL AND POLLUTION PREVENTION

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

13.0 DEFINITIONS

Sample Batch: samples of the same or similar matrix; for mercury analysis, a sample batch consists of 20 samples or less.

Laboratory Reagent Blank (LRB) (also known as Method Blank): an analyte-free matrix to which all reagents are added in the same volumes or proportions as used in the sample processing. The LRB is carried through the complete sample preparation and analytical procedure. The LRB is used to document contamination resulting from the analytical process.

Laboratory Control Sample (also known as Laboratory Fortified Blank, Spiked Blank, or QC Check Sample): sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes. It is generally used to establish intra-laboratory or analyst-specific precision and bias or to assess the performance of all or a portion of the measurement system.

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

Matrix Spike Duplicate (also known as Spiked Sample or Fortified Sample Duplicate): a second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

Method Detection Limit (MDL): the method detection limit is the minimum concentration of a substance that can be measured and reported with 99 percent confidence that the analyte concentration is greater than zero. It is determined from analysis of a sample in a given matrix containing the analyte. An acceptable MDL standard check must produce a signal at least 3 times the instrument's noise level. Also, a MDL check injection must be

made after each major instrument repair or changing of instruments (prior to sample analysis) to determine the performance sensitivity of the analysis.

Laboratory Duplicate: aliquots of sample taken from the same container under the same laboratory conditions and processed and analyzed under the same conditions but independently.

Calibration Standards: a series of known standard solutions used for calibration of the instrument within the measurable linear range. Calibration standards shall contain, in correct proportion, all reagents required by the method. A minimum of 5 calibration points are used for Mercury calibration. Acceptance of the calibration requires a correlation coefficient of 0.997 or better. No samples shall be analyzed without acceptable calibration.

Initial Calibration Verification (ICV): the initial calibration verification standard (different lot # or manufacturer from the initial calibration standard) shall verify the initial calibration curve. The initial calibration verification standard involves the analysis of all target analytes each time the initial calibration is performed.

Continuing Calibration Verification Standard (CCV): a standard solution that is used to check the validity of a calibration curve on a daily basis. It also provides information on satisfactory maintenance and adjustment of the instrument during sample analysis.

Initial calibration blank (ICB): a reagent blank solution, which is analyzed immediately following the ICV. The ICB is analyzed to check for drifts in calibration or possible analyte carry-over.

Continuing Calibration Blank (CCB): a reagent blank solution, which is analyzed immediately following the CCV. The CCB is analyzed to check for drifts in calibration or possible analyte carry-over.

14.0 REFERENCES

Department of Defense, *Quality Systems Manual for Environmental Laboratories* (DoD QSM), DoD Environmental Data Quality Workgroup, Department of Navy, Lead Service, Based on NELAC Voted Revision 5 June 2003, Version 4.1, April 22,2009.

Quick Trace Mercury Analyzer M-7500 Instrument Manual.

USEPA, *Methods for the Determination of Metals in Environmental Samples*. EPA/600/R94/111, Method 245.1.

USEPA, SW-846, Revision 3, Method 7470A.

USEPA, SW-846, Revision 3, Method 7471B.

Table 1: Quality Control Items, Frequency and Corrective Action

QA Items	Frequency	Acceptance Criteria	Corrective Action
Initial Calibration Verification (ICV)	Following Calibration	90-110%	Terminate analysis, correct problem, and recalibrate instrument
Initial Calibration Blank (ICB)	Following Calibration	< Reporting Limit of aqueous samples	Correct problem, re-analyze ICV and ICB
Continuing Calibration Verification (CCV)	Before and after each batch of 10 analytical samples (not including QC samples)	90-110%	Terminate analysis, correct problem, and recalibrate instrument. Re-analyze all samples following last acceptable calibration
Continuing Calibration Blank (CCB)	Before and after each batch of 10 analytical samples (not including QC samples)	< Reporting Limit of aqueous samples	Correct problem, re-analyze all samples following last acceptable calibration blank
Laboratory Control Sample (LCS)	One per batch or 20 samples or less	85-115%	Identify and resolve problem. Re-digest and re-analyze sample set
Laboratory Reagent Blank (Method Blank) (LRB)	One per batch or 20 samples or less	< Reporting Limit	Identify and eliminate source of contamination. Re-digest and re-analyze sample set
Matrix Duplicate (Dp)	One per 20 soil samples or 10 liquid samples, maybe replaced by MSD	DUP RPD < 20%	Evaluate to determine if due to matrix interference.
Matrix Spike (MS)	One per 20 soil samples or 10 liquid samples	80-120%	Evaluate to determine if due to matrix interference.
Matrix Spike Duplicate (MSD)	One per 20 soil samples or 10 liquid samples	DUP RPD <20%	Evaluate to determine if due to matrix interference.

Table 2: Quality Control Items, Frequency and Corrective Action for DoD Projects

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Initial calibration (ICAL) for all analytes CVAA: minimum 5 standards and a calibration blank	Daily ICAL prior to sample analysis.	If more than one calibration standard is used, $r \geq 0.995$.	Correct problem, then repeat ICAL.	Flagging criteria are not appropriate.	Problem must be corrected. No samples may be run until ICAL has passed.
Second source calibration verification (ICV)	One after each ICAL, prior to beginning a sample run.	Value of second source for all analytes(s) within ± 10% of true value.	Correct problem and verify second source standard. Rerun ICV. If that fails, correct problem and repeat ICAL.	Flagging criteria are not appropriate.	Problem must be corrected. No samples may be run until calibration has been verified.
Continuing calibration verification (CCV)	After every 10 field samples and at the end of the analysis sequence.	CVAA: within ± 20% of true value	Correct problem, rerun calibration verification. If that fails, then repeat ICAL. Reanalyze all samples since the last successful calibration verification.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply flag to all results for the specific analyte(s) in all samples since the last acceptable calibration verification.	Problem must be corrected. Results may not be reported without a valid CCV. Flagging is only appropriate in cases where the samples cannot be reanalyzed.
Method blank	One per preparatory batch.	No analytes detected > ½ RL and greater than 1/10 the amount measured in any sample or 1/10 the regulatory limit (whichever is greater). Blank result must not otherwise affect sample results.	Correct problem. If required, reprep and reanalyze method blank and all samples processed with the contaminated blank.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply flag to all results for the specific analyte(s) in all samples in the associated preparatory batch.	Problem must be corrected. Results may not be reported without a valid method blank. Flagging is only appropriate where the samples cannot be reanalyzed.
Calibration blank	Before beginning a sample run, after every 10 samples,	No analytes detected > LOD.	Correct problem. Re-prep and reanalyze calibration blank. All samples following	Apply flag to all results for specific analyte(s) in all samples associated with the	

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
	and at end of the analysis sequence.		the last acceptable calibration blank must be reanalyzed.	blank.	
LCS containing all analytes to be reported	One per preparatory batch.	QC acceptance criteria specified by DoD. 80-120% or laboratory generated in-house limits.	Correct problem, then reprep and reanalyze the LCS and all samples in the associated preparatory batch for failed analytes, if sufficient sample material is available.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply flag to specific analyte(s) in all samples in the associated preparatory batch.	Problem must be corrected. Results may not be reported without a valid LCS. Flagging is only appropriate in cases where the samples cannot be reanalyzed.
Matrix spike (MS)	One per preparatory batch per matrix.	For matrix evaluation, use QC acceptance criteria specified by DoD for LCS.	Examine the project-specific DQOs. If the matrix spike falls outside of DoD criteria, additional quality control tests are required to evaluate matrix effects.	For specific analyte(s) in the parent sample, apply flag if acceptance criteria are not met.	For matrix evaluation only. If MS results are outside the LCS limits, the data shall be evaluated to determine the source of difference and to determine if there is a matrix effect or analytical error.
Matrix spike duplicate (MSD) or sample duplicate	One per prepatory batch per matrix.	MSD: For matrix evaluation use QC acceptance criteria specified by DoD for LCS. MSD or sample duplicate: RPD $\leq$ 20% (between MS and MSD or sample and sample duplicate).	Examine the project-specific DQOs. Contact the client as to additional measures to be taken.	For specific analyte(s) in the parent sample, apply flag if acceptance criteria are not met.	The data shall be evaluated to determine the source of difference.
Results reported between DL and LOQ	NA	NA	NA	Apply flag to all results between DL and LOQ.	

Figure 1
Mercury Digestion

TIME START**: _____** DATE _____
TIME STOP: _____ TEMP: block #1_____ º C ANALYST_____
PREP BATCH: HGD-_____ block #2_____ º C REVIEWED BY _____
block #3_____ º C DATE _____

SAMPLE#	BTL ID	SAMPLE AMOUNT GRAMS (g)	%TOT. SOLIDS	DRY SAMPLE WT.	DILUTION FACTOR	FINAL VOLUME	REMARKS
LCS-	------		--------	----------		25g	
LRB-	------		--------	----------		25g	

NOTES: 1) Spike values (unless otherwise stated):

- 2.0 ppb for LCS: 0.50 ml of HPS solution (Lot# Exp)
- 2.0 ppb for liquid samples: 0.50 ml of HPS solution (Lot# Exp)
- 0.002 ppm for solid samples: 0.50 ml of HPS solution (Lot# Exp)

Figure 2

Date	Analyst	Standard ID and PPM conc. (bold)	Source	mls of 100 ppm working solution/ final volume	Expiration Date	Remarks
		HP working stock	HPS			
		0.00-H	HPS			
		0.10-H	HPS			
		020-H	HPS			
		0.50-H	HPS			
		1.00-H	HPS			
		2.00-H	HPS			
		6.00-H	HPS			
		10.0-H	HPS			
		CCV	HPS			
		ERA	ERA			
		5.00- S (ICV)	SPEX			
		HP working stock	HPS			
		0.00-H	HPS			
		0.10-H	HPS			
		0.20-H	HPS			
		0.50-H	HPS			
		1.00-H	HPS			
		2.00-H	HPS			
		6.00-H	HPS			
		10.0-H	HPS			
		CCV	HPS			
		ERA	ERA			
		5.00-S (ICV)	SPEX			
		HP working stock	HPS			
		0.00-H	HPS			
		0.10-H	HPS			
		0.20-H	HPS			
		0.50-H	HPS			
		1.00-H	HPS			
		2.00-H	HPS			
		6.00-H	HPS			
		10.0-H	HPS			
		CCV	HPS			
		ERA	ERA			
		5.00-S (ICV)	SPEX			
		HP working stock	HPS			
		0.00-H	HPS			
		0.10-H	HPS			
		0.20-H	HPS			
		0.50-H	HPS			
		1.00-H	HPS			
		2.00-H	HPS			
		6.00-H	HPS			
		10.0-H	HPS			
		CCV	HPS			
		ERA	ERA			
		5.00-(ICV)	SPEX			

Source ID	**Lot#**	**Expiration Date**
Spex	_____	_____
High Purity (HPS)	_____	_____

ERA _____ _____

STANDARD OPERATING PROCEDURE

POLYCHLORINATED BIPHENYLS (PCBS) BY GC METHOD 8082A

APPROVALS:

7/19/11

QA Officer — Date

7/19/11

Technical Director — Date

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Number	Description of Change	Date
001-010	Previous changes were not documented	
011	Updated to comply with DoD QSM and ISO 17025 standards.	6/3/11
012	Updated to include 8082A Method references	7/19/11
013		
014		
015		
016		
017		
018		
019		
020		
021		

1.0 SCOPE AND APPLICATION

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

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.

This method also includes different clean-up procedures used to assist in removing some of the more common found interferences.

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.

The Method Detection Limits (MDLs) for Aroclors are determined annually on all instruments analyzing PCBs. Estimated method detection limits are available on Merit's network and VLIMs.

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.

2.0 SUMMARY OF METHOD

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.

Aqueous samples are extracted at neutral pH with methylene chloride using Merit's SOP #: EXL-003 (PCB Extraction Liquid).

Solid samples are extracted with hexane using Merit's SOP#: EXL-004 (PCB Extraction Solid).

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 organochlorine or organophosphorus pesticides. Therefore, the analysis of pesticides is not covered by this SOP.

After the acid clean-up, a sulfur clean-up 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).

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).

The chromatographic data is used to determine the seven Aroclors in Section 1.0.

3.0 INTERFERENCES

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.

- Contaminated solvents, reagents, or sample processing hardware.
- Contaminated GC carrier gas, parts, column surfaces, or detector surfaces.
- Compounds extracted from the sample matrix to which the detector will respond.

[1] Reference for this procedure is SW-846, Revision 3, December 1996 Method 3510C, Liquid Liquid Separatory Funnel Extraction, and, Method 3550C, Ultrasonic Extraction.

Interferences by phthalate esters introduced during sample preparation can pose a major problem in PCB determinations.

- 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.

- 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 Number 2, Section 7.0 (sulfuric acid/permanganate cleanup), which is required for all PCB analysis.

- Cross-contamination of clean glassware is avoided by scrupulously cleaning and then baking glassware in a 550ºC oven for 4 – 12 hours.

    - 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.

    - 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 Section 7.0).

4.0 APPARATUS AND MATERIALS

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.

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.

- Narrow-bore columns are installed in split/splitless (Grob-type) injectors.
- 30m x 0.25mm ID fused silica capillary column chemically bonded with SE-54 (DB-5, 0.25um film thickness).

- 30m x 0.25mm ID fused silica capillary column chemically bonded with 35 percent phenyl methylpolysiloxane (DB-608, 0.25um film thickness)

- Column pair is mounted in a press-fit Y-shaped glass 3-way fused-silica connector (Supelco)

Column rinsing kit - Bonded-phase column rinse kit.

Glass vials for sample storage, cleaning, and standard preparation.

Hamilton Syringes (1ul to 1000 ul).

Sample Vials: 1.8 ml screw cap with PTFE liner and 4.0 ml calibrated screw cap.

Maintenance Logbook.

Disposable Pipettes.

Beakers.

5.0 REAGENTS

Reagent grade or pesticide grade chemicals are used in all tests. Unless otherwise indicated, it is intended that all reagents must 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 4 ± 2ºC 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.

Sample extracts are prepared by liquid - liquid extraction (SOP#: EXL-003 for waster samples or ultrasonic extraction (SOP#: EXL-004) 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 must be pesticide quality or equivalent.

- n-Hexane, C_6H_{14}.
- Methanol, CH_3OH.
- Acetone, CH_3COCH_3.
- Ethyl Ether (6%)

Deionized (DI) Water.

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.

Calibration standards for Aroclors.

- 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.

- The 1016/1260 mixture is used as a standard to demonstrate that a sample does not 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, if they are 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 6).

- Method 8082A 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." 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.

Copper balls, pre-cleaned. A method blank must be analyzed demonstrating that there is no interference.

Copper powder.

Sodium Sulfate Na_2SO_4, pre-cleaned with Methylene Chloride, a method blank must be analyzed demonstrating that there are no interferences.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

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.

Aqueous samples are extracted within 7 days from sample collection. Solid samples must be extracted within 14 days of sample collection.

Extracts are stored under refrigeration at 4 ± 2ºC and are analyzed within 40 days of extraction.

7.0 PROCEDURE

1. Samples are extracted using the SOP#'s EXL-003 and EXL-004.

   - Water samples are extracted at a neutral pH with methylene chloride using a separatory funnel.
   - Solid samples are extracted with ultrasonic extraction.
   - 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.

2. Extract clean-ups.

   - **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. (MANDATORY FOR ANALYSIS AND QC SAMPLES)

     - Place up to 2 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 must be worn at all times.
     - Place the cap on the vial and shake the extract with the acid causing a visible vortex. The acid will dissolve and carbonize the interferences commonly found in PCB samples.
     - Blanks and replicate analysis samples must be subjected to the same cleanup as the samples associated with them.
     - Allow the phase to separate for at least one minute. Examine the hexane (hexane) layer, it must not be highly colored, nor have a visible emulsion or cloudiness. If a clean phase separation is achieved, proceed to Number 2.
     - If the acid is "carbonized" or turns a dark brown color remove the sulfuric acid layer from the vial and dispose of it properly. Add another portion of the sulfuric acid and repeat bullets three and four under Number 2.

[2] Reference for Sulfuric Acid clean-up is SW-846, Revision 3, December 1996 Method 3665: Sulfuric Acid

- Transfer the hexane to a clean 4 ml vial. Take care not to include any of the acid layer in this clean vial, as it can cause damage to the instrumentation. Once the hexane layer is removed, perform a second extraction of the acid layer.

- Add an additional 1 ml of hexane to the sulfuric acid layer, cap and shake. This second extraction is done to ensure quantitated transfer of the PCBs, when needed. If still dirty, go to the alumina cleanup.

- **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. (MANDATORY FOR ANALYSIS AND QC SAMPLES)

  - 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.

  - 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.

  - If copper powder is used, follow Sulfur Clean-up and Alumina Clean-up and then carefully transfer the "cleaned" extract using a disposable pipette into another vial to prevent the "powder" from plugging up the auto syringe.

- **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.

  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.

[3] Reference for Sulfur clean-up is SW-846, Revision 3, December 1996 Method 3660B: Sulfur Clean-up using copper.
[4] Reference for Alumina clean-up is SW-846, Revision 3, December 1996 Method 3611B: Alumina Column Clean-up & Separation of Petroleum Products.

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).

- Place a clean glass wool plug in the bottom of a 50 ml disposable chromatographic column.
- On top of this plug, add 2 cm of anhydrous Na_2SO_4 and tap it down.
- Pour about 10 g of activated (130°C for 12 hours) Alumina (150 mesh) into the column.
- Tap it down and place 2 cm of anhydrous (130°C for 12 hours) Na_2SO_4 on top of the Alumina.
- Rinse the column with 40 ml hexane.

