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FINAL QUALITY ASSURANCE PROJECT PLAN ADDENDUM 1 AT FORMER SEWAGE TREATMENT PLANT WITH TRANSMITTAL NAS SOUTH WEYMOUTH MA
4/12/2011
TETRA TECH

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April 21, 2011

Project Number G02073

Mr. Brian Helland, RPM
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Philadelphia, Pennsylvania 19112

Reference: CLEAN Contract No. N62470-08-D-1001
Contract Task Order (CTO) No. WE11

Subject: Final Quality Assurance Project Plan, Addendum 1
Former Sewage Treatment Plant, Pre-Design Investigation
Naval Air Station South Weymouth, Weymouth, Massachusetts

Dear Mr. Helland:

Enclosed is the Final Quality Assurance Project Plan (QAPP), Addendum 1, Former Sewage Treatment Plant at Naval Air Station South Weymouth, Weymouth, Massachusetts. The field work is scheduled to begin on May 2, 2011.

On behalf of the Navy, the final QAPP Addendum 1, Former Sewage Treatment Plant, is being provided to the recipients listed below. If you have any questions regarding the document, please contact me at (978) 474-8403.

Very truly yours,

Phoebe A. Call

Phoebe A. Call
Project Manager

PAC/lh

Enclosures

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Quality Assurance Project Plan
Addendum 1

for

Former Sewage Treatment Plant
Naval Air Station South Weymouth
Weymouth, Massachusetts

Naval Facilities Engineering Command
Mid-Atlantic

Contract Number N62470-08-D-1001
Contract Task Order WE11

April 2011

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APRIL 2011

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1.0 INTRODUCTION

This Quality Assurance Project Plan (QAPP) Addendum 1 was prepared by Tetra Tech, Inc, (Tetra Tech) for the U.S. Department of Navy (Navy) to conduct additional activities to support the pre-design investigation (PDI) for the former Sewage Treatment Plant (STP) Site (the Site), at the Naval Air Station (NAS) South Weymouth, Massachusetts (the Base). The QAPP Addendum was prepared for the Navy's Naval Facilities Engineering Command (NAVFAC) Mid-Atlantic under Comprehensive Long-Term Environmental Action Navy (CLEAN) Contract No. N62470-08-D-1001, Contract Task Order (CTO) WE11. The Site is Installation Restoration (IR) Site 7.

This document supplements the *Final Quality Assurance Project Plan for Former Sewage Treatment Plant, at Former Naval Air Station South Weymouth, Weymouth, Massachusetts* (Tetra Tech NUS, Inc., February 2008), and includes additional delineation activities (direct push technology [DPT] drilling and soil sampling) based on the findings of the remedial action performed in 2009 (Tetra Tech EC Inc, 2010). The remedial action, which included excavation of shallow impacted soil and sediment, removal of soil stockpiles, and collection of confirmatory samples, was initiated in July 2009. Remedial action activities were completed in November 2009, consistent with the Record of Decision (ROD) and Remedial Action Work Plan. Additional soil sampling is required to address apparent petroleum contamination discovered in an upland area of the Site.

The STP QAPP addendum complies with the intent of the Unified Federal Policy (UFP) Quality Assurance Program Plans (QAPPs) and with the requirements of *QA/R-5, EPA Requirements for Quality Assurance Project Plans* (EPA, March 2001). The sections in this addendum correspond to sections in the Final QAPP (TtNUS, February 2008) with section-specific text added for DPT drilling and analysis of soil samples.

2.0 PROJECT MANAGEMENT AND OBJECTIVES

This QAPP Addendum 1 will be used by Tetra Tech in conjunction with the original 2008 QAPP to perform the data acquisition field activities to supplement the STP Site PDI.

2.1 PROJECT ORGANIZATION AND RESPONSIBILITIES

Tetra Tech continues to be responsible for the overall management of the project, including the performance of field activities presented in this QAPP Addendum 1. No changes were made to Section 2.1 in the QAPP addendum, with the exception of the substitution of key Tetra Tech project personnel listed in Table 2-1A.

2.2 PROJECT PLANNING AND SCOPING

The scope of the work covered by this QAPP Addendum 1 was developed by Navy with input from the U.S. Environmental Protection Agency (EPA) and the Massachusetts Department of Environmental Protection (MassDEP). In December 2009, a meeting was held by Tetra Tech and Navy to develop the scope of the work and identify additional project technical and QA/QC requirements. Table 2-2A lists the meeting participants and documents the planning session.

2.3 PROBLEM DEFINITION AND SITE HISTORY

Additions to the QAPP are listed in Section 2.3.3.

2.3.1 Former Sewage Treatment Plant Location, History, and Background

No changes were made to Section 2.3.1 in this QAPP Addendum 1.

2.3.2 Physical Characteristics of the Site

No changes were made to Section 2.3.2 in this QAPP Addendum 1.

2.3.3 Site Previous Investigations

No changes have been made to the original text of this section; the following paragraphs have been added:

The PDI was conducted to further delineate the types and extent of chemicals of concern (COCs) in soil and sediment requiring remediation, to verify that surface water is not a medium of concern, to evaluate groundwater flow and to inspect and determine whether there are potential migration pathways that have not been adequately investigated. The field activities were completed in February 2008; the final PDI Report was issued in February 2009 (LFR, 2009).

The Remedial Action Work Plan was completed in July 2009. The remedial action field activities began in July and were completed in November 2009. The remedial action included soil excavation and collection of confirmatory samples. When confirmatory sampling showed polycyclic aromatic hydrocarbon (PAH) contamination beyond the planned limits of excavation, further delineation was performed through test pit excavation and collection of soil samples. Staining was encountered in several test pits and analytical samples were collected from selected test pits (Figure 2-11). The test pit observations suggested that subsurface petroleum contamination was present within and beyond the A-2 excavation area and that further investigation was warranted to determine if the PAH exceedances were due to petroleum contamination (Tetra Tech EC, Inc., 2010). Headwall effluent pipes and arsenic in subsurface soil were also identified as potential data gaps to be addressed.

2.4 PROJECT QUALITY OBJECTIVES AND MEASUREMENT PERFORMANCE CRITERIA

Changes to the QAPP addendum are detailed in the following subsections.

2.4.1 Data Quality Objectives Development Process

The data quality objectives (DQOs) for this investigation were developed using the same process as for the PDI QAPP. The following subsections describe the DQOs for the data to be collected under this QAPP Addendum 1.

2.4.1.1 Step 1 - Statement of the Problem

The following information has been added to the decision statement.

Additional soil sampling and analysis is needed in order to delineate suspected petroleum contamination discovered during the 2009 remedial action and confirm that the residual PAH contamination is petroleum-related (see Section 2.5.2).

2.4.1.2 Step 2 - Identification of the Decision Statement

Based on the additional data described in this QAPP Addendum 1, decisions will be made that will affect the STP remedial action process. These additional decisions are described below.

- Based on the analytical results of the soil sampling, a decision will be made whether the residual PAH contamination is petroleum-related and whether a change in the delineation of the remediation areas is needed.
- Based on the analytical results of the soil sampling, a decision will be made whether to take further action under CERCLA or under the Massachusetts Contingency Plan (MCP), if the contamination is petroleum related.

2.4.1.3 Step 3 - Inputs to the Decisions

Inputs to the decisions include data to be generated during this additional investigation and data already available from the Phase II Remedial Investigation, the Feasibility Study, the PDI and the RA. The type of data generated includes laboratory-generated data for the analysis of soil samples and field data collected during drilling. All of the soil samples will be analyzed for volatile organic compounds (VOCs), PAHs, and MCP constituents (volatile petroleum hydrocarbons (VPH), and extractable petroleum hydrocarbons (EPH)). EPH petroleum fingerprint results (included in all EPH analyses) will be used to identify petroleum products such as kerosene, fuel oils #2, #4, #6, diesel fuel, jet fuel and some lubricant oils. In addition, a subset of the samples will also be analyzed for pesticides, polychlorinated biphenyls (PCBs), and total metals.