Note *The column must 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.*

- Using a long pasture pipette, place the sample extract on the column followed by rinse of the sample vial and the column with 2 ml hexane.
- Wash the column with 20 ml hexane and place the eluted hexane in a beaker labeled "Dirty Used Hexane". This washes the aliphatic interferences out of the sample.
- Elute 80 ml 6% ethyl ether in hexane through the column and collect it for the analysis of PCBs.
- Concentrate the eluted hexane to 0.5 ml inside the Zymark Evaporation Station.
- 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.
- Add 2 ml Sulfuric Acid (H_2SO_4) (concentrated) to the vial cap and shake. *Note: this carbonizes and dissolves much of the remaining interfering compounds*.
- Record alumina cleanup on bench sheet.

- **Dioxin cleanup:** This cleanup is similar to alumina but with a finer mesh column. The columns are pre-made and located in second drawer under the glassware ovens in the organic prep lab.
    - Set up is the same as alumina, except the columns are pre-made and placed in the slots in back.
    - Place clean beakers under the columns. All solvent extracted in this process will be kept. Label beakers with sample ID #.
    - Flush column with 120 ml hexane, this can take 4 columns worth of solvent. The column portion is thicker and media is finer so it requires more solvent to saturate.
    - Add sample to column, place columns over evaporation tubes, and flush column with collected hexane.
    - Evaporate samples in the evaporation tubes, to make room for additional hexane.
    - Once evaporated, place tubes back under their respective columns and add 120 ml of Hexane.
    - Evaporate to 0.5 ml, transfer and adjust to final of 1 ml of sample and analyze.
    - Add 2 ml Sulfuric Acid (H_2SO_4) (concentrated) to the vial cap and shake. *Note: this carbonizes and dissolves much of the remaining interfering compounds*.
    - Record dioxin cleanup on bench sheet and write "dx" on sample label.

3. GC conditions.

- **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.
- GC temperature programs and flow rates are listed in Table 1.

4. Calibration.

- Prepare calibration standards as described in the standard preparation logbook for PCBs/Pesticides (See Table 6). 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 must be established which optimize both peak resolution and sensitivity. The total run time must 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 must always be cleaned prior to performing the initial calibration.

- PCBs are quantitatively determined as Aroclors. The initial calibration consists of the following protocols:
  - 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.
  - 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." Positive identification of Aroclors other than 1016 or 1260, require the appropriate Aroclor standard to be run and samples re-analyzed.
  - 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.
- 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.
- Record the peak area for each characteristic Aroclor peak to be used for quantitation using the Chrom Perfect Software.
- A minimum of three 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 three to five 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.

- 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.

- Calculate the calibration factor (CF) for each characteristic Aroclor peak in each of the initial calibration standards using the equation below.

$$CF = \frac{\text{Peak Area (or Height) in the Standard}}{\text{Total Mass of the Standard Injected (in nanograms)}}$$

- 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 the seventh main bullet under Number 6. [5]

- 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 coefficient of determination (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.

5. Retention Time Windows.

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

[5] Reference for RSD values is SW-846, Revision 3, December 1996 Method 8000B Determinative Chromatographic Separations

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.

6. Gas chromatographic analysis of sample extracts.

- The same GC operating conditions used for the initial calibration are used for sample analyses and calibration verification.

- An analytical sequence of laboratory samples and QC samples is templated using 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.

- 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.

- The calibration factor for each analyte calculated from the calibration verification standard (CF_v) must not exceed a difference of more than ± 20 % when compared to the mean calibration factor from the initial calibration curve:

$$\% \text{ Difference} = \frac{\overline{CF} - CF_v}{\overline{CF}} \times 100$$

- 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 8 Quality Control Items, Frequency and Corrective Action.

- Inject a 1-2 uL (third main bullet under Number 6) aliquot of the concentrated sample extract.
- Qualitative identifications of target analytes are made by examination of the sample chromatograms, as described in Number 9.
- Quantitative results are determined for each identified Aroclor, using the procedures described in Number 10. If the responses in the sample chromatogram exceed the calibration range of the system, dilute the extract and reanalyze.
- 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.
- 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.
- 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.
- 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. Qualitative Identification (The equations governing the quantification, recovery and precision are referenced in the glossary section of the QA/QC manual).

- 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).

- 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.

- 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).

- Positive identifications require a second column confirmation. Both QC samples and calibrations are verified with the second (confirmation) column.

- Project-specific requirements must be followed when reporting data. If project-specific requirements have not been specified, method requirements must be followed. If the method does not include reporting requirements, then report the results from the primary column or detector, unless there is a scientifically valid and documented reason for not doing so.

8. Quantitation of PCBs

- 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.

- 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.

- 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 # ORL-003.

- Compound identifications are supported by at least one additional qualitative technique (i.e., second column confirmation).
    - For Ohio VAP samples and DoD Projects, both columns must meet the calibration and QC criteria.
- 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.

9. Chromatographic System Maintenance as Corrective Action.

- When system performance does not meet the established QC requirements, corrective action is required, and can include one or more of the following.
    - 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.
- Metal injector body.
    - 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.
    - 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.

- Consult the manufacturer's instructions regarding deactivating the injector port body. Glass injection port liners may require deactivation with a silanizing solution containing dimethyldichlorosilane.

♦ Column rinsing.

- The column is rinsed with hexane.

10. Calculations

Relative Percent Difference: $$RPD = \frac{(S - D)}{\left[\frac{S + D}{2}\right]} \times 100$$

Where: S = Initial sample result
D = Duplicate sample result

Spike Recovery Percent Recovery: $$\frac{SSR - SR}{SA} \times 100$$

Where: SSR = Spike sample result
SR = Sample (unspiked) result
SA = Spike added

8.0 QUALITY CONTROL

Quality control procedures necessary to evaluate the GC system operation include evaluation of retention time windows, calibration verification and chromatographic analysis of samples are listed in Table 8a and 8b. In addition the tables indicate the frequency of the QC item along with the course of corrective action.

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 must 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.

Method Detection Limit (MDL). The MDL is performed annually based on the procedure in SOP # QA-009. MDL are available on Merit's network and in VLIMs.

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 ± 3σ. The results for the water and solid matrices are given in Table 4.

The Continuing Calibration Verification (CCV) concentrate must 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.

- 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.

- If the averaged recovery of compounds found in the CCV is less than 80% or greater than 120% of the true value, the laboratory performance is judged to be out of control, and the problem must be corrected. Please refer to Table 8 Quality Control Items, Frequency and Corrective Action.

- Include a calibration standard after each group of 20 samples. The response factors for the calibration must be within 20 percent of the initial calibration. When this continuing calibration is out of this acceptance window, the laboratory must halt the analysis and take corrective action. Please refer to Table 8a and 8b Quality Control Items, Frequency and Corrective Action.

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.

- Documenting the effect of the matrix must 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 must 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 must be used for spiking. If samples are expected to contain target analytes, then laboratories can use one matrix spike and a duplicate analysis of an unspiked field sample.

- 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.

- 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.

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). TCX will be evaluated on a client/project specific basis. The surrogate standard is prepared by the GC analyst at a concentration of 0.03mg/l. and utilized by the extraction analyst. Table 5 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.

The MS/MSD and LCS spikes contain a mixture of Aroclor 1016/1260. This spike must 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.

The analyst will follow SOP# QA-007 and complete the appropriate review form upon completion of the analysis.

9.0 METHOD PERFORMANCE

Laboratory specific data are provided in this document.

The MDLs and PQLs can be found on Merit's network and in VLIMs.

Table 5 presents the lower and upper acceptance criteria for all surrogates.

10.0 EQUIPMENT MAINTENANCE AND TROUBLESHOOTING

Each instrument is assigned a maintenance logbook. All maintenance performed on the instrument must be recorded. Additionally, any modifications to the instrument settings must be noted in the specific instrument logbook. Maintenance procedures provided in the equipment manual must be followed. Maintenance includes: clipping/replacing the column, replacing the heat detector, solvent backflushing, cleaning injector port, and replacing the calibration standard. Refer to Number 9 in Section 7.0 for specific procedures.

11.0 SAFETY

Eye protection and gloves must be worn while performing the analyses. Every laboratory area has an eyewash, emergency shower, and fire extinguisher. The metals lab also has dust masks available for use with dust samples. The air system throughout 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. A reference file of material safety data sheets (MSDSs) is available to all personnel.

Specific attention be paid (but not limited) to:

- Sodium sulfate is mildly toxic by ingestion, not considered an explosion hazard, and oxides of sulfur and sodium may form when heated to decomposition. Keep in a tightly closed container, stored in a cool, dry, ventilated area. Protect against physical damage. Isolate from incompatible substances. Containers of this material may be hazardous when empty since they retain product residues (dust, solids); observe all warnings and precautions listed for the product.

- Hexane is extremely flammable liquid and vapor, causes irritation to skin, eyes, and respiratory tract, and overexposure may cause lightheadedness, nausea, headache, and blurred vision. Above flash point, vapor-air mixtures are explosive within flammable limits. Contact with oxidizing materials may cause extremely violent combustion. Sensitive to static discharge.

12.0 WASTE DISPOSAL AND POLLUTION PREVENTION

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

13.0 DEFINITIONS

Sample Batch: samples of the same or similar matrix; for this method, a sample batch consists of 20 samples or less.

Method Blank: an analyte-free matrix to which all reagents are added in the same volumes or proportions as used in the sample processing. The method blank is carried through the complete sample preparation and analytical procedure. The method blank is used to document contamination resulting from the analytical process.

Laboratory Control Spike (LCS): Milli-Q water (for water) and Organic-Free Soil (for soil) is spiked with 1016/1260 Aroclors (unless a specified Aroclor(s) is requested) and carried through the complete sample preparation and analytical procedure. The control spike is used to document the ability of an analyst to generate acceptable precision and bias to verify the analytical system performance, and to document method accuracy for each matrix.

Matrix Spike (MS): an aliquot of sample spiked with 1016/1260 Aroclors (unless a specified Aroclor(s) is requested). The spiking occurs prior to sample preparation and analysis. They are used to document the precision and bias of a method in a given sample matrix.

Matrix Spike Duplicate (MSD): intra-laboratory split samples spiked with 1016/1260 Aroclors (unless a specified Aroclor(s) is requested). The spiking occurs prior to sample preparation and analysis. They are used to document the precision and bias of a method in a given sample matrix.

Method Reporting Limit (MRL): the method reporting limit is a threshold value below which the laboratory reports a result as non-detect. The highest value reported for the method reporting limit is dependent upon project-specific action or decision levels. Method reporting limits are adjusted based on the sample matrix and any sample dilution/concentrations when necessary.

Method Detection Limit (MDL): the method detection limit is the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero. It is determined from analysis of a sample in a given matrix containing the analyte. Depending on project specifics, MDLs will be in the form of a MDL check standard or the MDL is subject to extraction procedures. An acceptable MDL standard check must produce a signal at least three times the instrument's noise level. Also, a MDL check injection must be made after each major instrument repair or changing of instruments (prior to sample analysis) to determine the performance sensitivity of the analysis.

Surrogate (SURR): an organic compound which is similar to the target analytes in chemical composition and behavior in the analytical process, but which is not normally found in environmental samples. Its use is to monitor the performance of the extraction, cleanup (as needed), the analytical system, and the effectiveness of the method. The surrogates are; 2,4,5,6-Tetrachloro-m-xylene and Decachlorobiphenyl.

Initial Calibration (ICAL): an analytical instrument is said to be calibrated when an instrumental response can be related to the concentration of Aroclors 1016/1260. This relationship is depicted graphically, and referred to as a "calibration curve". Initial calibration curves must be established based upon the requisite number of standards identified within the method for each target analyte. Alternative ICALs for Aroclors can be substituted for the 1016/1260 ICAL if specified by project or program.

Initial Calibration Verification (ICV): the initial calibration verification standard (different lot # or manufacture from the initial calibration standard) shall verify the initial calibration curve. The initial calibration verification standard involves the analysis of all target analytes each time the initial calibration is performed.

Continuing Calibration Verification Standard (CCV): a standard solution that is used to check the validity of a calibration curve on a daily basis. It also provides information on satisfactory maintenance and adjustment of the instrument during sample analysis.

14.0 REFERENCES

Department of Defense, *Quality Systems Manual for Environmental Laboratories* (DoD QSM), DoD Environmental Data Quality Workgroup, Department of Navy, Lead Service, Based on NELAC Voted Revision 5 June 2003, Version 4.1, April 22,2009.

USEPA, SW-846, Revision 3; Method 3510C.

USEPA, SW-846, Revision 2; Method 3550B.

USEPA, SW-846, Revision 1; Method 3665A.

USEPA, SW-846, Revision 2; Method 3611B.

USEPA, SW-846, Revision 2; Method 3660B.

USEPA, SW-846, Revision 2; Method 8000B.

USEPA, SW-846, Revision 1; Method 8082A.

Varian/Brueker User Manual 450 GC.

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) used for quantitation

Peak	*1016*	*1221*	*1232*	*1242*	*1248*	*1254*	*1260*
1	3.20	2.53	2.68	3.04	3.46	4.34	5.10
2	3.45	2.61	3.46	3.21	4.07	4.56	5.33
3	3.54	2.67	3.55	3.46	4.32	4.88	5.57
4	3.61		3.61	3.55	4.35	5.12	6.17
5	4.06		4.07	4.07	4.50	5.57	6.42

Table 2b. Summary of Characteristic PCB Peak Retention Times (DB-608 Column)

Peak	*1016*	*1221*	*1232*	*1242*	*1248*	*1254*	*1260*
1	3.11	2.89	3.11	3.53	3.88	4.90	5.62
2	3.52	3.04	3.52	3.89	4.51	4.96	5.70
3	3.88	3.10	3.88	4.04	4.77	5.45	6.14
4	4.04		4.04	4.77	4.82	5.56	6.60
5	4.17		4.82	4.82	5.45	6.10	7.02

Table 3. Retention Time Extraction Windows

Aroclor	*Main Peak Retention Time*			*σ (min)*	*Window (min)*
PCB-1016	3.459	3.455	3.45	0.004509	±0.013527
PCB-1260	5.567	5.572	5.564	0.004041	±0.012123

Table 4. Matrix Spike Accuracy and Precision Data

Aroclor	*Matrix*	*Spike*	*n*	*%Rec.*	*%RSD*	*LCL(%)*	*UCL(%)*	*LCL(%) DOD*	*UCL(%)DOD*
PCB-1016/1260	Water	0.5 µg/l	457	91.4	10.8	59.1	123.7	25/30	145/145
PCB-1016/1260	Soil	25.0 µg/kg	567	88.2	11.8	52.9	123.4	40/60	140/130

Key:
n: number of runs
% Rec: % Recovery
% RSD: % Relative Standard Deviation
LCL: Lower Control Limits
UCL: Upper Control Limits

Table 5. Surrogate Standard Recovery Ranges

Compound	*Matrix*	*Spike*	*n*	*%Rec.*	*%RSD*	*LCL(%)*	*UCL(%)*	*LCL(%) DOD*	*UCL (%) DOD*
TCX (Tetrachloro-m-xylene)	Water	0.01 µg/l	845	85.7	16.8	34.1	137.1		
	Soil	0.50 µg/kg	445	82.6	16.8	33.0	135.3		
DCBP (Decachlorobiphenyl)	Water	0.01 µg/l	810	81.9	18.8	30.0	138.6	40	135
	Soil	0.50 µg/kg	393	81.8	18.8	30.0	137.0	60	125

Key:
n: number of runs
% Rec: % Recovery
% RSD: % Relative Standard Difference
LCL: Lower Control Limits
UCL: Upper Control Limits

Table 6. 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[†]	0.05	0.1	0.3	0.5	0.8	1.0

[†]: The concentration for the 1016/1260 mixture is the concentration of each Aroclor.

Table 7. Standard Preparation for Calibration Mixtures

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 8. 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; perform some or all of the following: clip/replace column, replace heat detector, change injection septum, replace calibration standards, re-calibrate.
Continuing Calibration (CCV)	20 Samples / 12 hours	80 – 120%	Examine the entire analytical system; perform some or all of the following: clip/replace column, replace 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	Table 4	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	≤20% RPD	Relative Percent Differences (RPDs) are computed and included in the QC report
Method Blank	20 samples	< Reporting Limit	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 above the reporting limit, 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	Table 5	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.

Table 8b: Quality Control Items, Frequency and Corrective Action for DoD Projects

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Retention time (RT) window width calculated for each analyte and surrogate	At method set-up and after major maintenance (e.g., column change).	RT width is ± 3 times standard deviation for each analyte RT from a 72 hour study.	NA	NA	
Minimum five-point initial calibration (ICAL) for all analytes	ICAL prior to sample analysis.	One of the options below: Option 1: RSD for each analyte ≤ 20%; Option 2: linear least squares regressions: r ≥ 0.995; Option 3: non-linear regression: coefficient of determination (COD) r^2 ≥ 0.99 (6 points shall be used for second order; 7 points shall be used for third order).	Correct problem then repeat ICAL.	Flagging criteria are not appropriate.	Problem must be corrected. No samples may be run until ICAL has passed. Calibration may not be forced through the origin. Quantitation for multicomponent analytes such as chlordane, toxaphene, and Arocolors must be performed using a 5-point calibration. Results may not be quantitated using a single point.
Retention time window position establishment for each analyte and surrogate	Once per ICAL and at the beginning of the analytical shift.	Position shall be set using the midpoint standard of the ICAL curve when ICAL is performed, the initial CCV is used.	NA	NA	
Second source calibration verification (ICV)	Immediately following ICAL.	All project analytes within established retention time windows. GC methods: All project analytes within ± 20% of expected value from the ICAL	Correct problem, rerun ICV. If that fails, repeat ICAL.	Flagging criteria are not appropriate.	Problem must be corrected. No samples may be run until calibration has been verified.
Continuing calibration verification (CCV)	Prior to sample analysis, after every 10 field samples, and at the end of the analysis sequence.	All project analytes within established retention time windows. GC method: All project analytes within ± 20% of expected value from the ICAL.	Correct problem, then rerun calibration verification. If that fails, then repeat ICAL. Reanalyze all samples since the last successful calibration verification.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply flag to all results for the specific analyte(s)	Problem must be corrected. Results may not be reported without a valid CCV. Flagging is only appropriate in cases where the samples cannot be reanalyzed. Retention time windows are updated per the method.

Table 8b: Quality Control Items, Frequency and Corrective Action for DoD Projects

				in all samples since the last acceptable calibration verification.	
Method blank	One per preparatory batch.	No analytes detected > ½ RL and > 1/10 the amount measured in any sample or 1/10 the regulatory limit (whichever is greater). Blank result must not otherwise affect sample results.	Correct problem. If required, reprep and reanalyze method blank and all samples proceeded with the contaminated blank.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply flag to all results for the specific analyte(s) in all samples in the associated preparatory batch.	Problem must be corrected. Results may not be reported without a valid CCV. Flagging is only appropriate in cases where the samples cannot be reanalyzed.
Laboratory control sample (LCS) containing all analytes to be reported, including surrogates	One per preparatory batch.	QC acceptance criteria specified by DoD, if available. Otherwise, use in-house control limits. In-house control limits may not be greater than ± 3 times the standard deviation of the mean LCS recovery.	Correct problem, then reprep and reanalyze the lCS and all samples in the associated preparatory batch for failed analytes, if sufficient sample material is available.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply flag to specific analyte(s) in all samples in the associated preparatory batch.	Problem must be corrected. Results may not be reported without a valid LCS. Flagging is only appropriate in cases where the samples cannot be reanalyzed.
Matrix spike (MS)	One per preparatory per matrix.	For matrix evaluation, use LCS acceptance criteria specified by DoD, if available. Otherwise, use in-house LCS limits.	Examine the project-specific DQOs. Contact the client as to additional measures to be taken.	For specific analyte(s) in the parent sample, apply flag if acceptance criteria are not met.	For matrix evaluation only. If MS results are outside LCS limits, the data is evaluated to determine the source of difference and to determine if there is a matrix effect or analytical error.
Matrix spike duplicate (MSD) or sample duplicate	One per preparatory per matrix.	MSD: For matrix evaluation, use LCS acceptance criteria specified by DoD, if available. Otherwise, use in-house LCS control limits.	Examine the project-specific DQOs. Contact the client as to additional measures to be taken.	For specific analyte(s) in the parent sample, apply flag if acceptance criteria	The data shall be evaluated to determine the source of difference.

Table 8b: Quality Control Items, Frequency and Corrective Action for DoD Projects

		MSD or sample duplicate: RPD ≤ 30% (between MS and MSD or sample and sample duplicate).		are not met.	
Surrogate spike	All field and QC samples.	QC acceptance criteria specified by DoD, if available. Otherwise, use in-house control limits.	For QC and field samples, correct problem then reprep and reanalyze all failed samples for failed surrogates in the associated preparatory batch, if sufficient sample material is available. If obvious chromatographic interference with surrogate is present, reanalysis may not be necessary.	Apply flag to all associated analytes if acceptance criteria are not met.	Alternative surrogates are recommended when there is obvious chromatographic interference.
Confirmation of positive results (second column or second detector)	All positive results must be confirmed.	Calibration and QC criteria same ad for initial or primary column analysis. Results between primary and second column RPD ≤ 40%.	NA	Apply flag if RPD > 40%. Discuss in the case narrative.	Use project-specific reporting requirements if available; otherwise, use method reporting requirements; otherwise, report the result from the primary column.
Results reported between DL and LOQ	NA	NA	NA	Apply flag to all results between DL and LOQ.	

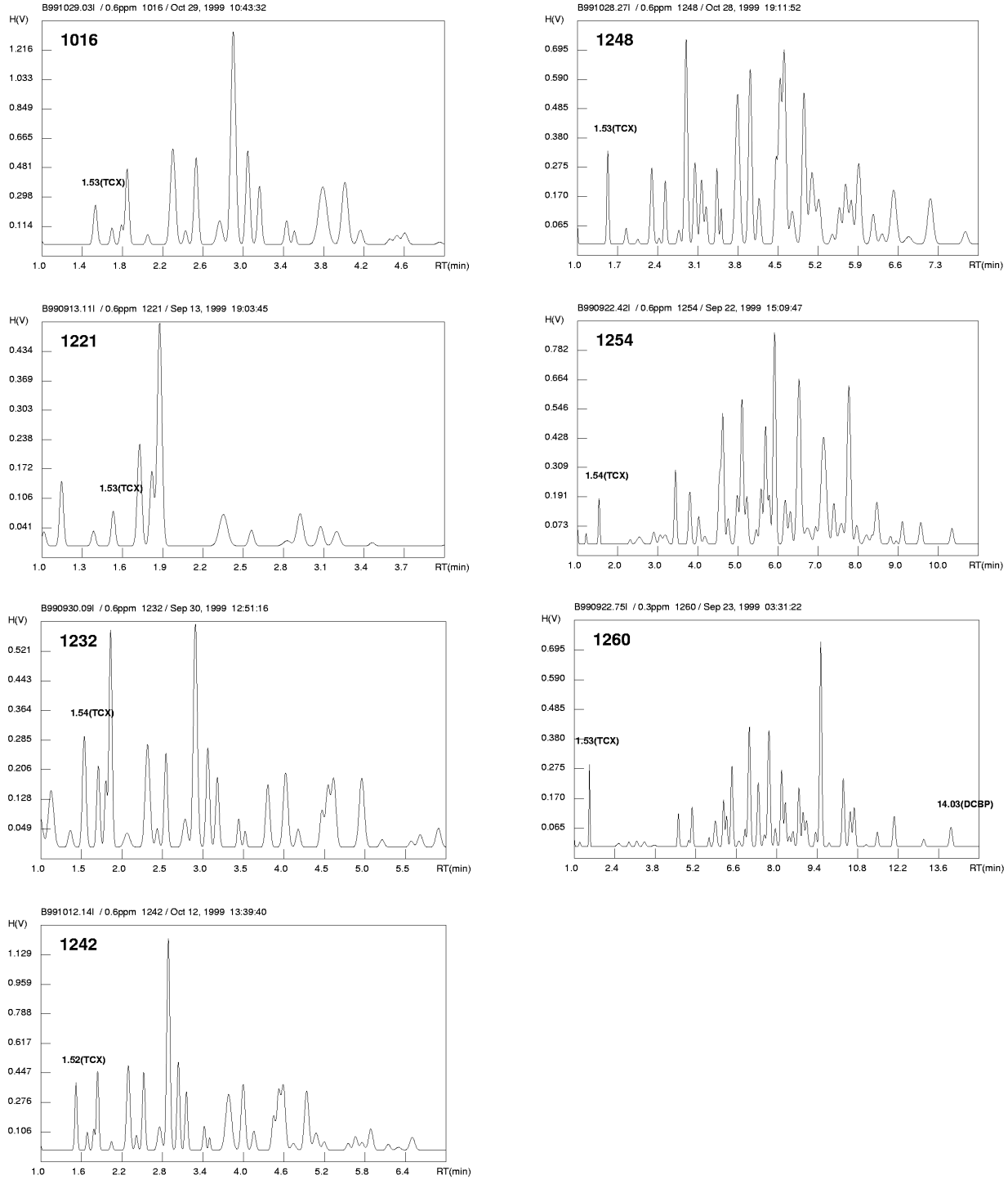

Figure 1. Example Aroclor chromatographic patterns from midpoint calibration standards for PCB 1016, 1221, 1232, 1242, 1248, 1254, and 1260 (column DB-5).

STANDARD OPERATING PROCEDURE

MANUAL INTEGRATION OF CHROMATOGRAPHIC DATA

APPROVALS:

6/7/11

QA Officer — Date

6/7/11

Technical Director — Date

Number	Description of Change	Date
001-003	Previous changes were not documented	
004	Updated to comply with DoD QSM and ISO 17025 standards.	6/7/11
003		
004		
005		
006		
007		
008		
009		
010		
011		
012		

1.0 SCOPE AND APPLICATION

This SOP defines the situations in which the automated integration of chromatographic data (volatile organics, semi-volatile organics, PCBs, and pesticides) by a computer data system may be manually corrected by an analyst in order to properly represent the data. This SOP also illustrates the procedure for such modifications as well as the subsequent means of documentation.

2.0 SUMMARY OF PROCEDURE

An automated data system may be unable to quantitatively characterize chromatographic data in instances where multiple compounds co-elute, the baseline exhibits significant noise/ramping, or matrix interferences are present in significant amounts. In these cases, a manual determination of the peak area is necessary in order to improve the accuracy of the results.

Manual integration procedures are not used to circumvent proper maintenance of the chromatographic system or quality control acceptance criteria.

For all DOD projects, the Case Narrative will include identification of samples and analytes for which manual integration is necessary.

Raw data records include a complete audit trail of the manipulations. The chromatograms before and after are kept on file to permit re-construction of results. This applies to all analytical runs, calibrations and QC samples.

General characteristics of acceptable manual integration procedures are listed below (*cf*. CLP methodologies). Specific examples are detailed in §3.0. Examples directly from analytical runs are also included in Appendices 1, 2, and 3.

- If the peak to be manually integrated is from a GC/MS data system, then the primary quantitation ion of the compound is to be integrated; otherwise, the total signal is integrated.
- The integrated area should contain that which can be attributed to the target compound of interest.
- The integrated area should exclude background noise at the baseline level.

In the event that the computer data system for Level III or CLP-like deliverables denotes instances of manual integration on its quantitation reports, this, along with the analyst's electronic signature in the LIM system, serves to document the existence of the manual integration. When the computer data system makes no such indication, the analyst should initial the hardcopy of the quantitation report. In any case, an SDG Narrative and all OHIO VAP work should also document and explain the manual integration.

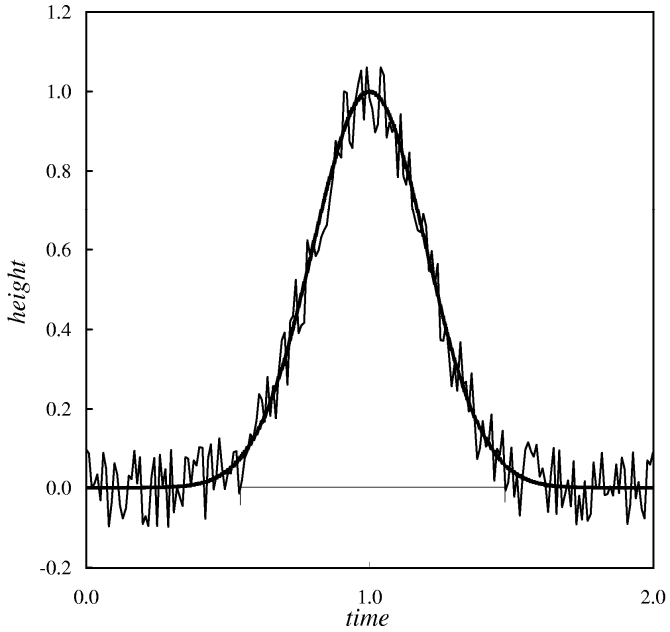

Figure 1. The effect of baseline noise superimposed upon a Gaussian chromatographic peak.

3.0 SPECIFIC APPLICATION EXAMPLES

Peak w/Noise: Figure 1 illustrates a case in which the actual chromatographic response is a superposition of a Gaussian peak and a random baseline noise (S/N = 10 for this example). In this instance, the computer integrator may be unable properly discern the peak beginning/ending, and may split the peak, resulting in a significant reduction of the reported area. Figure 1 shows an appropriate integration for this case: the integration baseline is co-linear with the approximate background baseline and it does not extend beyond the intercept of the peak signal and baseline.

Co-elution of Peaks: Figure 2 depicts a common case in which two chromatographic peaks have similar retention times and do no resolve completely. Resolution, in this case, is defined as the retention time difference between the two peaks relative to the standard deviation of two similar Gaussian peaks (*i.e.* $\Delta t/\sigma$). If the resolution is high enough to discern a local minimum between the two peaks, the integration of each peak is defined by a vertical line connecting the baseline to the local minimum, as illustrated. If the two similar peaks also have the

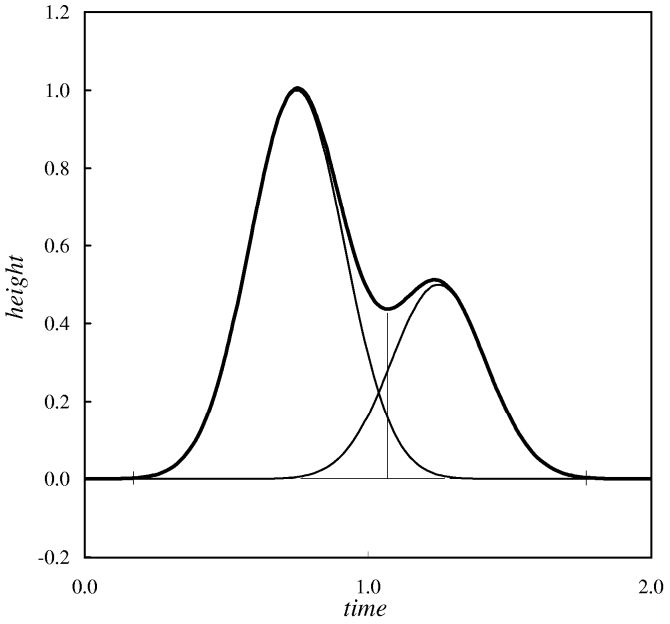

Figure 2. The influence of incomplete chromatographic resolution on two Gaussian peaks.

same peak height, this method is exact. When the relative peak heights are not the same, this method results in a positive bias for the larger peak, and a corresponding negative bias for the smaller peak. For the example shown, $\Delta t/\sigma = 3$ and $h_2/h_1 = 0.5$. This results in an over-prediction of the larger area by 4.8% and an under-prediction of the smaller area by 9.6%.

Linear Baseline Growth: Often, as illustrated by Figure 3, the chromatographic baseline may increase as an approximately piecewise-linear function of time. When there is enough information on either side of the peak of interest to approximate this baseline, the integration baseline should be co-linear with the background baseline. Any error introduced by this method is directly proportional to the extent, which the baseline growth deviates from a linear function.

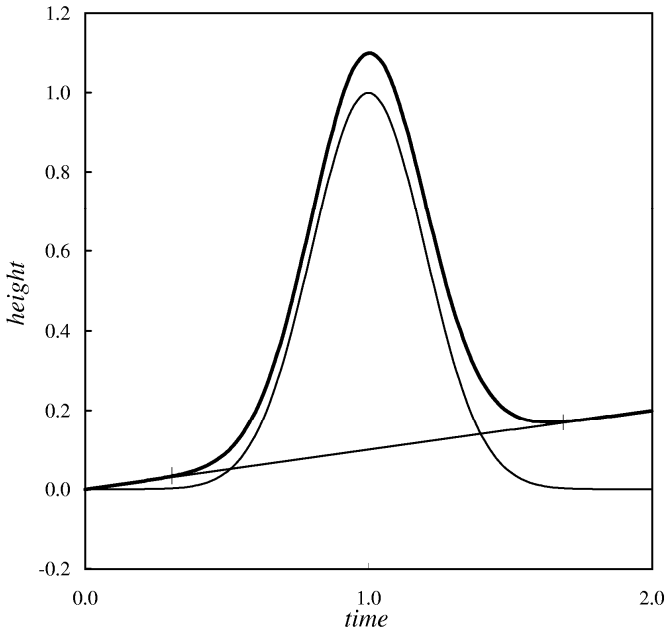

Figure 3. The effect of a linear baseline increase superimposed upon a Gaussian chromatographic peak.

Small Peak Superimposed Upon a Large Peak: This situation, as seen in Figure 4, typically occurs when a target compound elutes close to a solvent peak or in the presence of very large matrix interference peaks. This situation exhibits characteristics similar to those cases detailed in §3.2 and §3.3. When the relative magnitude of the secondary peak is small compared to the primary peak, however, the area of the smaller peak can be most accurately determined by applying the method of §3.3 and treating the boundary of the primary peak as the integration baseline for the secondary peak. The error associated with this method is greatest where the primary peak signal exhibits the greatest degree of nonlinearity (*i.e.* at the apex and the edges).

4.0 PROCEDURAL DEVIATIONS

Unusual instances of chromatographic behavior inconsistent with the principles detailed here may still be subject to manual integration, at the discretion of the analyst *and* with the approval of a supervisor.

In this case, in addition to the normal documentation procedures, a hardcopy of the data's state prior to manual integration should be retained and initialed by the analyst and supervisor. The rationale for the extraordinary manual integration should also be detailed in the SDG Narrative, where applicable.

5.0 VALIDATION OF MANUAL INTEGRATIONS

Manual integration have to be reviewed by another analyst (peer review) and 100% of all manual integration on QC samples need to be reviewed by management.

Management validates all of OHIO VAP data that has manual integrations. An excel list is generated on all OHIO VAP samples that contain manual integrations. This list is given to management for review. The validation is recorded in the table and placed into the appropriate sample file, and one copy is kept in a manual integration logbook.