Field and laboratory data will be used as described in Section 2.4.1.5. Details about the sample locations, number of samples, sampling and field measurement techniques, and analytical methods are presented in Section 3.0.

Decision inputs already available include the Site PRGs, which were developed during the FS for the COCs identified in the risk assessments performed for the Site and included in the ROD. Human health screening criteria (Regional Screening Levels, or RSLs) and base background values will be used to evaluate the sample results. MCP S-1 criteria were used in addition to the ROD-specified PRGs to evaluate the confirmatory sample and test pit sample results during the remedial action. The RSLs, base background values, and MCP S-1 criteria will be used as described in Section 2.4.1.5. Since this QAPP

Addendum 1 covers the collection of subsurface soil samples, ecological risk regulatory limits are not applicable.

2.4.1.4 Step 4 - Definition of the Boundaries of the Study

The geographical area to be evaluated for this QAPP Addendum 1 investigation consists of the upland portion of the STP Site, indicated as Area A-2 on Figure 2-11. Soil sampling will be performed in the area discussed in Section 2.5.2 and Section 3.1.2.

2.4.1.5 Step 5 - Decision Rules

To determine if the residual contamination is petroleum-related and if additional remediation or a change in the delineation of the remediation areas is needed, additional soil samples will be collected and analyzed for VOCs, PAHs, VPH, and EPH (which will include petroleum fingerprinting). In addition, to determine whether further action will be taken under CERCLA or the MCP, one sample from each boring will also be analyzed for PCBs, pesticides, and total metals. The decision rules will differ depending on whether a site PRG was developed for an analyte or not, as follows:

- Analytes with Site PRGs (COCs) – The new analytical results will be plotted on a site map along with existing data. The limits of any additional remediation will be drawn using the new and existing data, to encompass all sample locations and associated areas exceeding the site PRGs.

- Analytes with no Site PRG (non-COCs) – The new analytical results will be plotted on a site map along with existing data. VPH and EPH analytical data, which are MassDEP requirements, will be compared to MassDEP criteria. The EPH petroleum fingerprint results will be used to identify petroleum products. If a petroleum product is identified, then the source of the PAH contamination could be attributed to the identified petroleum product. Detections of VOCs and PAHs would be compared to CERCLA criteria (e.g. PRGs and RSLs). If VPH and EPH aliphatic/aromatic ranges are detected, EPH petroleum fingerprint results indicate the presence of petroleum products, and PAH concentrations do not exceed the CERCLA criteria, then the EPH, VPH, and PAH data would be considered representative of petroleum hydrocarbons and would be addressed under the MCP. If the results indicate that the contaminants are not petroleum-related, the results will be compared to screening criteria and base background, and human health risk will be evaluated under CERCLA as shown in the decision matrix presented on Figure 2-7A. A modification of the remediation area may be needed if the detected contaminant is present at a concentration that is determined to pose an unacceptable risk.

2.4.1.6 Step 6 - Limits on Decision Errors

No changes were made to Section 2.4.1.6 in this QAPP addendum.

2.4.1.7 Step 7 - Sampling Design

The sampling design for this QAPP Addendum 1 investigation was based on areas identified during the remedial action as requiring further delineation and potentially further remediation.

Specifics of the data collection design, rationale, and procedures are presented in Section 3.1.

2.4.2 Measurement Performance Criteria

The changes to Section 2.4.2 in this QAPP Addendum 1 are limited to the project quantitation limits shown in Table 2-4A.

2.4.3 Project Action Levels and Project Quantitation Limits

The project action levels and PQLs for QAPP Addendum 1 subsurface soils are listed in Table 2-4A.

2.5 EVALUATION OF SECONDARY DATA

In addition to the data sources identified in the QAPP, the confirmation data from the 2009 remedial action were evaluated for use in this QAPP Addendum 1. The sample locations were determined with the assistance of analytical data from the A-2 excavation and associated test pit activities (Figure 2-11 and Figure 2-12). No other changes were made to this section.

2.5.1 Media of Concern

Subsurface soil is considered to be the media of concern in this QAPP Addendum 1, based on field indications of petroleum-related contamination during the 2009 remedial action.

2.5.2 Remediation Areas and Areas Requiring Further Investigation

Potential sources of a petroleum release determined from as-built drawings include the following:

- Figure 2-10 (NAVFAC Drawing #2002855, March 1972) indicates a UST (and the piping connecting it to Building 87) located north of the east end of the former sludge drying bed. The UST area was included in the Round 3 excavation area, which removed soil to a depth of 2.5 feet bgs. Soil staining was found in the vicinity of Building 87 during the removal action, although the piping to the tank appeared to be intact.

- As petroleum products would foul the treatment system, they would not have been carried through the system. A significant oil release through the sanitary sewer system would have surcharged the primary settling tanks and weir and been released to the ground surface.

In addition, new areas requiring investigation were discovered during the completion of the remedial action. During the excavation in the A-2 area petroleum-impacted soil was identified by olfactory and visual observations. A review of Navy as-built drawings identified the area as the former Building 87-Addition. Exploratory test pits were completed in the area and the remains of a number of former structures were identified. A total of 25 additional test pits were completed around the structures and in the vicinity of Area A-2 (see Figure 2-11). The new areas requiring further investigation are described in Section 2.5.2.1 below.

2.5.2.1 Soil

Soil in the vicinity of Area A-2 has been determined to require characterization based on the test pit observations of petroleum odors, the test pit sample results and data gaps identified in comments on the Interim Remedial Action Completion Report (Tetra Tech EC, 2010). The lateral extent and thickness of contaminated soil will be determined by completing a series of soil borings. The proposed boring locations are described in Section 3.1.2.3. Subsurface soil samples will be collected to determine the presence and type of contaminants. Material within the pipes located within the headwall of the drainage ditch will be considered to be soil for the purpose of this document; the pipes will be sampled to determine if petroleum-contaminated material is present in the pipes which may need to be addressed.

2.5.2.2 Sediment

No changes were made to Section 2.5.2.2 in this QAPP Addendum 1. Sediment sampling is not included in this QAPP Addendum 1.

2.5.3 Remedial Action Objectives and Remedial Alternatives

No surface soil samples will be collected for this investigation, so ecological receptors and benchmarks will not be used to evaluate the data.

Based on the results of this subsurface soil investigation, remedial action objectives and alternatives may be adjusted as described below. As discussed during a project status meeting between Navy, EPA and MassDEP on November 24, 2009, an Explanation of Significant Differences may be required to document changes to the remedial action objectives and alternatives.

If the additional investigation determines the subsurface soil contaminants to be petroleum-related, the CERCLA remedial action will be considered complete and additional actions at the Site will be completed under the MCP process. If the additional investigation determines that the subsurface soil contaminants are not petroleum-related, remedial goals will be developed for the any newly identified COCs and the site activities will continue under the CERCLA process.

Petroleum fingerprinting is included in the EPH analysis in order to determine if PAH concentrations are from a petroleum-related source such as kerosene, fuel oils #2, #4, #6, diesel fuel, jet fuel and some lubricant oils. If a petroleum product is identified, then the source of the PAH contamination could be attributed to the identified petroleum product.

Detections of VOCs and PAHs will be compared to CERCLA criteria (e.g. PRGs and RSLs). If VPH and EPH aliphatic/aromatic ranges are detected, EPH petroleum fingerprint results indicate the presence of petroleum products, and PAH concentrations do not exceed the CERCLA criteria, then the EPH, VPH, and PAH data would be considered representative of petroleum hydrocarbons and would be addressed under the MCP.

The analytical results along with evidence of staining, etc. will be used to determine whether or not a sample is petroleum-based and thus should fall under the MCP. This determination will be made in consultation with EPA and MassDEP once the results are available.

No other changes were made to Section 2.5.3 in this QAPP addendum.