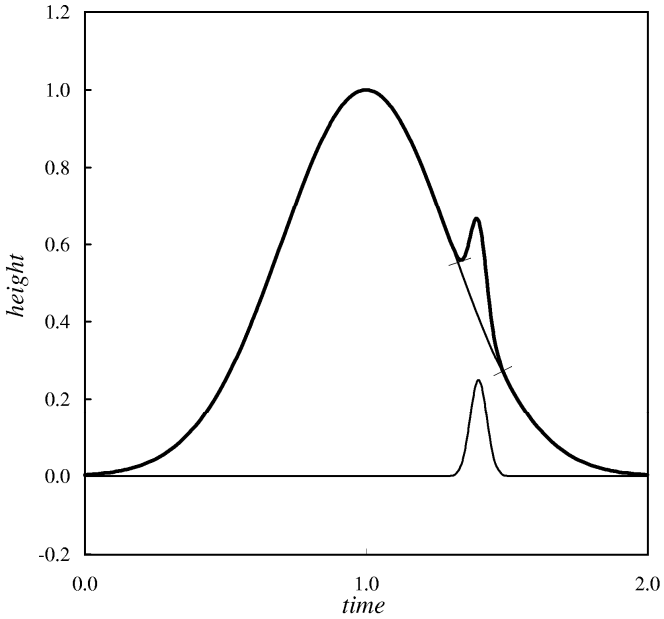

Figure 4. Integration of a small, narrow peak which elutes simultaneously with a large solvent/interference peak.

APPENDICES - PRACTICAL EXAMPLES OF MANUAL INTEGRATION PROCEDURES

Appendix 1. Integration of a Noisy Peak

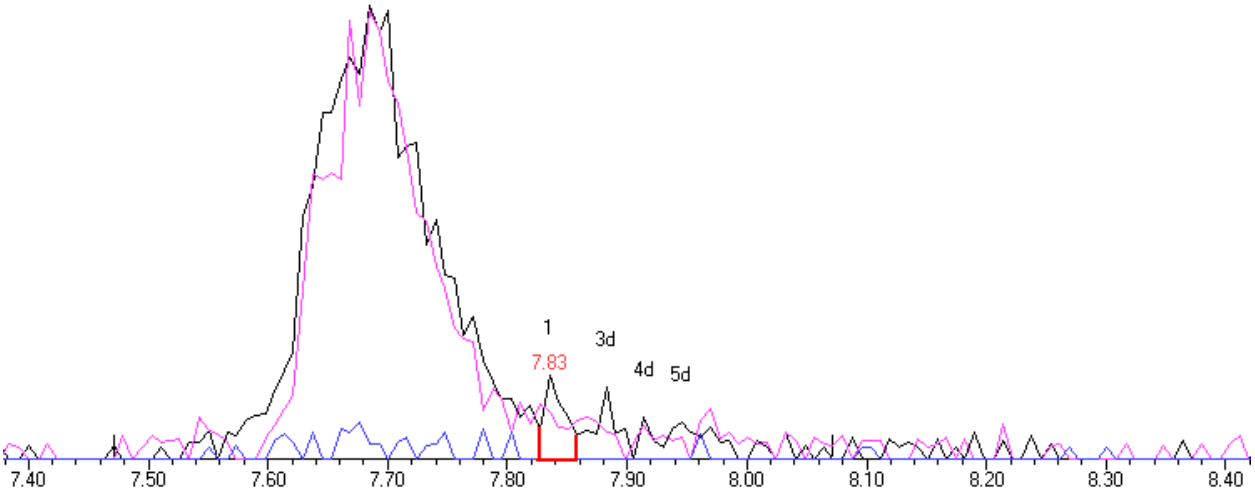

Figure 5a. Integration performed by the data system (acrylonitrile). A small satellite peak has been selected rather than the primary peak.

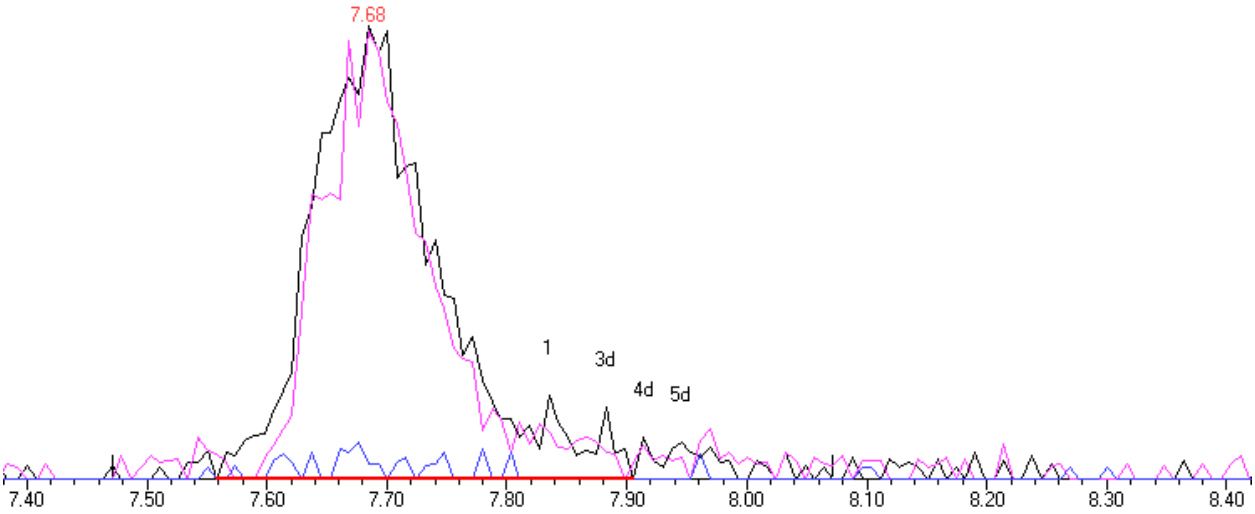

Figure 5b. Manual integration by the user includes the area under the primary peak (acrylonitrile), but does not exceed the intersections of the response with the zero response line.

Appendix 2. Incomplete Chromatographic Separation

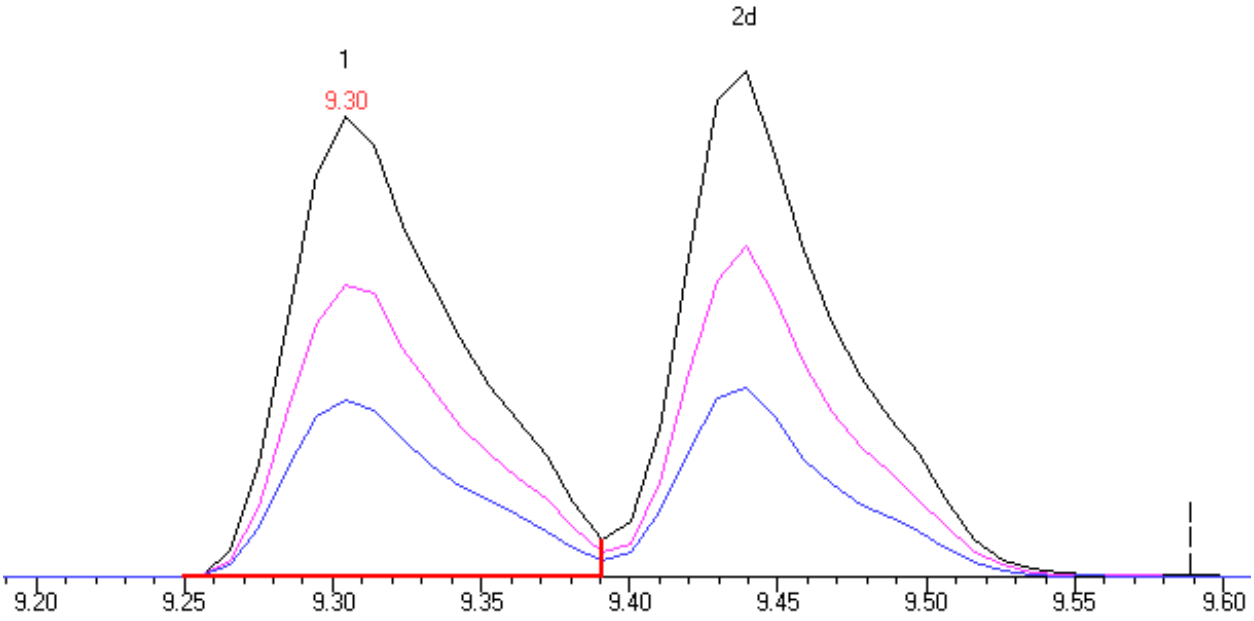

Figure 6a. Integration performed by the data system. The first peak (1,3-dichlorobenzene) is integrated up to the local minimum between the two peaks.

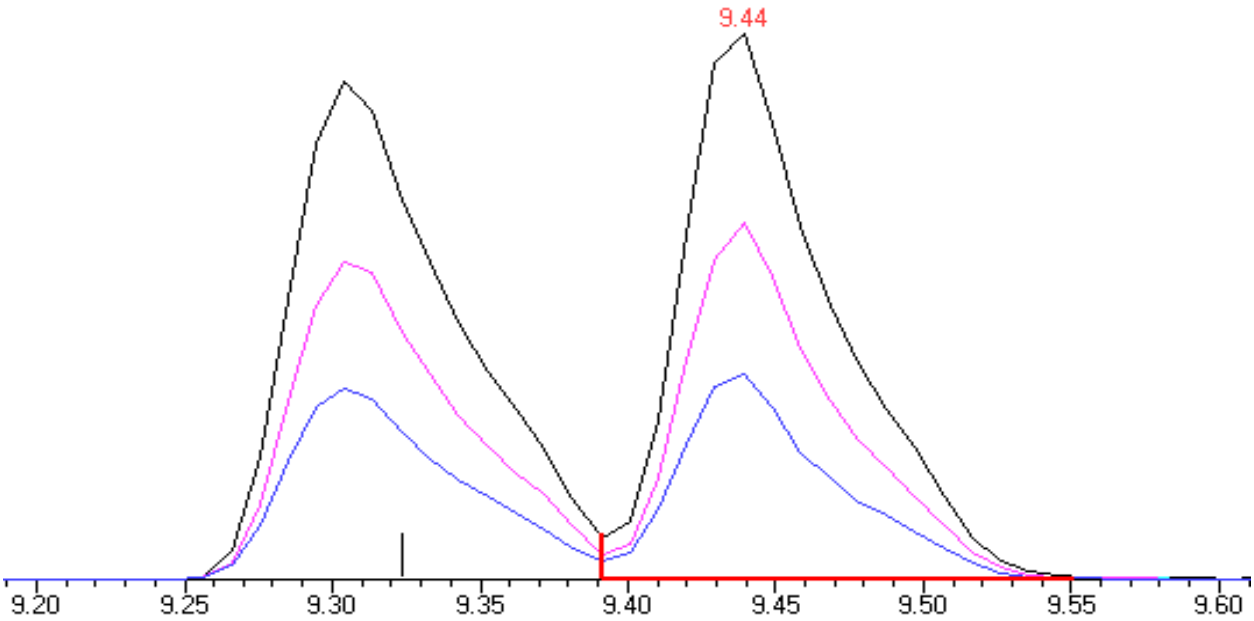

Figure 6b. Integration performed by the data system. The second peak (1,4-dichlorobenzene) is integrated from the local minimum between the two peaks up to the end of the second peak.

Appendix 3. Chromatographic Baseline Elevation

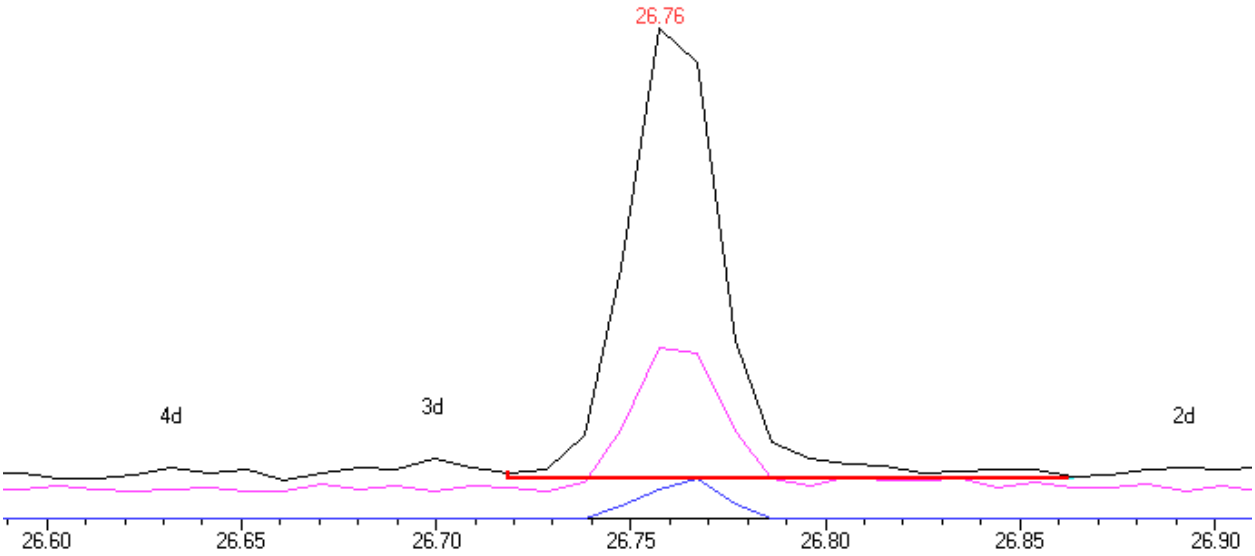

Figure 7a. Integration performed by the data system (bis-2-ethylhexyl phthalate). The integration baseline represents the mean response of the surrounding data. Integrated response: 19.6 ng/µl.

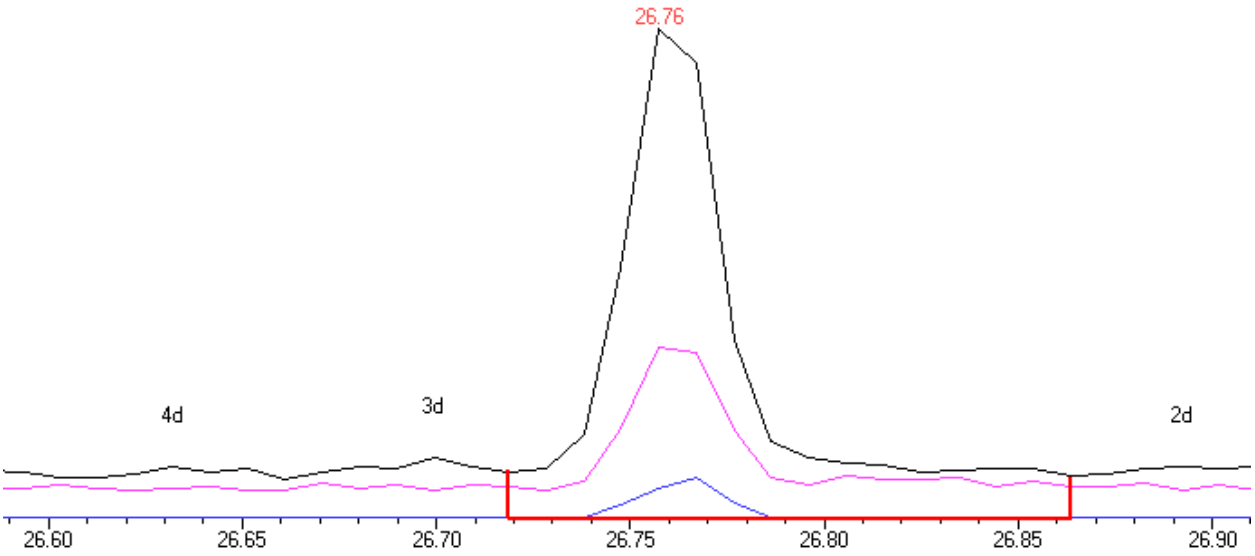

Figure 7b. Example of inappropriate integration (bis-2-ethylhexyl phthalate). The same time range as before is integrated, but it includes the extraneous area from the baseline. Integrated response: 28.1 ng/µl.

MERIT LABORATORIES, INC.

STANDARD OPERATING PROCEDURE

SEMIVOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY
METHOD SW-846 8270C

APPROVALS:

6/9/11

Barbara Richardson, QA Officer — Date

6/9/11

Maya V. Murshak, Technical Director — Date

Number	Description of Change	Date
001-010	Previous revisions not documented	
011	Updated to comply with DoD QSM and ISO 17025 standards.	6/9/11
012		
013		
014		
015		
016		
017		
018		
019		
020		

1.0 SCOPE AND APPLICATION

1.1 This SOP 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. This SOP is applicable to groundwater, surface water, aqueous sludges, water oily solvents, wastes, soil and sediment samples. 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.

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 gas chromatograph (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 practical quantitation limits (PQL) 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. PQLs will be proportionately higher for sample extracts that require dilution to avoid saturation of the detector.

- *Method Detection Limits (MDL) and Practical Quantitation Limits (PQL) are available in Merit's LIMs system.*

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 THE 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 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

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.

4.5 Maintenance logbooks

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 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} (see Table 2a). 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,

and 2-100 ng/µL for PNAs). 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 and PNA analysis can be found in the SVOC.QC-Reference Document.

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 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 HANDLING AND PRESERVATION

Unanalyzed samples are refrigerated at 4 ± 2 degrees Celsius and protected from light in amber sealed containers.

Aqueous samples are shall be extracted within 7 days from sample collection and analyzed within 40 days from extraction.

Soil samples shall be extracted within 14 days from sample collection and analyzed within 40 days thereafter.

7.0 PROCEDURE

Sample preparation

7.1.1 Soil and water are prepared via an extraction procedure (*cf.* SW-846 Methods 3500, 3510, 3550; SOP# EXL-005 and EXL- 006) prior to GC/MS analysis.

7.1.2 In cases where the sample is an oil or 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 or background contamination, average the three highest intensity scans for the DFTPP peak. 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.

7.3.1.3 The DFTPP mass intensity criteria in Table 4 are used as tuning acceptance criteria.

7.3.1.4 All subsequent standards, samples, MS/MSDs, and blanks associated with a DFTPP analysis must use the identical mass spectrometer instrument conditions.

7.3.1.5 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.

7.3.1.6 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 SPCCs are: N-nitroso-di-n-propylamine; hexachlorocyclopentadiene; 2,4-dinitrophenol; and 4-nitrophenol (*cf*. Table 2a).