2.6 PROJECT OVERVIEW AND SCHEDULE

This section presents a general overview of the activities that will be performed. Detailed descriptions for the individual tasks are included in Section 3.0. Only changes from the QAPP Addendum 1 are discussed in this section.

2.6.1 Project Overview

The tasks covered by this QAPP Addendum 1 are described below. See the QAPP for details regarding specific field tasks.

- Mobilize for field sampling.
- Procure and manage one or more subcontractor laboratories to analyze the Site samples.
- Conduct field sampling to delineate soil contamination. DPT drilling will be conducted to collect the subsurface soil samples, as described in Section 3.1.2.3.
- Perform off-site laboratory analysis of samples collected.
- Conduct GPS surveying of sample locations.
- Manage the minimal IDW expected to be generated from the collection of samples and daily decontamination.
- Demobilize.
- Provide sample management and tracking, including shipping samples to a laboratory for analysis and receiving data deliverables.
- Perform data validation of laboratory analytical data, integrate validated data sets into the Naval Installation Restoration Information Solution (NIRIS) system, and reduce and tabulate data for use in developing the PDI report.

- Prepare a field report summarizing all field activities, documenting any modifications to the QAPP Addendum 1, and presenting the results of the investigation. An internal draft, draft, draft final, and final report will be prepared.

2.6.2 Project Schedule

Actual dates for the project will be determined once the Final PDI QAPP Addendum 1 is approved or consensus is reached between Navy and the regulatory agencies.

3.0 FIELD DATA ACQUISITION

3.1 FIELD TASKS

This section has been modified to include additional soil sampling to delineate contamination found during the 2009 remedial action at STP.

The additional tasks covered under this QAPP Addendum 1 include:

- DPT drilling and subsurface soil sampling.

This DPT drilling and soil sampling activity is further described in new Section 3.1.2.3. Subsections 3.1.10 and 3.1.12 have been updated with additional task details; no other subsections in Section 3.1 have changed.

3.1.1 Mobilization/Demobilization

No changes were made to Section 3.1.1 in this QAPP addendum.

3.1.2 Sampling to Further Delineate Remediation Area

Subsection 3.1.2.3 has been added; the other portions of this section are not applicable to this QAPP Addendum 1.

3.1.2.3 Subsurface Soil Sampling

As discussed in Section 2.5.2, the 2009 remedial action encountered evidence of more contamination than was previously realized in an upland area of the Site. In order to delineate the extent of the petroleum-impacted soil contamination and confirm that other analytes, such as metals, are not a concern, additional subsurface soil samples are required in the vicinity of remediation Area A-2. See Section 2.5.

The sample designation and tracking system is described in Section 3.3.2 of the QAPP. A total of 23 soil borings and up to three subsurface headwall samples are planned for this field investigation.

DPT Sampling Process Design and Rationale

Sample locations are intended to investigate the lateral extent of contamination beyond the Area A-2 limits of excavation and to determine the vertical extent of the contamination. The total depth of each boring will either be 14 feet or 2 feet deeper than the bottom of contamination, if the bottom of the contamination as determined by field observations during drilling is deeper than 14 feet. The total depth of the borings will not exceed 20 feet. Samples will be collected generally from two intervals: at the depth of highest contamination, and below the depth of contamination or at the bottom of the boring. If no evidence of contamination is found, one sample will be collected at the bottom of the boring. Evidence of contamination will include either olfactory or visual observations, or photo-ionization detector (PID) readings above background. Samples from both intervals will be analyzed for VOCs, VPH/EPH and PAHs. The sample in each boring at the depth with the highest evidence of contamination will also be analyzed for pesticides, PCBs, and metals.

Several borings will also be used as confirmation samples for the 2009 excavations. Two borings, SB-10 and SB-21, will be used to collect confirmation samples from the southern edge of excavation. For these two borings, an additional sample will be collected at the excavation floor for full-suite analysis, if this interval is not the zone of highest contamination as noted above. One boring, SB-22, will be sampled using the same criteria as described for the investigation samples, but if field observations do not indicate contamination, two samples will be collected: the standard sample at the bottom of the boring, and one additional sample at the excavation floor (1.5 feet). The additional sample will be sent for full-suite analysis. Three borings, SB-25 through SB-27, will be sampled at the bottom of the excavation, estimated at 2.5 feet bgs, and analyzed for metals only.

Sampling rationales for each new soil boring, continuing the numbering sequence from the PDI, are provided below. See Figure 3-1A for details.

SB-05 is located to target the northern side of the former drying tank/primary clarifiers, between test pit TP-5, from which samples were not collected, and TP 11, which had a sample with no exceedances of MCP S-1 criteria nor was impacted soil encountered.

SB-06 is located to determine the northeast extent of contamination and if contamination extends under the road.

SB-07 and SB-08 are located to confirm that low contaminant concentrations in the area do not continue to the east under the road.

SB-09 is the southern-most location. It targets the TP-13 location, where field evidence indicated potential contamination (staining) but samples were not collected for laboratory analysis.

SB-10 is located along the east side of the northern edge of the sludge drying area. This is an area where subsurface soil samples have not been collected, but a surface soil sample PAH concentration exceeded a site PRG. It is intended to delineate the southern extent of contamination, as previous samples SB-01 and SB-04 located in the sludge drying bed to the south did not exceed the site PRGs. SB-10 will also be used as a confirmation sample for the A2 excavation and an additional sample will be collected for full-suite analysis at the bottom of the excavation, estimated at 2.5 feet bgs.

SB-11 is located to the east of the second former trickling filter. Analytical samples have not been collected previously from this area, although a nearby test pit (TP-21) did have potential contamination based on field observations. Subsurface soil samples were not collected from TP-21.

SB-12 and SB-13 are located to bracket the southwest and northwest extent of PAHs from TP-23, which was visually clean but had significant PAH concentrations (above CERCLA screening criteria but below the soil remediation goal from the ROD); and from TP-24, which had low PAH concentrations but had field observations of contamination. The locations are relatively close because previous boring STP-FSB-2 (50 feet to the west) did not have significant contamination.

SB-14 is located in the corner of the L-shaped building/structure to confirm the limits of excavation west of A2-B02.

SB-15 is located to determine the extent of contamination in the northwest portion of the excavation and to confirm the limits of excavation, as confirmatory samples were not collected in the northwest corner of the excavations.

SB-16 is located in the center of the former trickling filter, where previous results have indicated contaminant concentrations above the soil remediation goal. This boring is intended to determine the total depth of and fully characterize the vertical extent of contamination.

SB-17 is located north of TP-2, which had samples exceeding CERCLA screening criteria but below the soil remediation goal; west of TP-6, which had potential contamination but no analytical samples were

collected;, and slightly north of the Round 3 excavation. It is intended to determine the extent of contamination in this area.

SB-18 is located between the two digesters. This area was included in the Round 3 excavation, but analytical samples have not previously been collected from this location.

SB-19 is located along the edge of the excavation, northeast of test pit 22 (concentrations above soil remediation goal) and between test pits 20 and 21 (no analytical samples collected). It will be located within the excavation footprint to evaluate concentrations at depth.

SB-20 is located immediately to the east of Building 87 to determine the vertical extent of contamination in this area.

SB-21 is located at the west side of the northern edge of the sludge drying beds. It is intended as a confirmation sample for the excavation. An additional sample will be collected for full-suite analysis at the depth of the bottom of the excavation, estimated to be 1 ft bgs.

SB-22 is located slightly north of TP-22 and is intended to determine the extent of contamination associated with the A2-B02 area. Samples will be collected using the same criteria as described for the investigation samples, but if field observations do not indicate contamination, two samples will be collected: one at the bottom of the boring, and one at the depth of the excavation floor, estimated to be 1.5 ft bgs.

SB-23 is located between the northwest corner of the sludge drying bed and boring SB-12 in order to confirm the southern limit of contamination in this area.