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 SW-846 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 Tables 2a and 2b) 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.

7.3.5.4 For DoD project requirements refer to Table 5b.

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. The retention time extraction windows are set 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 SW-846 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 coefficient of determination (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).

7.3.7.4 Refer to Table 5b for DoD project requirements.

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

7.4.4.1 An SPCC 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

7.4.5.1 After the system performance check is met, the CCCs listed in Tables 2a and 2b 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.

7.4.5.4 Refer to Table 5b for DoD project requirements.

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). SVOC Dilution Reference Document 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 extracted ion current potential (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 Tables 5a and 5b). 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, $k_1 \equiv \langle RF \rangle$, 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).

8.0 QUALITY CONTROL

All of the quality control items employed and evaluated are provided in Table 5a and 5b. In addition, the tables indicate the frequency of each QC item along with appropriate courses of corrective action. Control limits for surrogates and matrix spikes are listed in Table 6. The analyst will follow SOP # QA-007 and complete the appropriate review form upon completion of the analysis.

9.0 METHOD PERFORMANCE

The precision and accuracy of the method depends upon the overall performance of the sample preparation and analysis. Laboratory specific performance data is provided on in Merit's LIMs system. Each sample batch contains a method blank, laboratory control sample and matrix spike

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

10.0 EQUIPMENT MAINTENANCE AND TROUBLESHOOTING

Each instrument is assigned a maintenance logbook. All maintenance performed on the instrument must be recorded. Additionally, any modifications to the instrument settings shall be noted in the specific instrument logbook. Maintenance procedures provided in the equipment manual shall be followed. Maintenance may include, cleaning the MS source, clipping/replacing the column, or replacing the calibration standard.

11.0 SAFETY

Eye protection and gloves must be worn while performing the analyses. Every laboratory area has eyewash, emergency shower, and fire extinguisher. The metals lab also has dust masks available for use with dust samples. The air system throughout 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.

A reference file of material safety data sheets (MSDSs) is available to all personnel. Specific attention shall be paid (but not limited) to:

12.0 WASTE DISPOSAL AND POLLUTION PREVENTION

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

13.0 DEFINITIONS

Sample Batch: Samples of the same or similar matrix; for this method, a sample batch consists of 20 samples or less.

Method Blank: An analyte-free matrix to which all reagents are added in the same volumes or proportions as used in the sample processing. The method blank is carried through the complete sample preparation and analytical procedure. The method blank is used to document contamination resulting from the analytical process.

Laboratory Control Spike (LCS): Milli-Q water (for water) or Organic-Free Soil (for soil) is spiked with the target analytes and carried through the complete sample preparation and analytical procedure.

The control spike is used to document the ability of an analyst to generate acceptable precision and bias, to verify the analytical system performance, and to document method accuracy for each matrix.

Laboratory Control Spike Duplicate (LCSD): A duplicate Milli-Q water (for water) or Organic-Free Soil (for soil) is spiked with the target analytes and carried through the complete sample preparation and analytical procedure. The control spike duplicate is used to document the precision and bias of a method. This QC type is only performed when sufficient amount of sample is unavailable for performing a matrix spike and matrix spike duplicate.

Matrix Spike (MS): An aliquot of sample spiked with a known concentration of target analytes. The spiking occurs prior to sample preparation and analysis. It is used to document the precision and bias of a method in a given sample matrix.

Matrix Spike Duplicate (MSD): Intra-laboratory split samples spiked with identical concentration of target analytes. The spiking occurs prior to sample preparation and analysis. They are used to document the precision and bias of a method in a given sample matrix.

Method Reporting Limit (MRL): The method reporting limit is a threshold value below which the laboratory reports a result as a non-detect. The highest value reported for the method reporting limit is dependant upon project-specific action or decision levels. Method reporting limits are adjusted based on the sample matrix and any sample dilution/concentrations when necessary.

Method Detection Limit (MDL): The method detection limit is the minimum concentration of a substance that can be measured and reported with 99 percent confidence that the analyte concentration is greater than zero. It is determined from analysis of a sample in a given matrix containing the analyte. Depending on project, specific MDL checks are either in the form of an MDL check standard or the MDL is subject to extraction procedures. An acceptable MDL standard check must produce signals for the qualifier ions. An MDL standard injection must be made after each major instrument repair or changing of instruments (prior to sample analysis) to determine the performance sensitivity of the analysis.

Surrogate (SURR): Organic compound which is similar to the target analytes in chemical composition and behavior in the analytical process, but which is not normally found in environmental samples. Its use is to monitor the performance of the extraction, cleanup (as needed), the analytical system, and the effectiveness of the method. The acid surrogates are at twice the concentration of the Base/Neutral surrogates. The acid surrogate compounds are: 2-Fluorophenol, Phenol d_5, and 2,4,6-Tribromophenol. The base/neutral surrogates are: Nitrobenzene

$d_{5,}$ 2-Fluorobiphenyl, and p-Terphenyl $d_{14.}$ o-Terphenyl d_{14} is also added when the samples are analyzed for PAHs in selected ion monitoring (SIM) mode.

Initial Calibration (ICAL): An analytical instrument is said to be calibrated when an instrumental response can be related to the concentration of an analyte. This relationship is depicted graphically and referred to as a "calibration curve". Initial calibration curves must be established based upon the requisite number of standards identified within the method for each target analyte.

Initial Calibration Verification (ICV): The initial calibration verification standard (different lot # or manufacturer from the initial calibration standard) shall verify the initial calibration curve. The initial calibration verification standard involves the analysis of all target analytes each time the initial calibration is performed.

Continuing Calibration Verification Standard (CCV): A standard solution that is used to check the validity of a calibration curve on a daily basis. It also provides information on satisfactory maintenance and adjustment of the instrument during sample analysis. A CCV must be made during each 12 hour shift.

DFTPP: Decafluorotriphenylphosphine. This compound is used in tuning the GC/MS. To acquire the mass spectrum of DFTPP, three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction to eliminate column bleed or instrument background noise is accomplished using a single scan acquired no more than 20 scans prior to the elution of DFTPP. The DFTPP standard must also contain Pentachlorophenol, Benzidine, and DDT to assess GC column performance and injection port inertness. Benzidine and Pentachlorophenol must have tailing factors less than 2. Breakdown of DDT to DDD and DDE must be less than 20%

Internal standard (ISTD): Internal Standard involves the comparison of instrument responses from the target compounds in the sample to the responses of specific standards added to the sample extract prior to injection. The ratio of the peak area of the target compound in the sample extract to the peak area of the internal standard in the sample extract is compared to a similar ratio derived for each calibration standard. The internal standards are; 1,4-Dichlorobenzene $d_{4,}$ Naphthalene $d_{8,}$ Acenaphthene $d_{10,}$ Phenanthrene $d_{10,}$ Chrysene d_{12} and Perylene $d_{12.}$ In addition, Benzo[a]anthracene d_{12} is added when the samples are analyzed for PAHs in selected ion monitoring (SIM) mode.

System Performance Check Compounds (SPCC): SPCCs are system performance compounds that are a part of the Continuing Calibration Verification standard (CCV). The SPCCs must meet a

minimum response factor of 0.050. The SPCC criteria also apply to the average response factor of the initial calibration curve.

Calibration Check Compounds (CCC): CCCs are calibration check compounds that are a part of the Continuing Calibration Verification standard (CCV). The CCC percent difference must be less than or equal to 20%.

Instrument Blanks: Contamination by carryover can occur whenever high-concentration and low-concentration samples are sequentially analyzed. Whenever an unusually concentrated sample is encountered, it can be followed by the analysis of an instrument blank (methylene chloride + Internal Standards) to check for cross-contamination.

14.0 REFERENCES

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Table 1a. Summary of Retention Times† and Characteristic Ions for Base/Neutral/Acid Semi-Volatile Organics

#	**Compound**	t_R	$t_R/t_{R,I}$	$t_R-t_{R,I}$	1^0	2^0	3^0	4^0
		(min)	**(-)**	***(min)***	***m/z***	***m/z***	***m/z***	***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)ether	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	

#	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*
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	
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 ether	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	

#	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*
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)anthracene	19.5	0.961	-0.80	256	241	239	
97)	Benzo(k)fluoranthene	19.47	0.959	-0.83	252	253	126	
98)	Benzo(a)pyrene	20.16	0.993	-0.14	252	253	126	

#	**Compound**	t_R	$t_R/t_{R,I}$	$t_R-t_{R,I}$	1^0	2^0	3^0	4^0
		(min)	**(-)**	**(*min*)**	***m/z***	***m/z***	***m/z***	***m/z***
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 Applicable Performance Compounds - Base/Neutral/Acid Analysis

#†	COMPOUND	CCC	SPCC	ISD	SSD	MS
1	1,4-DICHLOROBENZENE-D4			✔		
6	2-Fluorophenol				✔	
8	Phenol-d5				✔	
9	Phenol **	✔				✔
11	2-Chlorophenol **					✔
14	1,4-Dichlorobenzene **	✔				✔
22	N-Nitrosodi-n-propylamine**		✔			✔
23	NAPHTHALENE-D8			✔		
24	Nitrobenzene-d5				✔	
28	2-Nitrophenol	✔				
31	2,4-Dichlorophenol	✔				
32	1,2,4-Trichlorobenzene **					✔
37	Hexachlorobutadiene	✔				
39	4-Chloro-3-methylphenol **	✔				✔
41	ACENAPHTHALENE-D10			✔		
43	Hexachlorocyclopentadiene		✔			
44	2,4,6-Trichlorophenol	✔				
46	2-Fluorobiphenyl				✔	
50	Acenaphthylene	✔				
54	Acenaphthene **					✔
55	2,4-Dinitrophenol		✔			
57	4-Nitrophenol **		✔			✔
58	2,4-Dinitrotoluene **					✔
66	2,4,6-Tribromophenol				✔	
67	PHENANTHRENE-D10			✔		
69	N-Nitrosodiphenylamine	✔				
77	Pentachlorophenol **	✔				✔
83	Fluoranthene	✔				
84	Terphenyl-d14				✔	
85	CHRYSENE-D12			✔		
87	Pyrene **					✔
95	Di-n-octyl phthalate	✔				
96	PERYLENE-D12			✔		
100	Benzo(a)pyrene	✔				

†: Compound identification numbers listed are from calibration BX010711.M.

Key

CCC: Calibration Check Compound

SPCC: System Performance Check Compound

ISD: Internal Standard Compound

SSD: Surrogate Standard Compound

MS: Matrix Spiking Compound

Table 2b. Summary of Applicable Performance Compounds - Polynuclear Aromatic Analysis

#†	COMPOUND	CCC	SPCC	ISD	SSD	MS
1	1,4-DICHLOROBENZENE-D4			✔		
2	NAPHTHALENE-D8			✔		
3	Nitrobenzene-d5				✔	
4	Naphthalene	✔	✔			✔
6	ACENAPHTHALENE-D10			✔		
7	2-Fluorobiphenyl				✔	
8	Acenaphthylene		✔			
9	Acenaphthene **	✔				✔
11	PHENANTHRENE-D10			✔		
12	Phenanthrene		✔			
14	Fluoranthene	✔				✔
15	CHRYSENE-D12			✔		
16	Pyrene **	✔				✔
17	Terphenyl-d14				✔	
20	PERYLENE-D12			✔		
21	Benzo(b)fluoranthene		✔			
23	Benzo(a)pyrene	✔				✔

†: Compound identification numbers listed are from calibration PN010526.M.

Key

CCC: Calibration Check Compound

SPCC: System Performance Check Compound

ISD: Internal Standard Compound

SSD: Surrogate Standard Compound

MS: Matrix Spiking Compound

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: the above is subject to change based on GC and/or sample 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

Table 5a. 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.
DFTPP	12-hour	Table 4	Re-attempt injection; clean MS source, re-tune; failure requires the re-analysis of all associated analytical runs.
SPCC/CCC	12-hour	SPCC RF <0.050 CCC $\leq$ 20%	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	Table 6	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	<RL	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 (*i.e*. non phthalate esters), the blank should be re-extracted and re-analyzed. If additional sample exists, the

QC Item	Frequency	Acceptance Criteria	Corrective Action
			samples associated with a failed, re-extracted blank should also be re-extracted and re-analyzed.
Internal Standard	All samples	Section 7.5.5	Adverse matrix effects on areas/recoveries are demonstrated either by screening the extract or re-analyzing the extract 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. Internal standards recoveries below 50% require re-analysis
Surrogate Standard	All samples	Table 6	Adverse matrix effects on areas/recoveries are demonstrated either by screening the extract or 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. Two out three surrogates are to be within limits, as long as the third surrogate is above 10%.
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 5b. Quality Control Items, Frequency, and Corrective Action for DoD Projects

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Tuning	Prior to ICAL and at the beginning of each 12-hour period.	Refer to method for specific ion criteria.	Retune instrument and verify. Rerun affected samples.	Flagging criteria are not appropriate.	Problem must be corrected. No samples may be accepted without a valid tune.
Breakdown check (DDT)	At the beginning of each 12-hour period, prior to analysis of samples.	Degradation ≤ 20% for DDT. Benzidine and pentachlorophenol should be present at their normal responses, and should not exceed a tailing factor of 2.	Correct problem then repeat breakdown check.	Flagging criteria are not appropriate.	No samples shall be run until degradation ≤ 20%.
Minimum five-point initial calibration (ICAL) for all analytes	ICAL prior to sample analysis.	1. Average response factor (RF) for SPCCs: VOCs ≥ 0.30 for chlorobenzene and 1,1,2,2-tetrachlorolethane; ≥ 0.1 for chloromethane, bromoform, and 1,1-dichloroethane. SVOCs ≥ 0.050. 2. RSD for RFs for CCCs: VOCs and SVOCs ≤ 30% and one option below: Option 1: RSD for each analyte ≤ 15%; Option 2: linear least squares regression r ≥ 0.995; Option 3:non-linear regression– coefficient of determination	Correct problem then repeat ICAL.	Flagging criteria are not appropriate.	Problem must be corrected. No samples may be run until ICAL has passed. Calibration may not be forced through the origin.

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
		(COD) r2 ≥ 0.99 (6 points shall be used for second order, 7 points shall be used for third order).			
Second source calibration verification (ICV)	Once after each ICAL.	All project analytes within ± 20% of true value.	Correct problem and verify second source standard. Rerun second source verification. If that fails, correct problem and repeat ICAL.	Flagging criteria are not appropriate.	Problem must be corrected. No samples may be run until calibration has been verified.
Retention time window position establishment for each analyte and surrogate	Once per ICAL.	Position shall be set using the midpoint standard of the ICAL curve when ICAL is performed. On days when ICAL is not performed, the initial CCV is used.	NA.	NA.	
Evaluation of relative retention times (RRT)	With each sample.	RRT of each target analyte within ± 0.06 RRT units.	Correct problem, then rerun ICAL.	Flagging criteria are not appropriate.	Laboratories may update the retention times based on the CCV to account for minor performance fluctuations or after routine system maintenance (such as column clipping). With each sample, the RRT shall be compared with the most recently updated RRT. If the RRT has changed by more than ±0.06 RRT

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
					units since the last update, this indicates a significant change in system performance and the laboratory must take appropriate corrective actions as required by the method and rerun the ICAL to reestablish the retention times.
Continuing calibration verification (CCV)	Daily before sample analysis and every 12 hours of analysis time.	1. Average RF for SPCCs : VOCs ≥ 0.30 for chlorobenzene and 1,1,2,2-tetrachlorolethane; ≥ 0.1 for chloromethane, bromoform, and 1,1-dichloroethane. SVOCs ≥ 0.050. 2. %Difference/Drift for all target compounds and surrogates: VOCs and SVOCs ≤ 20%D (Note: D = difference when using RFs or drift when using least squares regression or non-linear calibration).	DoD project level approval must be obtained for each of the failed analytes or corrective action must be taken. Correct problem, then rerun calibration verification. If that fails, then repeat ICAL. Reanalyze all samples since last acceptable CCV.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply Q-flag to all results for the specific analyte(s) in all samples since last acceptable CCV.	Problem must be corrected. Results may not be reported without a valid CCV. Flagging is only appropriate in cases where the samples cannot be reanalyzed.
Internal standards verification	Every field sample, standard, and	Retention time ± 30 seconds from retention time of the	Inspect mass spectrometer and GC for	If corrective action fails in field samples,	Sample results are not acceptable without a valid IS

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
	QC sample.	midpoint standard in the ICAL; EICP area within -50% to +100% of ICAL midpoint standard.	malfunctions. Reanalysis of samples analyzed while system was malfunctioning is mandatory.	apply Q-flag to analytes associated with the non-compliant IS. Flagging criteria are not appropriate for failed standards.	verification.
Method blank	One per preparatory batch.	No analytes detected > ½ RL and > 1/10 the amount measured in any sample or 1/10 the regulatory limit (whichever is greater). Blank result must not otherwise affect sample results. For common laboratory contaminants, no analytes detected > RL (see Box D-1).	Correct problem, then see criteria in Box D-1. If required, reprep and reanalyze method blank and all samples processed with the contaminated blank.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply B-flag to all results for the specific analyte(s) in all samples in the associated preparatory batch.	Problem must be corrected. Results may not be reported without a valid method blank. Flagging is only appropriate in cases where the samples cannot be reanalyzed.
LCS containing all analytes to be reported, including surrogates	One per preparatory batch.	QC acceptance criteria specified by DoD, if available. Otherwise, use in-house control limits. In-house control limits may not be greater than ± 3 times the standard deviation of the mean LCS recovery. See Box D-3 and Appendix G.	Correct problem, then reprep and reanalyze the LCS and all samples in the associated preparatory batch for failed analytes, if sufficient sample material is available (see full explanation in Appendix G).	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply Q-flag to specific analyte(s) in all samples in the associated preparatory batch.	Problem must be corrected. Results may not be reported without a valid LCS. Flagging is only appropriate in cases where the samples cannot be reanalyzed.
Matrix Spike	One per	For matrix	Examine the	For the specific	For matrix

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
(MS)	preparatory batch per matrix (see Box D-7).	evaluation, use LCS acceptance criteria specified by DoD, if available. Otherwise, use in-house LCS control limits.	project-specific DQOs. Contact the client as to additional measures to be taken.	analyte(s) in the parent sample, apply J-flag if acceptance criteria are not met.	evaluation only. If MS results are outside the LCS limits, the data shall be evaluated to determine the source of difference and to determine if there is a matrix effect or analytical error.
Matrix spike duplicate (MSD) or sample duplicate	One per preparatory batch per matrix (see Box D-7).	MSD: For matrix evaluation, use LCS acceptance criteria specified by DoD, if available. Otherwise, use in-house LCS control limits. MSD or sample duplicate: RPD ≤ 30% (between MS and MSD or sample and sample duplicate).	Examine the project-specific DQOs. Contact the client as to additional measures to be taken.	For the specific analyte(s) in the parent sample, apply J-flag if acceptance criteria are not met.	The data shall be evaluated to determine the source of difference.
Surrogate spike	All field and QC samples.	QC acceptance criteria specified by DoD, if available. Otherwise, use in-house control limits.	For QC and field samples, correct problem then reprep and reanalyze all failed samples for failed surrogates in the associated preparatory batch, if sufficient sample material is available. If obvious chromatographic interference with	Apply Q-flag to all associated analytes if acceptance criteria are not met.	Alternative surrogates are recommended when there is obvious chromatographic interference.

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
			surrogate is present, reanalysis may not be necessary.		
Matrix spike duplicate (MSD) or sample duplicate	One per preparatory batch per matrix (see Box D-7).	MSD: For matrix evaluation, use LCS acceptance criteria specified by DoD, if available. Otherwise, use in-house LCS control limits. MSD or sample duplicate: RPD ≤ 30% (between MS and MSD or sample and sample duplicate).	Examine the project-specific DQOs. Contact the client as to additional measures to be taken.	For the specific analyte(s) in the parent sample, apply J-flag if acceptance criteria are not met.	The data shall be evaluated to determine the source of difference.

Table 6. Summary of Control Limits: Surrogate and Matrix Spiking Compounds Percent Recovery[†]

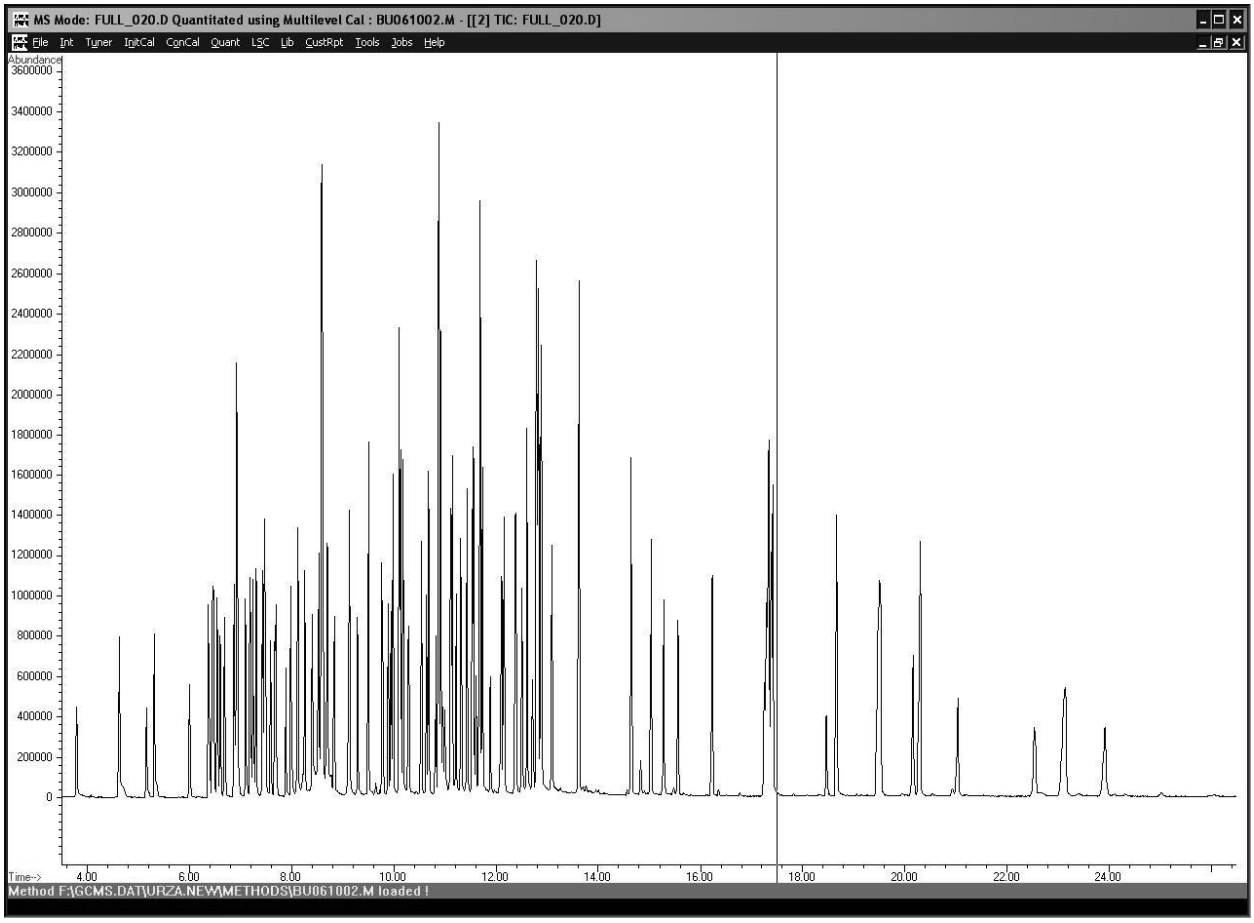
#[‡]	COMPOUND	Water Matrix		Solid Matrix	
		LCL (%)	UCL (%)	LCL (%)	UCL (%)
6	2-Fluorophenol	10.0	110.0	13.2	121.0
8	Phenol-d5	10.0	110.0	16.9	113.0
24	Nitrobenzene-d5	10.0	114.0	18.5	120.0
46	2-Fluorobiphenyl	10.0	116.0	10.0	115.0
66	2,4,6-Tribromophenol	10.0	123.0	13.0	122.0
84	Terphenyl-d14	10.0	141.0	10.3	137.0
9	Phenol **	10.0	110.0	16.3	118.6
11	2-Chlorophenol **	14.0	123.0	18.3	116.5
14	1,4-Dichlorobenzene **	16.8	110.0	13.2	110.0
22	N-Nitrosodi-n-propylamine**	31.3	119.6	24.7	126.0
32	1,2,4-Trichlorobenzene **	20.5	110.0	15.6	110.0
39	4-Chloro-3-methylphenol **	20.8	120.7	18.1	120.8
54	Acenaphthene **	26.4	118.0	19.0	137.0
57	4-Nitrophenol **	10.0	110.0	10.0	114.0
58	2,4-Dinitrotoluene **	24.0	110.0	14.7	112.6
77	Pentachlorophenol **	10.0	110.0	10.0	110.0
87	Pyrene **	23.0	127.5	16.2	142.0
n/a	Diesel Range Organics	30.0	130.0	30.0	130.0

[†]: Results based on recovery data from 2001.

[‡]: Compound identification numbers listed are from calibration BX010711.M.

All target compounds must be included in the spike for DoD projects. DoD acceptance criteria is provided in the DoD QSM.

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 3 for BNA Analysis.

STANDARD OPERATING PROCEDURE

PURGE AND TRAP FOR AQUEOUS AND HIGH CONCENTRATION SOIL SAMPLES METHOD 5030B/5035

APPROVALS:

6/3/11

QA Officer Date

6/3/11

Technical Director Date

Number	Description of Change	Date
001-005	Previous changes were not documented	
006	Updated to comply with DoD QSM and ISO 17025 standards.	6/3/11
007		
008		
009		
010		
011		
012		
013		
014		
015		
016		

1.0 SCOPE AND APPLICATION

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 Gas Chromotography/Mass Spectrometry (GC/MS) Method 8260B. 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. 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. 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. This SOP is not for use with samples that come into the lab for OHIO VAP work.

2.0 SUMMARY OF METHOD

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. 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. 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. 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.

3.0 INTERFERENCES

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.

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.

Contamination by carryover can occur whenever high-concentration and low-concentration samples are analyzed sequentially. Whenever an unusually concentrated sample is analyzed, it must 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.

The laboratory where volatiles analysis is performed must be completely free of solvents. Special precautions must be taken to determine methylene chloride. The analytical and sample storage areas must 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 must 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.

4.0 APPARATUS AND MATERIALS

Microsyringes - 10-µL, 25-µL, 100-µL, 250-µL, and 500-µL.

Gas tight 5ml syringes.

Vials – 40-mL, for GC autosampler (Archon).

Magnetic stir bars.

Scale capable of displaying weight to the nearest hundredth of a gram.

Purge-and-trap device. The purge-and-trap device consists of three separate pieces of equipment: the sample purger, the trap, and the desorber.

- The Vocarb3000 trap by Supelco is used. It is preconditioned at 270°C for 60 minutes upon installment as suggested by supplier.

Gas Chromatograph.

Mass Spectrometer.

pH paper.

5.0 REAGENTS

Organic-free reagent water - All references to water in this method refer to organic-free reagent water.

Purge and Trap grade methanol.

Sodium Bisulfate.

See SOP ORL-007 for specifications on internal and surrogate standards.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

Aqueous Samples

- Samples must be stored in capped bottles, with minimum headspace, at (4 ± 2)°C in an area free of solvent fumes.

- All samples must 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. The pH is recorded on the volatile sample prep log (Figure 1).

Soil Samples

- 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.
  - 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.

- (10 ± 0.5)g of sample are weighed out and added to the vial in the field.
- Upon arrival to the lab, samples are stored at (4 ±2)°C.

♦ High concentration soil samples collected without a preservative.

- When high concentration soil samples are collected without the use of a preservative, an EnCore sample container/sampler is employed.
  - 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 must be preserved in methanol within 48 hours of the sampling time. This preservation is documented in the High Level Extraction Sheet (Figure 3).
- Weigh out (10 ±0.5)g of soil sample into a 40-mL vial and add 10-mL of Methanol.
- Sonicate for twenty minutes.
- Sample extracts are transferred to 4 ml vials and stored at (4 ± 2)°C.
- Frozen samples are not acceptable for all OHIO VAP samples.

♦ 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 this 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 must be considered before selecting a sampling and preservation technique and may include procedures not in this SOP.
- 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, and Low Level Extraction Log (Figure 2).

- (1-5 ± 0.5)g of sample are weighed out and added to the vial in the field.
- Upon arrival to the lab, samples are stored at (4 ±2)°C.

♦ Low concentration soil samples collected without a preservative.

- When low concentration soil samples are collected without the use of a preservative, an EnCore sample container/sampler is employed.
  - 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 must be preserved with sodium bisulfate within 48 hours of the sampling time. This preservation is documented in the Low Level Extraction Log (Figure 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.
- The preserved samples are stored at (4 ± 2)°C.

7.0 PROCEDURE

1. The purge-and-trap technique for aqueous samples is found in Number 2 and method for analysis of solvent extracts from the High Concentration Method in Method 5035 is found in Number 3. The gas chromatographic determinative steps are found in SOP ORL-007. The method is also applicable to the analysis of gasoline, using SOP ORL-010.

2. This section provides guidance on the analysis of aqueous samples and samples that are water miscible, by purge-and-trap analysis.

♦ Initial calibration. Calibrate system in accordance with Method 8260B.

♦ If necessary or for project specific purposes, screen samples prior to purge-and-trap analysis to provide guidance on whether sample dilution is necessary and may prevent contamination of the purge-and-trap system. Screen the sample by GC/MS.

♦ Sample introduction and purging.

- Assemble the purge-and-trap device. The operating conditions for the GC and GC/MS are given in method SOP ORL-007.
- GC or GC/MS calibration verification criteria must be met (SOP ORL-007) before analyzing samples.

- 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.

- 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 must be done with duplicate VOA.

- Add 10.0 µL of surrogate and internal spiking solution as well as any matrix spike if applicable as described in SOP ORL-007.

- Inject the aliquot into a 40-mL VOA and immediately place cap with septum and tighten.

- Purge for 11.0 minutes at room temperature in the 40ml vial.

♦ Sample desorption.

- Non-cryogenic interface - After the recommended purge (see above), place the purge-and-trap system in the desorb mode and preheat the trap to 190 °C 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.

♦ Trap Reconditioning.

- After desorbing the sample, recondition the trap by baking it at 210 ºC for 3 minutes.

3. This section provides guidance on the analysis of solvent extracts from High Concentration Samples prepared by Method 5035.

♦ The GC or GC/MS system must be set up as in specific determinative method (SOP ORL-007).

♦ 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 SOP ORL-007.

♦ Measure out a 100µL aliquot of the methanol phase of the sample.

♦ 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.

♦ Purge for 11.0 minutes at room temperature in the 40ml vial.

- Desorb the sample and recondition the trap.

4. This section provides guidance on the analysis of Low Concentration Samples prepared by Method 5035.

   - The GC or GC/MS system must be set up as in specific determinative method (SOP ORL-007).
   - Internal standards, surrogates and matrix spikes (if applicable) must be added automatically by the autosampler or manually by puncturing the septum using a small gauge needle.
   - Prior to purging the sample is preheated to 40°C for 1.0 minute while being agitated by the magnetic stir bar.
   - Purge for 11.0 minutes at 40°C while being agitated by the magnetic stir bar in the 40ml vial.
   - Desorb the sample and recondition the trap.

5. Tedlar Bag Air Analysis

   - The GC or GC/MS system must be set up as in specific determinative method (SOP ORL-007).
   - 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 SOP ORL-007.
   - Take a gas tight syringe with a needle 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.
   - Insert the needle of the syringe through the septa of the Tedlar Bag and with draw 5 cc into the syringe.
   - Bubble into 40 ml VOA bottle with 5 ml of DI water and surrogates and internal standards then cap promptly.
   - Purge for 11.0 minutes at room temperature in the 40ml vial.
   - Desorb the sample and recondition the trap.

6. Sample analysis. The samples prepared by this method will be analyzed according to method 8260B SOP.

8.0 QUALITY CONTROL

Refer to method SOP ORL-007 for specific quality control procedures. Quality control items employed and evaluated are provided in Table 1 and Table 2. In addition, the table indicates the frequency of each QC item along with appropriate courses of corrective action. The analyst will follow SOP # QA-007 and complete the appropriate review form upon completion of the analysis.

9.0 METHOD PERFORMANCE

Refer to the determinative methods for performance data.

10.0 EQUIPMENT MAINTENANCE AND TROUBLESHOOTING

Each instrument is assigned a maintenance logbook. All maintenance performed on the instrument must be recorded. Additionally, any modifications to the instrument settings shall be noted in the specific instrument logbook. Maintenance procedures provided in the equipment manual shall be followed. Maintenance may include, cleaning the MS source, clipping/replacing the column, or replacing the calibration standard.

11.0 SAFETY

Eye protection and gloves must be worn while performing Volatile analyses. Every Laboratory area has eyewash, emergency shower, and fire extinguisher. The air system throughout 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. A reference file of material safety data sheets (MSDSs) is available to all personnel.

Specific attention be paid (but not limited) to:

- 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.

- 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

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

13.0 DEFINITIONS

An analytical batch is defined as a group of samples (not to exceed 20 samples) analyzed per sequential run. Depending on client or program requirements, an analytical batch may or may not include matrix spikes as part of the 20 samples.

Method Blank (MB): an analyte-free matrix to which all reagents are added in the same volumes or proportions as used in the sample processing. The method blank is carried through the complete sample preparation and analytical procedure. The method blank is used to document contamination resulting from the analytical process.

Laboratory Control Sample (LCS) (also known as Laboratory Fortified Blank, Spiked Blank, or QC Check Sample): a sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes. It is generally used to establish intra-laboratory or analyst-specific precision and bias or to assess the performance of all or a portion of the measurement system.

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

Matrix Spike Duplicate (also known as Spiked Sample or Fortified Sample Duplicate): A second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

14.0 REFERENCES

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USEPA, SW-846, 1996, REVISION 3; METHOD 5000.

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USEPA, SW-846, 1996, REVISION 3; METHOD 8260B.

Table 1 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 must 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 must 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) must 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 must 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 2: Quality Control Items, Frequency, and Corrective Action for DoD Projects					
QC Check	**Minimum Frequency**	**Acceptance Criteria**	**Corrective Action**	**Flagging Criteria**	**Comments**
Tuning	Prior to ICAL and at the beginning of each 12-hour period.	Refer to method for specific ion criteria.	Retune instrument and verify. Rerun affected samples.	Flagging criteria are not appropriate.	Problem must be corrected. No samples may be accepted without a valid tune.
Minimum five-point initial calibration (ICAL) for all analytes	ICAL prior to sample analysis.	1. Average response factor (RF) for SPCCs: VOCs ≥ 0.30 for chlorobenzene and 1,1,2,2-tetrachlorolethane; ≥ 0.1 for chloromethane, bromoform, and 1,1-dichloroethane. SVOCs ≥ 0.050. 2. RSD for RFs for CCCs: VOCs and SVOCs ≤ 30% and one option below: Option 1: RSD for each analyte ≤ 15%; Option 2: linear least squares regression r ≥ 0.995; Option 3: non-linear regression– coefficient of determination (COD) r2 ≥ 0.99 (6 points shall be used for second order, 7 points shall be used for third order).	Correct problem then repeat ICAL.	Flagging criteria are not appropriate.	Problem must be corrected. No samples may be run until ICAL has passed. Calibration may not be forced through the origin.
Second source calibration verification (ICV)	Once after each ICAL.	All project analytes within ± 20% of true value.	Correct problem and verify second source standard. Rerun second source verification. If that fails, correct problem and repeat ICAL.	Flagging criteria are not appropriate.	Problem must be corrected. No samples may be run until calibration has been verified.
Retention time window position establishment for each analyte and surrogate	Once per ICAL.	Position shall be set using the midpoint standard of the ICAL curve when ICAL is performed. On days when ICAL is not performed, the initial CCV is used.	NA.	NA.	