SB-24 is located in the northern portion of the A-2 excavation area, in the vicinity of confirmation sample A2-B01 (concentrations below the soil remediation goal but above CERCLA screening criteria) and just north of test pit TP-20, which had field observations of contamination throughout the test pit but no samples were collected for laboratory analysis.

SB-25 through SB-27 are located in the Round 3 excavation footprint in areas not otherwise covered by the other soil boring locations proposed in this QAPP Addendum, in order to determine if the subsurface contains elevated arsenic concentrations. The samples will be collected at the bottom of the excavation and analyzed for metals.

If significant contamination is detected in a boring, based on field (PID readings, visual, or olfactory) observations, an additional boring will be drilled further away from the excavations.

DPT Sampling Procedures

The subsurface soil sampling procedures will be as follows:

A total of 23 soil borings will be advanced using Direct Push Technology (DPT) drilling methods. The drilling apparatus will use Macro-Core® samplers fitted with detachable aluminum or steel drive points or dual tube technology. The specific equipment used will be determined based on field conditions.

Soil cores will be collected using a 1.5-inch inside diameter (ID) acetate sleeve in 2-foot lengths. Additional borings may be required to collect sufficient soil sample volumes. Soils will be logged to provide a complete lithologic record of the subsurface materials and described according to the Unified Soil Classification System. As each acetate sleeve is opened, the soils will be screened for organic vapors using a PID. The breathing zone of the field personnel will be periodically monitored for organic vapors, in accordance with the site-specific Health and Safety Plan.

A log of each borehole will be maintained by the field geologist to describe lithologies encountered, depth of geologic contacts, water levels, sample depths, soil characteristics, PID/FID jar headspace as well as screening readings, and any other pertinent observations made during drilling. Boring logs will also include information on sample number, type, and depth; and sample interval and recovery.

Headwall Samples

Up to three samples, HW-01 through HW-03 will be collected from the piping at the headwall of the drainage ditch if sufficient sample material is available. Samples will be analyzed for VOCs, VPH/EPH, PAHs, pesticides, PCBs, and metals. If insufficient volume is available for all analyses, a sampling hierarchy will be followed: aliquots will be collected for EPH and PAH to determine if any contamination should be evaluated under the MCP or CERCLA, then VOC and VPH, then pesticides, PCBs, and then metals.

General Sample Collection Procedures

VOC and VPH soil samples will be collected as follows:

Soil samples for VOC/VPH analysis will be collected using a cut syringe or equivalent device and placed in 40-mL VOC vials with septa caps, according to the EPA SW846 Method 5035A. No additional labels will be added to the pre-weighed VOC vials received from the laboratory.

1. Label three pre-tare weighed 40-mL amber vials containing 1 gram (g) of sodium bisulfate ($NaHSO_4$) and 5 mL of reagent grade water with the sample location number and a bottle letter such as A, B, C, (for the VOC analysis); and two pre-tare weighed 40-mL amber vials containing 5 mL of methanol with the sample location number and the letters D and E (for VOC and/or VPH analyses). Some laboratories will send VOC vials with 10 or 15 ml methanol. The ratio of soil to methanol must be 1:1; consequently, if the vials contain 5 ml of methanol, the soil aliquot must be approximately 5 g, if vials contain 10 ml of methanol, a 10 g soil aliquot must collected, and if VOC vials contain 15 ml of methanol, 15 g of soil must be collected.

2. Collect approximately 5 grams (g) of material by coring or stabbing the soil or sediment with a 10 milliliter (mL) pre-cut syringe. Extrude the sample into one of the 40 mL VOC vials containing $NaHSO_4$ and 5 ml of reagent grade water or 5 ml of methanol. The soil must be immersed in the water or methanol; recollect the sample using a smaller volume if necessary. Avoid touching the threads on the vial's neck or loss of water or methanol by evaporation. Cap the vial and invert it several times to mix the sample. Repeat this sample collection step for all five of the VOC vials as needed to collect the required mass of soil. Approximately 5 g of soil should be collected in the vial containing $NaHSO_4$ and 5 ml of reagent-grade water; 10 g of soil should be collected in the vial containing 10 ml of methanol. **If NAPL is noted within the soils then a reduced volume of approximately 1 to 2 g should be collected in the vial containing methanol as a separate "medium concentration" (NAPL) sample.**

3. Weigh each sample vial to the nearest 0.01 g and record the weight in the field log sheet. Pack and ship the preserved samples to the laboratory several times per week. Include the field log sheet containing the sample weight information with the samples.

<u>Each VOC/VPH soil sample will include a separate aliquot to be used for percent moisture analysis</u>. The percent moisture sample will be collected by filling one 2 oz container with sample representing the same location where the 40 mL VOC/VPH vial sample was collected. Every effort will be made to obtain the percent moisture soil aliquot as close as possible to the location where the VOC/VPH sample aliquots were collected.

The following procedures will be used to collect soil samples for laboratory analyses of EPH, PAHs, PCBs, pesticides, and metals. Collection of soil samples for these parameters will be performed after the aliquots for jar headspace screening, VOC/VPH, and percent moisture have been collected.

1. Label appropriate sample jars with the sample location number, sampler's name, date, and analytical fractions.

2. Transfer the soil from the plastic liner sleeve into a decontaminated stainless-steel bowl using sterile spatulas/scoops or decontaminated stainless steel trowels, and homogenize the sample.

3. Remove any large particles such as gravel or artificial fill too large to be sent for analysis. Note the removal of material on the boring log.

4. Fill the appropriate sample containers.

5. For field duplicate samples, after homogenization fill one set of sample containers for the original sample and fill another set of sample containers for the field duplicate sample on an analyte by analyte basis.

6. Ensure that the samples are properly labeled, maintained in coolers with ice, and that chain-of-custody procedures (described in Section 4.0) are followed. Package and ship the sample coolers to the appropriate laboratory for overnight delivery.

Care should be taken in handling all soil samples to ensure that the exteriors of the sample containers are clean and free of soils before shipping. The laboratory analytical samples will be kept on ice in matrix-specific coolers and will be shipped with appropriate QA/QC samples, as described in Section 3.3.3.

The following tables have been added to cover the subsurface soil sampling: Table 3-1A presents a summary of the proposed sampling stations and associated laboratory analyses to be performed for the subsurface soil samples. Table 3-2A lists the analytical methods to be used for the subsurface soil samples. Table 3-3A presents the summary of field and laboratory quality control samples. The types of sample containers, preservatives, and holding times are presented in Table 3-4A.

QA/QC samples will also be collected as part of the soil investigation, including field duplicates, trip blanks for VOC and VPH, rinsate blanks, field blanks, and laboratory QC samples. QA/QC samples are described in Section 3.4, and Table 3-3A presents the quality control sample summary. The types of

sample containers, preservatives, and holding times for each analytical group are presented in Table 3-4A.

All soil samples will be identified in accordance with the sample location identification system presented in Section 3.3.2 of the QAPP. Soil samples will be handled and delivered in accordance with the chain-of-custody procedures detailed in Section 3.3.3 of the QAPP. All pertinent sampling data will be recorded on appropriate sample log sheets (Appendix B) and in the site logbook. Any field deviations shall be recorded on a Field Modification Record.

3.1.3 Sampling to Confirm that Surface Water is Not a Medium of Concern

This section is not applicable to this QAPP Addendum 1.

3.1.4 Synoptic Water Level Round

This section is not applicable to this QAPP Addendum 1.

3.1.5 Staff Gauge and Piezometer Installation

This section is not applicable to this QAPP Addendum 1.

3.1.6 Site Inspection

This section does not change for this QAPP Addendum 1.

3.1.7 Land Surveying

This section does not change for this QAPP Addendum 1.

3.1.8 Calibration Procedures

This section does not change for this QAPP Addendum 1.

3.1.9 Preventative Maintenance

This section does not change for this QAPP Addendum 1.

3.1.10 Decontamination Procedures

No changes were made to the QAPP regarding decontamination of non-disposable sampling equipment. The following discussion of drilling equipment has been added.