Table 2: Quality Control Items, Frequency, and Corrective Action for DoD Projects					
QC Check	**Minimum Frequency**	**Acceptance Criteria**	**Corrective Action**	**Flagging Criteria**	**Comments**
Evaluation of relative retention times (RRT)	With each sample.	RRT of each target analyte within ± 0.06 RRT units.	Correct problem, then rerun ICAL.	Flagging criteria are not appropriate.	Laboratories may update the retention times based on the CCV to account for minor performance fluctuations or after routine system maintenance (such as column clipping). With each sample, the RRT shall be compared with the most recently updated RRT. If the RRT has changed by more than ±0.06 RRT units since the last update, this indicates a significant change in system performance and the laboratory must take appropriate corrective actions as required by the method and rerun the ICAL to reestablish the retention times.
Continuing calibration verification (CCV)	Daily before sample analysis and every 12 hours of analysis time.	1. Average RF for SPCCs : VOCs ≥ 0.30 for chlorobenzene and 1,1,2,2-tetrachlorolethane; ≥ 0.1 for chloromethane, bromoform, and 1,1-dichloroethane. 2. %Difference/Drift for all target compounds and surrogates: VOCs ≤ 20%D (Note: D = difference when using RFs or drift when using least squares regression or non-linear calibration).	DoD project level approval must be obtained for each of the failed analytes or corrective action must be taken. - Correct problem, then rerun calibration verification. If that fails, then repeat ICAL. Reanalyze all samples since last acceptable CCV.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply flag to all results for the specific analyte(s) in all samples since last acceptable CCV.	Problem must be corrected. Results may not be reported without a valid CCV. Flagging is only appropriate in cases where the samples cannot be reanalyzed.
Internal standards verification	Every field sample, standard, and QC sample.	Retention time ± 30 seconds from retention time of the midpoint standard in the ICAL; EICP area within -50% to +100% of ICAL midpoint standard.	Inspect mass spectrometer and GC for malfunctions. Reanalysis of samples analyzed while system was malfunctioning is mandatory.	If corrective action fails in field samples, apply flag to analytes associated with the non-compliant IS. Flagging criteria are not appropriate for failed standards.	Sample results are not acceptable without a valid IS verification.

Table 2: Quality Control Items, Frequency, and Corrective Action for DoD Projects					
QC Check	**Minimum Frequency**	**Acceptance Criteria**	**Corrective Action**	**Flagging Criteria**	**Comments**
Method blank	One per preparatory batch.	No analytes detected > ½ RL and > 1/10 the amount measured in any sample or 1/10 the regulatory limit (whichever is greater). Blank result must not otherwise affect sample results. For common laboratory contaminants, no analytes detected > RL.	Correct problem. If required, reprep and reanalyze method blank and all samples processed with the contaminated blank.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply flag to all results for the specific analyte(s) in all samples in the associated preparatory batch.	Problem must be corrected. Results may not be reported without a valid method blank. Flagging is only appropriate in cases where the samples cannot be reanalyzed.
LCS containing all analytes to be reported, including surrogates	One per preparatory batch.	QC acceptance criteria specified by DoD, if available. Otherwise, use in-house control limits. In-house control limits may not be greater than ± 3 times the standard deviation of the mean LCS recovery.	Correct problem, then reprep and reanalyze the LCS and all samples in the associated preparatory batch for failed analytes, if sufficient sample material is available	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply flag to specific analyte(s) in all samples in the associated preparatory batch.	Problem must be corrected. Results may not be reported without a valid LCS. Flagging is only appropriate in cases where the samples cannot be reanalyzed.
Matrix Spike (MS)	One per preparatory batch per matrix.	For matrix evaluation, use LCS acceptance criteria specified by DoD, if available. Otherwise, use in-house LCS control limits.	Examine the project-specific DQOs. Contact the client as to additional measures to be taken.	For the specific analyte(s) in the parent sample, apply flag if acceptance criteria are not met.	For matrix evaluation only. If MS results are outside the LCS limits, the data shall be evaluated to determine the source of difference and to determine if there is a matrix effect or analytical error.

Table 2: Quality Control Items, Frequency, and Corrective Action for DoD Projects					
QC Check	**Minimum Frequency**	**Acceptance Criteria**	**Corrective Action**	**Flagging Criteria**	**Comments**
Matrix spike duplicate (MSD) or sample duplicate	One per preparatory batch per matrix.	MSD: For matrix evaluation, use LCS acceptance criteria specified by DoD, if available. Otherwise, use in-house LCS control limits. MSD or sample duplicate: RPD ≤ 30% (between MS and MSD or sample and sample duplicate).	Examine the project-specific DQOs. Contact the client as to additional measures to be taken.	For the specific analyte(s) in the parent sample, apply flag if acceptance criteria are not met.	The data shall be evaluated to determine the source of difference.
Surrogate spike	All field and QC samples.	QC acceptance criteria specified by DoD, if available. Otherwise, use in-house control limits.	For QC and field samples, correct problem then reprep and reanalyze all failed samples for failed surrogates in the associated preparatory batch, if sufficient sample material is available. If obvious chromatographic interference with surrogate is present, reanalysis may not be necessary.	Apply flag to all associated analytes if acceptance criteria are not met.	Alternative surrogates are recommended when there is obvious chromatographic interference.
Results reported between DL and LOQ	NA.	NA.	NA.	Apply flag to all results between DL and LOQ.	

Figure 1: Volatiles Sample Preparation

VOLATILES
Sample Prep

Date: _____
Analyst: _____
Batch QC ID#: _____

#	Merit #	Matrix	Surrogate ID	Vol. (ul)	Spike ID	Vol. (ul)	Time Start / End	PH	Notes
	BFB								
	SPCC								
	LCS								
	LCSD								
	BLK								
1									
2									
3									
4									
5									
6									
7									
8									
9									
10									
11									
12									
13									
14									
15									
16									
17									
18									
19									
20									
21									
22									
23									
24									
25									

Reviewed by: _____

Date: _____

Prepared by Merit Laboratories, Inc.

FIGURE 2. METHOD 5035 (LOW LEVEL) EXTRACTION SHEET

Method 5035 (Low Level)
Extraction Sheet

Analyst: _____
Date: _____
Batch QC ID #_____

Merit Number	Tare wt (g)	Vial wt (g)	Sample wt.(g)	Time Start / End	Decontaminated	Decontamination Date	Notes

Figure 3. Method 5035 (High Level) Extraction Sheet

Method 5035 (High Level)
Extraction Sheet

Analyst: _____
Date: _____
Batch QC ID#_____

Merit Number	Tare wt (g)	Vial wt (g)	Sample wt.(g)	Methanol (mL)	Sonicate (min)	Time Start / End	Notes

STANDARD OPERATING PROCEDURE

VOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY
METHOD SW-846 8260B

APPROVALS:

Barbara Richardson, QA Officer — 6/9/11 Date

Maya V. Murshak, Technical Director — 6/9/11 Date

Number	Description of Change	Date
001-011	Previous revisions not documented	
0012	Updated to comply with DoD QSM and ISO 17025 standards.	6/9/11
013		
014		
015		
016		
017		
018		
019		

1.0 SCOPE AND APPLICATION

This SOP is used to determine volatile organic compounds (VOC) in a variety of matrices, 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.

There are various techniques by which these compounds may be introduced into the GC/MS system. Purge-and-trap, by SW-846 Methods 5030 (aqueous samples) and 5035 (solid, waste, and oil samples), are the most commonly used technique for volatile organic analytes. SW-846 Method 5000 provides general information on the selection of other introduction methods.

The practical quantitation limit (PQL) for an individual compound is instrument dependent and also dependent on the choice of the 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 When lower reportable detection limits (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. 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.

Method Detection Limits (MDL) and Practical Quantitation Limits (PQL) are available in Merit's LIMs system.

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.

This SOP is not for use with samples that come into the lab for OHIO VAP work.

2.0 SUMMARY OF THE METHOD

VOC 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 interfaced to the gas chromatograph.

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.

The method includes specific calibration and quality control steps that supersede the general requirements provided in SW-846 Method 8000.

3.0 INTERFERENCES

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 will be concentrated in the trap during the purge operation.

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

Gas chromatograph/mass spectrometer system

- 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.
- 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.
- 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 4.
- GC/MS interface - The capillary column is interfaced through a direct connection to the GC/MS system.

- 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.

Purge-and-trap device.
Microsyringes - 2 to 500-µL.
Balance - Analytical, capable of weighing 0.0001 g, and top-loading, capable of weighing 0.1 g.
Glass bottles - 40-mL, with PTFE-lined screw-caps.
pH paper.

5.0 REAGENTS

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.

Organic-free reagent water - All references to water in this method refer to organic-free reagent water.

Stock standard solutions.

- 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.
- Supplemental compounds added to calibration mixes are generally prepared gravimetrically from neat standard references (in order to create a high-concentration stock solution).
- 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.
- Stock standard solutions are replaced prior to expiration, or sooner if comparison with quality control check samples indicate a problem.

Internal standard solutions - The internal standards used are pentafluorobenzene, 1,4-difluorobenzene, chlorobenzene-d_5, and 1,4-dichlorobenzene-d_4 (see Table 2). 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).

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. For DoD projects, each standard shall contain all target compounds.

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).

Matrix spike (MS), matrix spike duplicate (MSD) and laboratory control standards (LCS) - 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. For DoD projects, matrix spiking solutions shall contain all target compounds.

- 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).
- For SIM (selective ion monitoring) analysis, compounds of interest are spiked at concentrations of 0.1 ppb (µg/L).

Methanol, CH_3OH - Pesticide quality or equivalent, demonstrated to be free of analytes. Store apart from other solvents.

6.0 SAMPLE HANDLING AND PRESERVATION

Unanalyzed samples are refrigerated at 4 ± 2 degrees Celsius in sealed vials or containers.

Aqueous samples are preserved to a pH <2with HCl and/or $Na_2S_2O_3$ (unless unpreserved requested) and collected in a 40 ml. Preserved samples must be analyzed within 14 days from sample collection; unpreserved samples must be analyzed within 7 days from sample collection.

Soil samples collected Encore™ Samplers must be preserved within 48 hours and analyzed within 14 days. Soil samples collected in glass jars shall be kept refrigerated and analyzed within 14 days from sample collection. For additional information on sample collection, handling and preservation for soil samples see SOP #ORL-005.

7.0 PROCEDURE

Sample introduction.

- 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).

- Purge-and-trap - This is generally used for 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# ORL-005).

GC/MS operating conditions - see Table 3 for routine operating conditions for VOC analysis.

- For SIM, the MS is put into the SIM 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.

Initial calibration.

- Each GC/MS system must be hardware-tuned to meet the criteria in Table 4 for 4-bromofluorobenzene. Analysis does not begin until these criteria are met.

    - 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.

    - 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.

    - 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.

    - The BFB mass intensity criteria in Table 4 are used as tuning acceptance criteria.

- All subsequent standards, samples, MS/MSDs, and blanks associated with a BFB analysis must use the identical mass spectrometer instrument conditions, Exception: for SIM, tune is run using full scan acquisition and subsequent samples are acquired using SIM.

♦ 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 5 details the dilutions necessary to create a set of calibration standards. Figure 1 shows a chromatogram of a midpoint calibration standard.

♦ 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.

♦ System performance check compounds (SPCCs).

- A system performance check must be performed to ensure that minimum *RF*s are met before the calibration curve is used. For volatiles, the SPCCs are: chloromethane, 1,1-dichloroethane, bromoform, chlorobenzene, and 1,1,2,2-tetrachloroethane (Table 2). No response factor criteria are applied to SIM analysis.
- 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.
- 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.

♦ Calibration check compounds (CCCs).

- 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.
- 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 2) must be less than or equal to 30%.
- 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.

♦ 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.

♦ 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.

- Refer to SW-846 Method 8000 if a least-squares regression is used to determine a linear or quadratic fit to the calibration data. Quadratic polynomials are generally fit through the origin in order to prevent the symptomatic aphysical prediction of high concentrations at very low responses. The coefficient of determination 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.
- 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*.
- 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).

- GC/MS calibration verification - Calibration verification consists of three steps that are performed at the beginning of each 12-hour analytical shift.
- 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 4 before sample analysis begins. These must be *injected* within 12 hours of the injection time for the BFB.
- 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 SIM procedures. The results from the calibration standard analysis must meet the verification acceptance criteria provided below for the SPCC and CCC compounds.
- 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.
- System performance check compounds (SPCCs).
  - 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).
  - If the minimum response factors are not met, the system must be evaluated, and corrective action must be taken before sample analysis begins.
- Calibration check compounds (CCCs).
  - After the system performance check is met, the CCCs listed in Table 2 are used to check the validity of the initial calibration. Percent drift is used to evaluate the CCC response and it must be ≤20%.
  - 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. Drift is defined as the normalized deviation of the measured from the spike value of a target component: $\%D = \left|C - C_{spike}\right| / C_{spike}$.

- 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.

GC/MS analysis of samples.

- 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.
- 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 5 has a list of commonly used dilutions as well as the required amount of sample, water, and internal standard for each dilution.
- Add 10 µL of 25 mg/L internal/surrogate standard mixture to each sample. For SIM analysis, internal and surrogate standards are spiked at 0.1µg/L.
- 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.
- 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 6a and 6b). 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.

Qualitative analysis.

- 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 Figures 1a and 1b. Compounds are identified when the following criteria are met.

- 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.
- 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.
- 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%.)
- 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.
- 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.
- 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.
- 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 judgment and accept an identified hit, allowing the potential for a false positive.

- 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.

Quantitative analysis.

- 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.
- 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, $k_2 \equiv 0$.
- 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 tentatively identified compound (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.

- 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).

8.0 QUALITY CONTROL

All of the quality control items employed and evaluated are provided in Table 6a and 6b. In addition, the table indicates the frequency of each QC item along with appropriate courses of corrective action. Control limits for surrogates and matrix spikes are listed in Table 7. The analyst will follow SOP # QA-007 and complete the appropriate review form upon completion of the analysis.

9.0 METHOD PERFORMANCE

The precision and accuracy of the method depends upon the overall performance of the sample preparation and analysis. Laboratory specific performance data is provided for Merit's LIMs system. Each sample batch contains a method blank, laboratory control sample and matrix spike samples. Performance Evaluation samples are analyzed periodically in order to prove the performance of the method.

10.0 EQUIPMENT MAINTENANCE AND TROUBLESHOOTING

Each instrument is assigned a maintenance logbook. All maintenance performed on the instrument must be recorded. Additionally, any modifications to the instrument settings shall be noted in the specific instrument logbook. Maintenance procedures provided in the equipment manual shall be followed. Maintenance may include, cleaning the MS source, clipping/replacing the column, or replacing the calibration standard.

11.0 SAFETY

Eye protection and gloves must be worn while performing the analyses. Every laboratory area has eyewash, emergency shower, and fire extinguisher. The metals lab also has dust masks available for use with dust samples. The air system throughout 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.

A reference file of material safety data sheets (MSDSs) is available to all personnel. Specific attention shall be paid (but not limited) to:

a. Methanol may react violently with acids, acid chlorides, acid anhydrides, oxidizing agents, reducing agents and alkali metals. Protect from moisture. Highly flammable.

b. 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.

12.0 WASTE DISPOSAL AND POLLUTION PREVENTION

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

13.0 DEFINITIONS

4-Bromofluorobenzene (BFB), is used to verify that the GC/MS is properly tuned and ready for calibration and sample analyses. BFB is directly injected at 25-50 ng and precedes all other analyses. A twelve hour analysis time window is used before another BFB injection is required.

An Initial Calibration Verification standard (ICV) is analyzed before the analysis of samples as a check on the calibration curve. The ICV shall be of a second source, meaning a separate vendor and/or lot # shall be used to prepare this standard. A second source is needed to validate the integrity and concentration of the standards used for calibration.

An Initial Calibration Blank (ICB) is also analyzed before samples to confirm that the deionized water (DI H2O) used for standards, blanks, and dilutions are free from contamination. An ICB for soil samples also includes organic free sand and/or methanol used for standard and QC preparation, as well as sample dilutions and volume adjustments; the control sand and methanol must also be documented as free from contamination.

A Calibration Check Verification standard (CCV) is analyzed at the beginning of each sequence (following the BFB injection) shift and every 12 hour shift thereafter. A CCV is made up from the same standards used for calibration and is used to ensure that the calibration and retention times are stable.

An analytical batch is defined as a group of samples (not to exceed 20 samples) analyzed per sequential run. Depending on client or program requirements, an analytical batch may or may not include matrix spikes as part of the 20 samples.

Internal standards (ISTD) are added to each sample, blank, spike, and check standard. The ISTDs used are Fluorobenzene, Chlorobenzene-d_5, and 1,4-Dichlorobenzene-d_4. The ISTD is used for internal calibration

as a reference peak and to check purging efficiency.

Surrogate standards (SSTD) are also added to each sample, blank, spike, and check standard. The SSTDs used are Toluene-d_4, 4-Bromofluorobenzene, 1,2-Dichloroethane-d_4, and Dibromofluoromethane. The SSTD is used as matrix interference and as a method control check.

Method Blank (MB): An analyte-free matrix to which all reagents are added in the same volumes or proportions as used in the sample processing. The method blank is carried through the complete sample preparation and analytical procedure. The method blank is used to document contamination resulting from the analytical process.

A Continuing Calibration Blank (CCB) is analyzed every 12 hour shift after the MB has been analyzed and before sample reanalyzes to ensure the system is still free from contamination.

Instrument blanks are analyzed whenever instrument contamination is a suspected possibility. The purpose of an IB is to prevent carry over from a standard, spike, or contaminated sample into another sample or blank. The acceptance criteria for an IB is the same as for a MB or CCB (for example: if an IB contains detections above acceptance criteria and a MB and/or sample following the IB exhibit the same contamination above acceptance criteria, then the instrument shall be considered contaminated). The samples and/or MBs shall be reanalyzed after the instrument is confirmed free from contamination.

Laboratory Control Spike (LCS): Milli-Q water (for water) and Organic-Free Soil (for soil) is spiked with all target compounds and carried through the complete sample preparation and analytical procedure. The control spike is used to document the ability of an analyst to generate acceptable precision and bias to verify the analytical system performance, and to document method accuracy for each matrix.

Matrix Spike (MS): An aliquot of sample spiked with all target compounds. The spiking occurs prior to sample preparation and analysis. They are used to document the precision and bias of a method in a given sample matrix.

Matrix Spike Duplicate (MSD): Intra-laboratory split samples spiked with all target compounds. The spiking occurs prior to sample preparation and analysis. They are used to document the precision and bias of a method in a given sample matrix.

14.0 REFERENCES

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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-trifluoroethane	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 (MTBE)	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	

#	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*
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
47	Tetrachloroethene	5.29	1.300	1.22	166	129	164	
48	CHLOROBENZENE-D5	5.76	1.000	0.00	82	117	119	
49	4BROMOFLUOROBENZENE	6.38	1.108	0.62	174	95	176	
50	trans-1,4-Dichloro-2-butene	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

#	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*
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.

: For DoD projects, all target compounds will be included in the matrix spike and matrix spike duplicate

Table 2. 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.

: For DoD projects, all target compounds will be included in the matrix spike and matrix spike duplicate

Key

CCC: Calibration Check Compound

SPCC: System Performance Check Compound

ISD: Internal Standard Compound

SSD: Surrogate Standard Compound

MS: Matrix Spiking Compound

Table 3. 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 4. 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 5. 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 6a. 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	Table 5	Re-attempt injection; clean MS source, re-tune; failure requires the re-analysis of all associated analytical runs.
SPCC/CCC	12-hour	SPCC- section 7.34 CCC- section 7.3.5	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	Table 7	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	<RL	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	Section 7.5.5	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

QC Item	Frequency	Acceptance Criteria	Corrective Action
			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	Table 7	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 6b. Quality Control Items, Frequency, and Corrective Action for DoD Projects

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Tuning	Prior to ICAL and at the beginning of each 12-hour period.	Refer to method for specific ion criteria.	Retune instrument and verify. Rerun affected samples.	Flagging criteria are not appropriate.	Problem must be corrected. No samples may be accepted without a valid tune.
Minimum five-point initial calibration (ICAL) for all analytes	ICAL prior to sample analysis.	1. Average response factor (RF) for SPCCs: VOCs ≥ 0.30 for chlorobenzene and 1,1,2,2-tetrachlorolethane; ≥ 0.1 for chloromethane, bromoform, and 1,1-dichloroethane. SVOCs ≥ 0.050. 2. RSD for RFs for CCCs: VOCs and SVOCs ≤ 30% and one option below: Option 1: RSD for each analyte ≤ 15%; Option 2: linear least squares regression r ≥ 0.995; Option 3:non-linear regression– coefficient of determination (COD) r2 ≥ 0.99 (6 points shall be used for second order, 7 points shall be used for third order).	Correct problem then repeat ICAL.	Flagging criteria are not appropriate.	Problem must be corrected. No samples may be run until ICAL has passed. Calibration may not be forced through the origin.
Second source calibration verification (ICV)	Once after each ICAL.	All project analytes within ± 20% of true value.	Correct problem and verify second source standard.	Flagging criteria are not appropriate.	Problem must be corrected. No samples may be run

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
			Rerun second source verification. If that fails, correct problem and repeat ICAL.		until calibration has been verified.
Retention time window position establishment for each analyte and surrogate	Once per ICAL.	Position shall be set using the midpoint standard of the ICAL curve when ICAL is performed. On days when ICAL is not performed, the initial CCV is used.	NA.	NA.	
Evaluation of relative retention times (RRT)	With each sample.	RRT of each target analyte within ± 0.06 RRT units.	Correct problem, then rerun ICAL.	Flagging criteria are not appropriate.	Laboratories may update the retention times based on the CCV to account for minor performance fluctuations or after routine system maintenance (such as column clipping). With each sample, the RRT shall be compared with the most recently updated RRT. If the RRT has changed by more than ±0.06 RRT units since the last update, this indicates a significant change in system performance and the laboratory must take appropriate corrective actions

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
					as required by the method and rerun the ICAL to reestablish the retention times.
Continuing calibration verification (CCV)	Daily before sample analysis and every 12 hours of analysis time.	1. Average RF for SPCCs : VOCs ≥ 0.30 for chlorobenzene and 1,1,2,2-tetrachlorolethane; ≥ 0.1 for chloromethane, bromoform, and 1,1-dichloroethane. SVOCs ≥ 0.050. 2. %Difference/Drift for all target compounds and surrogates: VOCs and SVOCs ≤ 20%D (Note: D = difference when using RFs or drift when using least squares regression or non-linear calibration).	DoD project level approval must be obtained for each of the failed analytes or corrective action must be taken. Correct problem, then rerun calibration verification. If that fails, then repeat ICAL. Reanalyze all samples since last acceptable CCV.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply Q-flag to all results for the specific analyte(s) in all samples since last acceptable CCV.	Problem must be corrected. Results may not be reported without a valid CCV. Flagging is only appropriate in cases where the samples cannot be reanalyzed.
Internal standards verification	Every field sample, standard, and QC sample.	Retention time ± 30 seconds from retention time of the midpoint standard in the ICAL; EICP area within -50% to +100% of ICAL midpoint standard.	Inspect mass spectrometer and GC for malfunctions. Reanalysis of samples analyzed while system was malfunctioning is mandatory.	If corrective action fails in field samples, apply Q-flag to analytes associated with the non-compliant IS. Flagging criteria are not appropriate for	Sample results are not acceptable without a valid IS verification.

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
				failed standards.	
Method blank	One per preparatory batch.	No analytes detected > ½ RL and > 1/10 the amount measured in any sample or 1/10 the regulatory limit (whichever is greater). Blank result must not otherwise affect sample results. For common laboratory contaminants, no analytes detected > RL (see Box D-1).	Correct problem, then see criteria in Box D-1. If required, reprep and reanalyze method blank and all samples processed with the contaminated blank.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply B-flag to all results for the specific analyte(s) in all samples in the associated preparatory batch.	Problem must be corrected. Results may not be reported without a valid method blank. Flagging is only appropriate in cases where the samples cannot be reanalyzed.
LCS containing all analytes to be reported, including surrogates	One per preparatory batch.	QC acceptance criteria specified by DoD, if available. Otherwise, use in-house control limits. In-house control limits may not be greater than ± 3 times the standard deviation of the mean LCS recovery. See Box D-3 and Appendix G.	Correct problem, then reprep and reanalyze the LCS and all samples in the associated preparatory batch for failed analytes, if sufficient sample material is available (see full explanation in Appendix G).	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply Q-flag to specific analyte(s) in all samples in the associated preparatory batch.	Problem must be corrected. Results may not be reported without a valid LCS. Flagging is only appropriate in cases where the samples cannot be reanalyzed.
Matrix Spike (MS)	One per preparatory batch per matrix (see Box D-7).	For matrix evaluation, use LCS acceptance criteria specified by DoD, if available. Otherwise, use in-house LCS control limits.	Examine the project-specific DQOs. Contact the client as to additional measures to be taken.	For the specific analyte(s) in the parent sample, apply J-flag if acceptance criteria are not met.	For matrix evaluation only. If MS results are outside the LCS limits, the data shall be evaluated to determine the source of difference and to determine if

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
					there is a matrix effect or analytical error.
Matrix spike duplicate (MSD) or sample duplicate	One per preparatory batch per matrix (see Box D-7).	MSD: For matrix evaluation, use LCS acceptance criteria specified by DoD, if available. Otherwise, use in-house LCS control limits. MSD or sample duplicate: RPD ≤ 30% (between MS and MSD or sample and sample duplicate).	Examine the project-specific DQOs. Contact the client as to additional measures to be taken.	For the specific analyte(s) in the parent sample, apply J-flag if acceptance criteria are not met.	The data shall be evaluated to determine the source of difference.
Surrogate spike	All field and QC samples.	QC acceptance criteria specified by DoD, if available. Otherwise, use in-house control limits.	For QC and field samples, correct problem then reprep and reanalyze all failed samples for failed surrogates in the associated preparatory batch, if sufficient sample material is available. If obvious chromatographic interference with surrogate is present, reanalysis may not be necessary.	Apply Q-flag to all associated analytes if acceptance criteria are not met.	Alternative surrogates are recommended when there is obvious chromatographic interference.
Matrix spike duplicate (MSD) or sample duplicate	One per preparatory batch per matrix (see Box D-7).	MSD: For matrix evaluation, use LCS acceptance criteria specified by DoD, if available. Otherwise, use in-house LCS	Examine the project-specific DQOs. Contact the client as to additional measures to be taken.	For the specific analyte(s) in the parent sample, apply J-flag if acceptance criteria are not	The data shall be evaluated to determine the source of difference.

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
		control limits. MSD or sample duplicate: RPD ≤ 30% (between MS and MSD or sample and sample duplicate).		met.	

Table 7. Summary of Control Limits: Surrogate and Matrix Spiking Compounds Percent Recovery[†]

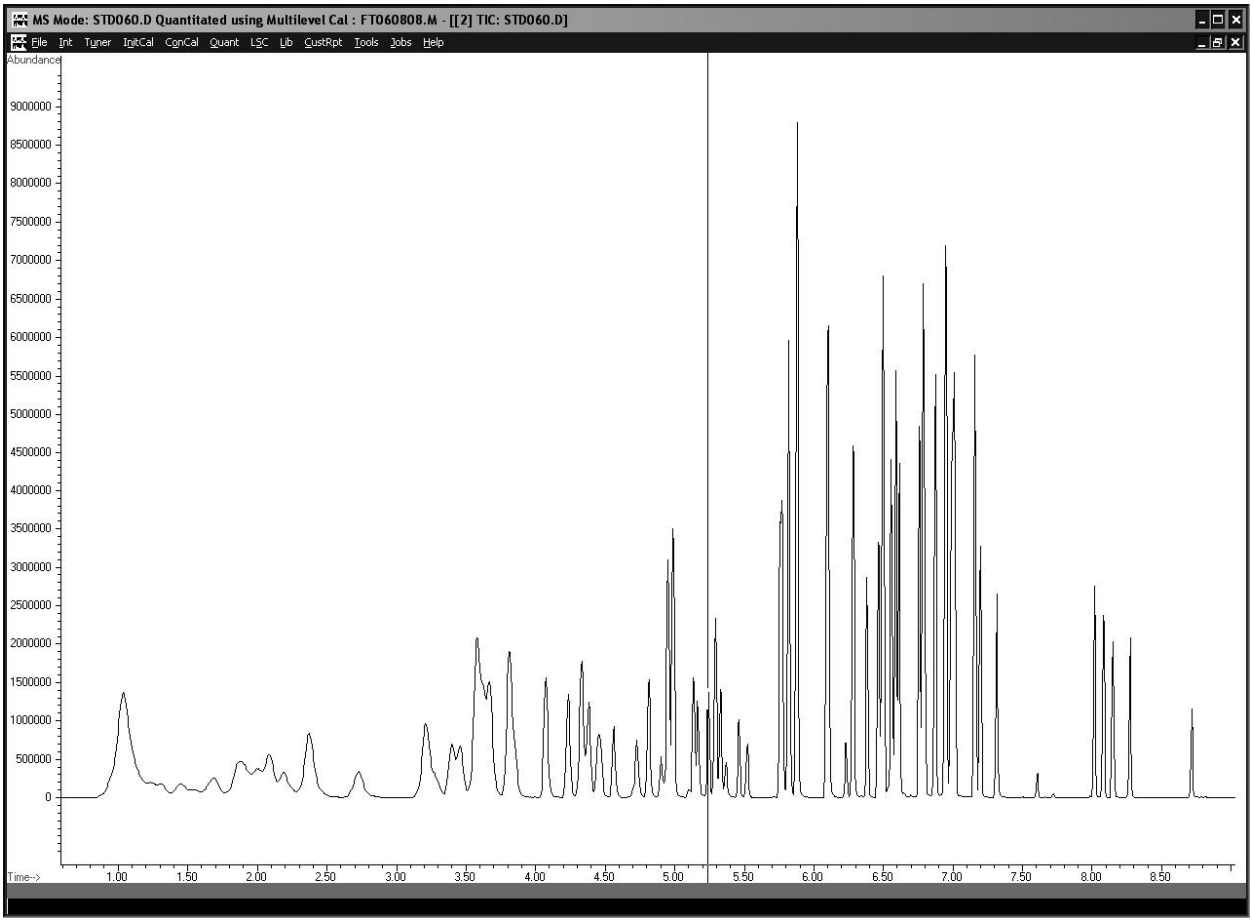
#[‡]	COMPOUND	Water Matrix		Solid Matrix	
		LCL (%)	UCL (%)	LCL (%)	UCL (%)
2	1,2-DICHLOROETHANE-D4	66.4	124.8	70.0	136.3
26	TOLUENE-D8	82.5	118.4	84.0	138.0
43	4BROMOFLUOROBENZENE	78.4	119.6	59.0	122.8
16	1,1-Dichloroethene (CCC/MS)	59.9	145.0	59.0	172.0
30	Benzene (MS)	73.7	127.0	66.0	142.0
32	Trichloroethene (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.

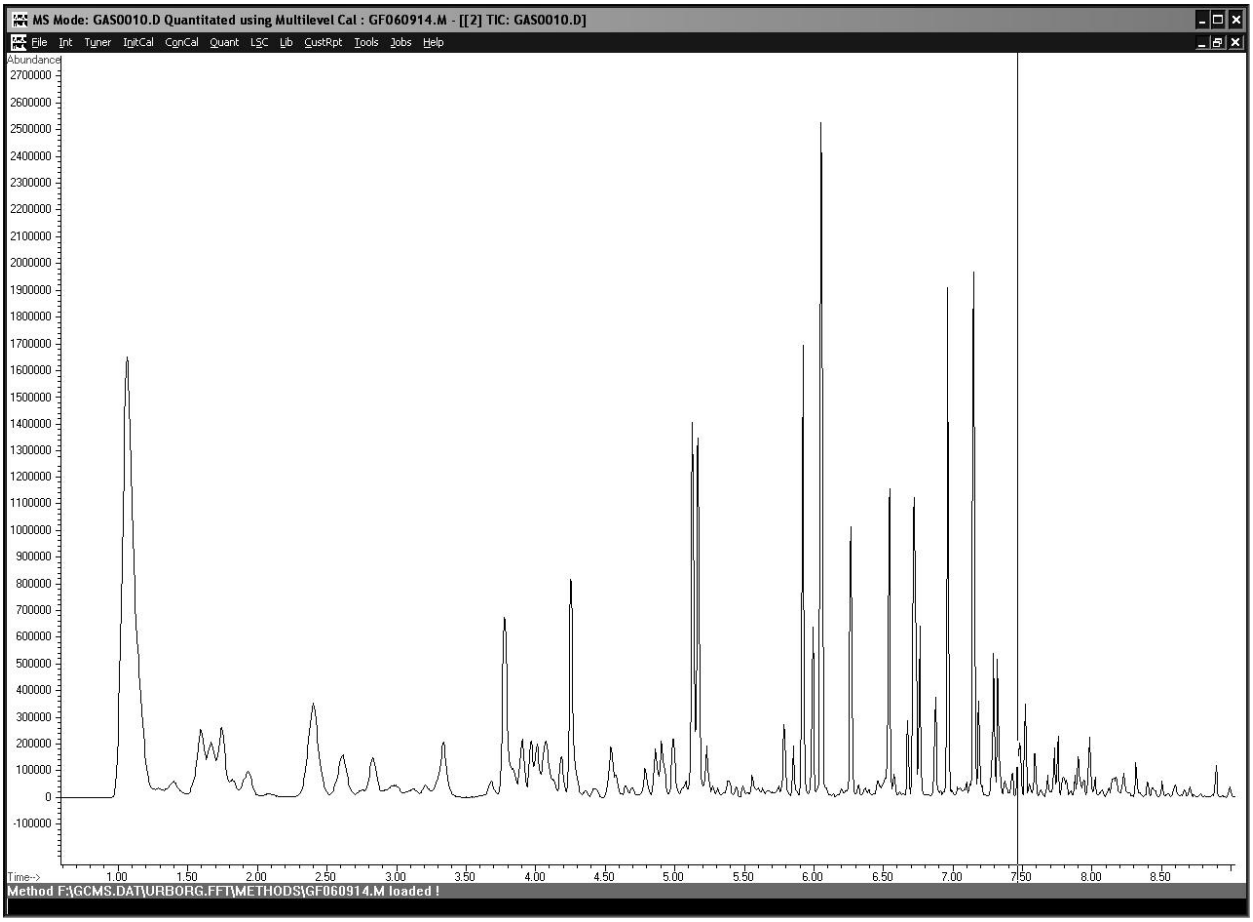
: For DoD projects, all target compounds must be included in the spikes. LCS acceptance criteria specified in the DoD QSM or in-house LCS control limits shall be used.

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†



†:GAS_010.D from calibration GF060914.M (1.0 mg/L). GC/MS acquisition parameters are given by Table 4.