Equipment used by the drilling subcontractor will be decontaminated prior to use at the Site, between work locations, and prior to leaving the Site. Decontamination of equipment will be performed using a pressure washer or a steam cleaner. Small non-disposable equipment may be decontaminated manually at each location if pressure-washing or steam cleaning is not practical and equipment is not visually impacted by contamination. The drilling subcontractor will be responsible for designing and locating the decontamination pad that will be used to decontaminate their equipment.

The drilling specification will require the drilling subcontractor to have sufficient downhole equipment available so as not to impede progress of work.

3.1.11 Investigation Derived Waste Management

This section does not change for this QAPP Addendum 1.

3.1.12 Standard Operating Procedures

The following SOP has been added and is included in Appendix A along with other pertinent SOPs:

SOP	DESCRIPTION
SA-2.5	Direct Push Technology

The additional paperwork associated with this task (boring logs) is provided in Appendix B along with other pertinent field forms.

3.2 ANALYTICAL TASKS

Chemical analyses will be performed by Katahdin Analytical Services (KAS) which has DOD ELAP accreditation for each method required and is also certified by the state of Massachusetts.

The analyses will be performed in accordance with the method listed on Table 3-2A and the requirements of the technical specification for laboratory services developed for this work. KAS-specific SOPs are included in Appendix C.

PQLs for subsurface soil samples are specified in Table 2-4A. Subsurface soil samples will be analyzed for VOCs, PAHs, EPH, VPH, Pesticides, PCBs, and metals. This QAPP Addendum does not include sampling for the other media covered in the PDI QAPP. KAS-specific quality control details for the analytes are included in Table 3-6A.

3.3 SAMPLE COLLECTION, DOCUMENTATION, HANDLING, TRACKING, AND CUSTODY PROCEDURES

Additions or other changes to sampling collection, documentation, handling, tracking, and custody procedures are detailed in the subsections below.

3.3.1 Sample Collection Documentation

This section does not change for this QAPP Addendum 1.

3.3.2 Sample Designation and Tracking System

Sample designations for subsurface soil borings will follow the system outlined in the QAPP, with the addition of a depth identifier. The medium identifier for subsurface soil borings will be “SB” and for headwall piping samples will be “HW.” The alpha-numeric coding for the samples will be as follows:

AAA	-	AA	- (AAANNN)	-	(NNNN)
(Site ID)	-	(Medium)	- (Location)	-	(depth)

For example, a soil sample collected from the SB-06 sample location at a depth of 10 to 12 feet will be labeled STP-SB-06-1012. The sample collected from the HW-01 location, if the pipe is at a depth of 3.5 feet, will be labeled STP-HW-01-03.50

Location identifiers for soil borings will start with 05 (i.e. STP-SB-05-0110) because SB-01 through SB-04 have been used previously.

Quality control sample designation will be the same as detailed in the PDI QAPP.

3.3.3 Sample Handling and Chain-of-Custody Procedures

This section does not change for this QAPP Addendum 1.

3.4 QUALITY CONTROL SAMPLES

The following is an addition for this QAPP Addendum 1:

Trip blanks Trip blanks are used for VOC and VPH to assess the potential for sample contamination due to contaminant migration during sample shipment and storage. Trip blanks will consist of two vials containing 1 g NaHSO4 in 5 mL of volatile-free deionized water and one vial containing 5 mL of methanol. The vials will remain in the shipping container from the time the sampling kit leaves the laboratory until it is received back from the field. Trip blanks will be required at a frequency of one set per cooler in which VOC or VPH samples are shipped.

3.5 DATA MANAGEMENT TASKS

No changes were made to Section 3.5 in this QAPP Addendum 1.

3.5.1 Field Documentation

This section does not change for this QAPP Addendum 1.

3.5.2 Fixed Laboratory Data Package Deliverables

This section does not change for this QAPP Addendum 1.

3.5.3 Data Reporting Formats

This section does not change for this QAPP Addendum 1.

3.5.4 Data Handling and Management

This section does not change for this QAPP Addendum 1.

3.5.5 Data Tracking and Control

This section does not change for this QAPP Addendum 1.

4.0 ASSESSMENT AND OVERSIGHT

4.1 PERFORMANCE OF SYSTEM AUDITS

No changes to this section were required for QAPP Addendum 1.

4.2 INTERNAL QUALITY CONTROL

No changes to this section were required for QAPP Addendum 1.

4.3 CORRECTIVE ACTION

No changes to this section were required for QAPP Addendum 1.

4.4 PROJECT REPORT

Issues identified during the assessment and oversight activities described above as well as any corrective action affecting the planned data collection activities will be documented in the project report for the activities covered in this QAPP Addendum 1. The project report will also summarize all field activities; document any modifications to the QAPP Addendum 1; and present the results of the investigation, data review (Section 5.0), and data evaluation. The report will recommend changes to the regulatory process (e.g. CERCLA or MCP), as appropriate, based on the evaluation of the data. Site observations will be documented and figures developed showing locations of monitoring wells, samples, and site features, etc. All new data will be evaluated and presented in summary tables. All subcontractor reports (e.g. analytical lab results) will be included as appendices. The report will follow a format similar to the PDI report and will have the same review process. No other changes to this section were required for QAPP Addendum 1.

5.0 DATA REVIEW ELEMENTS

5.1 DATA VERIFICATION

No changes to this section were required for QAPP Addendum 1.

5.2 DATA VALIDATION

The laboratory VOC, VPH, EPH, and PAH data will be reviewed by Tetra Tech staff using the method specific criteria described in Table 5-1 and Region I EPA-NE Data Validation Functional Guidelines for Evaluating Environmental Analyses, Part II, December 1996 (U.S. EPA, 1996) will be applied using these criteria.

The laboratory pesticide and PCB data will be reviewed by Tetra Tech staff using the method specific criteria described in Table 5-1 and Region I EPA-NE Data Validation Functional Guidelines for Evaluating Environmental Analyses, Part III, February 2004 (U.S. EPA, 2004) will be applied using these criteria.

The laboratory metals data will be reviewed by Tetra Tech staff using the method specific criteria described in Table 5-1 and Region I EPA-NE Data Validation Functional Guidelines for Evaluating Environmental Analyses, Part IV, November 2008 (U.S. EPA, 2008) will be applied using these criteria.

See Table 5-1 for a data validation summary. No other changes to this section are required for this QAPP Addendum 1.

5.3 DATA USABILITY ASSESSMENT

The following is added to the existing description of the data usability assessment.

The field report will discuss the overall precision, accuracy/bias, representativeness, comparability, completeness and sensitivity for each type of samples collected and also for each type of analysis performed, and for the levels of contamination detected and quantitated by the laboratory. The report will describe data use limitations of project data if criteria for the data quality indicators were not met. The field report content and deliverables are described in Section 4.4.

TABLES

TABLE 2-1A
QAPP ADDENDUM 1

KEY PROJECT PERSONNEL
FORMER SEWAGE TREATMENT PLANT SITE
NAS SOUTH WEYMOUTH, WEYMOUTH, MASSACHUSETTS

Name	Title	Affiliation	Location	Phone	E-Mail
U. S. Navy Project Personnel					
Mr. Brian Helland	Remedial Project Manager	BRAC PMO Northeast	Philadelphia, PA	(215) 897-4912	brian.helland@navy.mil
Mr. David Barney	BRAC Environmental Coordinator	BRAC PMO Northeast	NAS South Weymouth, MA	(617) 753-4656	david.a.barney@navy.mil
TtNUS, Inc. Project Personnel					
Ms. Phoebe Call	Project Manager	Tetra Tech NUS, Inc.	Wilmington, MA	(978) 474-8403	phoebe.call@tetratech.com
Ms. Lucy Guzman	Project Chemist	Tetra Tech NUS, Inc.	Wilmington, MA	(978) 474-8416	lucy.guzman@tetratech.com
Ms. Jennifer Lambert	Task Manager/ Hydrogeologist	Tetra Tech NUS, Inc.	King of Prussia, PA	(610) 382-3779	jennifer.lambert@tetratech.com
Ms. Kayleen Jalkut	Field Operations Leader	Tetra Tech NUS, Inc.	Wilmington, MA	(978) 474-8417	kayleen.jalkut@tetratech.com
TtNUS, Inc. Program Personnel					
Mr. John Trepanowski, P.E.	CLEAN Program Manager	Tetra Tech NUS, Inc.	King of Prussia, PA	(610) 382-1532	john.trepanowski@tetratech.com
Mr. Garth Glenn	CLEAN Deputy Program Manager	Tetra Tech NUS, Inc.	Norfolk, VA	(757) 461-3926	garth.glenn@tetratech.com
Mr. Tom Johnston, PhD	CLEAN QA Manager	Tetra Tech NUS, Inc.	Pittsburgh, PA	(412) 921-8615	tom.johnston@tetratech.com
Mr. Matt Soltis	CLEAN Health and Safety Manager	Tetra Tech NUS, Inc.	Pittsburgh, PA	(412)921-8912	matt.soltis@tetratech.com

TABLE 2-2A
QAPP ADDENDUM 1

PROJECT SCOPING SESSION
FORMER SEWAGE TREATMENT PLANT SITE
NAS SOUTH WEYMOUTH, WEYMOUTH, MASSACHUSETTS

Project Name: PRE-DESIGN INVESTIGATION WP/QAPP, Addendum 1 **Projected Date(s) of Sampling:** TBD **Project Manager:** Phoebe Call	**Site Name:** Former Sewage Treatment Plant **Site Location:** NAS S. Weymouth, Weymouth, MA
Date of Session: December 9, 2009 **Scoping Session Purpose:** Discuss overall requirements	

Name	Title	Affiliation	Phone #	E-mail Address	Project Role
Phoebe Call	Project Manager	Tetra Tech	978.474.8403	phoebe.call@tetratech.com	Project Manager
Jennifer Lambert	Task Manager	Tetra Tech	610.382.3779	jennifer.lambert@tetratech.com	Work Plan Developer
Brian Helland	Remedial Project Manager	BRAC PMO Northeast	215.897.4912	brian.helland@navy.mil	Remedial Project Manager
David Barney	BRAC Environmental Coordinator	BRAC PMO Northeast	617.753.4656	david.a.barney@navy.mil	BRAC Environmental Coordinator

Comments/Decisions:

- Identified additional resources to assist with QAPP development: 1992 Chlorine Cylinder removal report, additional data from Tetra Tech EC (TtEC) removal action. TtEC will provide spatial data (test pit coordinates, structure basemap) and analytical data as they becomes available.
- Data quality should be sufficient to use for risk assessments if needed.
- Comprehensive sample analysis will be used to rule out contaminants and focus on areas to be delineated. May need to revise the ROD if additional contaminants are found.

Action Items:

- TtNUS will develop a budget and scope of work for work plan development, fieldwork, and a field report.
- May need access for locations on the east side of the access road to STP.

TABLE 2-4A
QAPP ADDENDUM 1

SUBSURFACE SOIL FIXED LABORATORY PARAMETERS
FORMER SEWAGE TREATMENT PLANT SITE
NAS SOUTH WEYMOUTH, WEYMOUTH, MASSACHUSETTS

Chemical	Method	Site PRG[1] (mg/kg)	EPA RSL, Residential Soil[2, 3, 4] (mg/kg)	MCP S-1 Soil & GW-1[3, 5] (mg/kg)	Project[6] Action Level (mg/kg)	Project Action Level Basis[7]	LOQ Goal[8] (mg/kg)
VOCs							
1,1,1-Trichloroethane	SW846 8260B	--	870	30	30	S-1/GW-1	10
1,1,2,2-Tetrachloroethane	SW846 8260B	--	0.56	0.005	0.005	S-1/GW-1	0.002 [9]
1,1,2-Trichloroethane	SW846 8260B	--	1.1	0.1	0.1	S-1/GW-1	0.033
1,1-Dichloroethane	SW846 8260B	--	3.3	0.4	0.4	S-1/GW-1	0.13
1,1-Dichloroethene	SW846 8260B	--	24	3	3	S-1/GW-1	1
1,2,4-Trichlorobenzene	SW846 8260B	--	6.2	2	2	S-1/GW-1	0.66
1,2-Dichlorobenzene	SW846 8260B	--	190	9	9	S-1/GW-1	3
1,2-Dichloroethane	SW846 8260B	--	0.43	0.1	0.1	S-1/GW-1	0.033
1,2-Dichloropropane	SW846 8260B	--	0.89	0.1	0.1	S-1/GW-1	0.033
1,3-Dichlorobenzene	SW846 8260B	--	--	1	1	S-1/GW-1	0.33
1,4-Dichlorobenzene	SW846 8260B	--	2.4	0.7	0.7	S-1/GW-1	0.24
2-Butanone (MEK)	SW846 8260B	--	2800	4	4	S-1/GW-1	1.33
2-Hexanone	SW846 8260B	--	21	--	21	RSL	7
4-Methyl-2-pentanone (MIBK)	SW846 8260B	--	530	0.4	0.4	S-1/GW-1	0.13
Acetone	SW846 8260B	--	6100	6	6	S-1/GW-1	2
Benzene	SW846 8260B	--	1.1	2	1.1	RSL	0.36
Bromodichloromethane	SW846 8260B	--	0.27	0.1	0.1	S-1/GW-1	0.03
Bromoform	SW846 8260B	--	61	0.1	0.1	S-1/GW-1	0.03
Bromomethane	SW846 8260B	--	0.73	0.5	0.5	S-1/GW-1	0.16
Carbon disulfide	SW846 8260B	--	82	--	82	RSL	27.3
Carbon tetrachloride	SW846 8260B	--	0.61	10	0.61	RSL	0.21
Chlorobenzene	SW846 8260B	--	29	1	1	S-1/GW-1	0.3
Chloroethane	SW846 8260B	--	1500	--	1500	RSL	500
Chloroform	SW846 8260B	--	0.29	0.4	0.29	RSL	0.1
Chloromethane	SW846 8260B	--	12	--	12	RSL	4
cis-1,2-Dichloroethene	SW846 8260B	--	78	0.3	0.3	S-1/GW-1	0.1
cis-1,3-Dichloropropene	SW846 8260B	--	1.7	0.01	0.01	S-1/GW-1	0.004 [9]
Cyclohexane	SW846 8260B	--	700	--	700	RSL	233.33
Dibromochloromethane	SW846 8260B	--	0.68	0.005	0.005	S-1/GW-1	0.002 [9]
Dichlorodifluoromethane	SW846 8260B	--	18	--	18	RSL	6
Ethylbenzene	SW846 8260B	--	5.4	40	5.4	RSL	1.8
Isopropylbenzene	SW846 8260B	--	210	--	210	RSL	70
Methyl acetate	SW846 8260B	--	7800	--	7800	RSL	2600
Methylcyclohexane	SW846 8260B	--	--	--	--	--	--
Methylene chloride	SW846 8260B	--	11	0.1	0.1	S-1/GW-1	0.03
Methyl-tert-butyl ether	SW846 8260B	--	43	0.1	0.1	S-1/GW-1	0.03
Styrene	SW846 8260B	--	630	3	3	S-1/GW-1	1
Tetrachloroethene	SW846 8260B	--	0.55	1	0.55	RSL	0.18
Toluene	SW846 8260B	--	500	30	30	S-1/GW-1	10
trans-1,2-Dichloroethene	SW846 8260B	--	15	1	1	S-1/GW-1	0.33
trans-1,3-Dichloropropene	SW846 8260B	--	1.7	0.01	0.01	S-1/GW-1	0.004 [9]
Trichloroethene	SW846 8260B	--	2.8	0.3	0.3	S-1/GW-1	0.1
Trichlorofluoromethane	SW846 8260B	--	79	--	79	RSL	26
Vinyl chloride	SW846 8260B	--	0.06	0.6	0.06	RSL	0.02
Xylenes (total)	SW846 8260B	--	63	400	63	RSL	21

TABLE 2-4A
QAPP ADDENDUM 1

SUBSURFACE SOIL FIXED LABORATORY PARAMETERS
FORMER SEWAGE TREATMENT PLANT SITE
NAS SOUTH WEYMOUTH, WEYMOUTH, MASSACHUSETTS

Chemical	Method	Site PRG[1] (mg/kg)	EPA RSL, Residential Soil[2, 3, 4] (mg/kg)	MCP S-1 Soil & GW-1[3, 5] (mg/kg)	Project[6] Action Level (mg/kg)	Project Action Level Basis[7]	LOQ Goal[8] (mg/kg)
PAHs							
2-Methylnaphthalene	SW846 8270D SIM	--	31	0.7	0.7	S-1/GW-1	0.24
Acenaphthene	SW846 8270D SIM	--	340	4	4	S-1/GW-1	1.32
Acenaphthylene	SW846 8270D SIM	--	340	1	1	S-1/GW-1	0.33
Anthracene	SW846 8270D SIM	--	1700	1000	1000	S-1/GW-1	334
Benzo(a)anthracene*	SW846 8270D SIM	14.5	0.15	7	0.15	RSL	0.05
Benzo(a)pyrene*	SW846 8270D SIM	1.829	0.015	2	0.015	RSL	0.005 [10]
Benzo(b)fluoranthene*	SW846 8270D SIM	14.5	0.15	7	0.15	RSL	0.05
Benzo(g,h,i)perylene	SW846 8270D SIM	--	170	1000	170	RSL	57
Benzo(k)fluoranthene	SW846 8270D SIM	--	1.5	70	1.5	RSL	0.5
Chrysene	SW846 8270D SIM	--	15	70	15	RSL	5
Dibenzo(a,h)anthracene	SW846 8270D SIM	--	0.015	0.7	0.015	RSL	0.005 [10]
Fluoranthene	SW846 8270D SIM	--	230	1000	230	RSL	77
Fluorene	SW846 8270D SIM	--	230	1000	230	RSL	77
Indeno(1,2,3-cd)pyrene	SW846 8270D SIM		0.15	7	0.15	RSL	0.05
Naphthalene	SW846 8270D SIM	--	3.6	4	3.6	RSL	1.2
Phenanthrene	SW846 8270D SIM	--	170	10	10	S-1/GW-1	3.33
Pyrene	SW846 8270D SIM	--	170	1000	170	RSL	57
Metals							
Aluminum	SW846 6020A	--	7700	--	7700	RSL	2567
Antimony	SW846 6020A	--	3.1	20	3.1	RSL	1
Arsenic*	SW846 6020A	9.08	0.39	20	0.39	RSL	0.13 [11]
Barium	SW846 6020A	--	1500	1000	1000	S-1/GW-1	330
Beryllium	SW846 6020A	--	16	100	16	RSL	5.3
Cadmium	SW846 6020A	--	7	2	2	S-1/GW-1	0.67
Calcium	SW846 6020A	--	--	--	--	--	--
Chromium (total)	SW846 6020A	--	0.29	30	0.29	RSL	0.097 [10]
Cobalt	SW846 6020A	--	2.3	--	2.3	RSL	0.77
Copper	SW846 6020A	--	310	--	310	RSL	100
Iron	SW846 6020A	--	5500	--	5500	RSL	1800
Lead	SW846 6020A	--	400	300	300	S-1/GW-1	100
Magnesium	SW846 6020A	--	--	--	--	--	--
Manganese	SW846 6020A	--	180	--	180	RSL	60
Mercury	SW846 7471B	--	2.3	20	2.3	RSL	0.77
Nickel	SW846 6020A	--	150	20	20	S-1/GW-1	6.7
Potassium	SW846 6020A	--	--	--	--	--	--
Selenium	SW846 6020A	--	39	400	39	RSL	13
Silver	SW846 6020A	--	39	100	39	RSL	13
Sodium	SW846 6020A	--	--	--	--	--	--
Thallium	SW846 6020A	--	--	8	8	S-1/GW-1	2.7
Vanadium	SW846 6020A	--	39	600	39	RSL	13
Zinc	SW846 6020A	--	2300	2500	2300	RSL	770
Pesticides							
4,4' DDE	SW846 8081B	--	2	3	2	RSL	0.67
4,4'-DDD	SW846 8081B	--	1.4	4	1.4	RSL	0.47
4,4'-DDT*	SW846 8081B	2.8	1.7	3	1.7	RSL	0.57
Aldrin	SW846 8081B	--	0.029	0.04	0.029	RSL	0.0097

TABLE 2-4A
QAPP ADDENDUM 1

SUBSURFACE SOIL FIXED LABORATORY PARAMETERS
FORMER SEWAGE TREATMENT PLANT SITE
NAS SOUTH WEYMOUTH, WEYMOUTH, MASSACHUSETTS

Chemical	Method	Site PRG[1] (mg/kg)	EPA RSL, Residential Soil[2, 3, 4] (mg/kg)	MCP S-1 Soil & GW-1[3, 5] (mg/kg)	Project[6] Action Level (mg/kg)	Project Action Level Basis[7]	LOQ Goal[8] (mg/kg)
alpha-BHC	SW846 8081B	--	0.077	--	0.077	RSL	0.026
alpha-Chlordane	SW846 8081B	--	1.6	0.7	0.7	S-1/GW-1	0.23
Beta-BHC	SW846 8081B	--	0.27	--	0.27	RSL	0.09
delta-BHC	SW846 8081B	--	0.077	--	0.077	RSL	0.026
Dieldrin*	SW846 8081B	0.876	0.03	0.05	0.03	RSL	0.01
Endosulfan I	SW846 8081B	--	37	0.5	0.5	S-1/GW-1	0.17
Endosulfan II	SW846 8081B	--	37	0.5	0.5	S-1/GW-1	0.17
Endosulfan sulfate	SW846 8081B	--	37	0.5	0.5	S-1/GW-1	0.17
Endrin	SW846 8081B	--	1.8	8	1.8	RSL	0.6
Endrin aldehyde	SW846 8081B	--	1.8	8	1.8	RSL	0.6
Endrin ketone	SW846 8081B	--	1.8	8	1.8	RSL	0.6
gamma-BHC (Lindane)	SW846 8081B	--	0.52	0.003	0.003	S-1/GW-1	0.001 [9]
gamma-Chlordane	SW846 8081B	--	1.6	0.7	0.7	S-1/GW-1	0.23
Heptachlor	SW846 8081B	--	0.11	0.2	0.11	RSL	0.037
Heptachlor epoxide	SW846 8081B	--	0.053	0.09	0.053	RSL	0.018
Methoxychlor	SW846 8081B	--	31	200	31	RSL	10
Toxaphene	SW846 8081B	--	0.44	--	0.44	RSL	0.15
PCBs							
Aroclor-1016	SW846 8082A	--	0.39	--	0.39	RSL	0.13
Aroclor-1221	SW846 8082A	--	0.14	--	0.14	RSL	0.047
Aroclor-1232	SW846 8082A	--	0.14	--	0.14	RSL	0.047
Aroclor-1242	SW846 8082A	--	0.22	--	0.22	RSL	0.073
Aroclor-1248	SW846 8082A	--	0.22	--	0.22	RSL	0.073
Aroclor-1254	SW846 8082A	--	0.11	--	0.11	RSL	0.037
Aroclor-1260	SW846 8082A	--	0.22	--	0.22	RSL	0.073
Total Polychlorinated Biphenyls	SW846 8082A	--	0.22	2	0.22	RSL	0.073 [9]
VPH							
C5-C8 Aliphatic Hydrocarbons	MADEP VPH	--	--	100	100	S-1/GW-1	33
C9-C10 Aromatic Hydrocarbons	MADEP VPH	--	--	100	100	S-1/GW-1	33
C9-C12 Aliphatic Hydrocarbons	MADEP VPH	--	--	1000	1000	S-1/GW-1	330
EPH							
C11-C22 Aromatic Hydrocarbons	MADEP EPH	--	--	1000	1000	S-1/GW-1	330
C19-C36 Aliphatic Hydrocarbons	MADEP EPH	--	--	3000	3000	S-1/GW-1	1000
C9-C18 Aliphatic Hydrocarbons	MADEP EPH	--	--	1000	1000	S-1/GW-1	330
TEPH (Unfractionated) Fingerprint Analysis	MADEP EPH	--	--	--	--	NA	NA

NOTES:

1. Site PRGs are the PRGs selected in the Record of Decision (U.S. Navy, 2008).
2. EPA Regions 3, 6, and 9 Regional Screening Levels (RSLs) for Chemical Contaminants at Superfund Sites – Residential Soil values (May, 2010) (EPA, 2010). One-tenth RSLs are presented for the non-carcinogenic RSLs to correspond to a hazard quotient of 0.1. The carcinogenic RSL values presented correspond to a cancer risk level of 10^{-6}.
3. The following notes apply to the values for the chemicals specified:
   cis- and trans-1,3-Dichloropropene - Value is for 1,3-dichloropropene.
   alpha- and gamma-Chlordane - Value is for chlordane.
   delta-BHC - Value is for alpha-BHC.
4. The following notes apply to the values for the chemicals specified:
   Acenaphthylene - Value is for acenapththene.

TABLE 2-4A
QAPP ADDENDUM 1

SUBSURFACE SOIL FIXED LABORATORY PARAMETERS
FORMER SEWAGE TREATMENT PLANT SITE
NAS SOUTH WEYMOUTH, WEYMOUTH, MASSACHUSETTS

Chemical	Method	Site PRG(1) (mg/kg)	EPA RSL, Residential Soil(2, 3, 4) (mg/kg)	MCP S-1 Soil & GW-1(3, 5) (mg/kg)	Project(6) Action Level (mg/kg)	Project Action Level Basis(7)	LOQ Goal(8) (mg/kg)

Benzo(g,h,i)perylene - Value is for pyrene.
Phenanthrene - Value is for pyrene.
PCBs - Value is for high-risk PCBs.
1,2,4-Trichlorobenzene and Aroclor-1254 - one tenth the Residential Soil noncarcinogenic value is less than the carcinogenic value; therefore, one-tenth the non-carcinogenic value is presented.

5. Massachusetts Contingency Plan, 310 CMR 40, Table 2: MCP Method 1 Soil Category S-1 Standards, available at http://www.mass.gov/dep/cleanup/laws/0975_6a.htm (values as of 10/13/10).
6. Project Action Level (PAL) is the lowest of the Site PRG, the EPA RSL, the MCP S-1 Soil & GW-2 standard, and the MCP S-1 Soil & GW-3 standard.
7. Basis abbreviations: RSL - EPA RSL, Residential Soil value; S-1/GW-1 - MCP S-1 Soil & GW-2 standard; S-1/GW-1 - MCP S-1 Soil & GW-3 standard.
8. The LOQ Goal is set at one-third the concentration of the PAL.
9. LOQ exceeds Goal but does not exceed Project Action Level.
10. LOQ exceeds Goal and PAL, but LOD does not exceed Project Action Level.
11. LOQ exceeds Goal, and LOQ and LOD exceed PAL.

ABBREVIATIONS:

-- Not Available
mg/kg - milligrams per kilogram
LOQ - Limit of Quantitation
PAL - Project Action Limit
PRG - Preliminary Remediation Guideline
RSL - Regional Screening Level
SIM - Selected Ion Monitoring
NA - not applicable

Method References:

- SW846 - Test Methods for Evaluating Solid Wastes. EPA Office of Solid Waste. Third Edition, including all promulgated revisions.

TABLE 2-8
ADDENDUM 1

MEASUREMENT PERFORMANCE CRITERIA
FIELD QC SAMPLES
FORMER SEWAGE TREATMENT PLANT SITE
NAS SOUTH WEYMOUTH, WEYMOUTH, MASSACHUSETTS

QC Sample	Analytical Group	Frequency	Data Quality Indicators (DQIs)	Measurement Performance Criteria (MPC)	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
Rinsate Blank	VOCS, PAHS, Pesticide, PCBs, Metals, VPHs, and EPHs	One per 20 field samples	Accuracy/Bias/ Contamination	No target analytes ≥ ½ QL (>QL for common laboratory contaminants), unless target analytes in field samples are > 10x those in rinsate blank.	S & A
Field Duplicates	VOCS, PAHS, Pesticide, PCBs, VPHs, and EPHs	One per 10 field samples	Precision	Relative percent difference (RPD) ≤ 50%. If sample results are < 2x QL, professional judgment is used.	S & A
	Metals	One per 10 field samples	Precision	Values ≥ 5x QL: RPD ≤ 50%. Values < 5x QL: Absolute Difference ≤ 4x QL.	S & A
Temperature Indicator	VOCS, PAHS, Pesticide, PCBs, Metals, VPHs, and EPHs	One per cooler	Representativeness	Temperature between 2 and 6 degrees Celsius (4 ± 2 °C).	S
All samples	VOCS, PAHS, Pesticide, PCBs, Metals, VPHs, and EPHs	All samples	Sensitivity	MDL and QL < PSLs listed in Worksheet #15a.	A
All samples	VOCS, PAHS, Pesticide, PCBs, Metals, VPHs, and EPHs	All samples	Data Completeness	95% overall.	S & A

Note: The MPCs for Katahdin Analytical Services laboratory QC samples are presented in Table 3-6.

TABLE 3-1A
QAPP ADDENDUM 1

SUMMARY OF LABORATORY ANALYSES BY MEDIA
FORMER SEWAGE TREATMENT PLANT SITE
NAS SOUTH WEYMOUTH, WEYMOUTH, MASSACHUSETTS

Sample Matrix	Sample Location[1]	BOTH INTERVALS PER BORING				ONE INTERVAL PER BORING		
		Organics				Organics		Inorganics
		EPH[2]	PAHs	VPH	VOCs	PCBs	Pesticides	Metals
Subsurface Soil	STP-SB-05	x	x	x	x	x	x	x
	STP-SB-06	x	x	x	x	x	x	x
	STP-SB-07	x	x	x	x	x	x	x
	STP-SB-08	x	x	x	x	x	x	x
	STP-SB-09	x	x	x	x	x	x	x
	STP-SB-10	x	x	x	x	x	x	x
	STP-SB-11	x	x	x	x	x	x	x
	STP-SB-12	x	x	x	x	x	x	x
	STP-SB-13	x	x	x	x	x	x	x
	STP-SB-14	x	x	x	x	x	x	x
	STP-SB-15	x	x	x	x	x	x	x
	STP-SB-16	x	x	x	x	x	x	x
	STP-SB-17	x	x	x	x	x	x	x
	STP-SB-18	x	x	x	x	x	x	x
	STP-SB-19	x	x	x	x	x	x	x
	STP-SB-20	x	x	x	x	x	x	x
	STP-SB-21	x	x	x	x	x	x	x
	STP-SB-22	x	x	x	x	x	x	x
	STP-SB-23	x	x	x	x	x	x	x
	STP-SB-24	x	x	x	x	x	x	x
Sample Matrix	**Sample Location**	**EPH[2]**	**PAHs**	**VPH**	**VOCs**	**PCBs**	**Pesticides**	**Metals**
Subsurface Soil - Excavation Floor		Full-Suite Confirmation - Organics						Inorganics
	STP-SB-10	x	x	x	x	x	x	x
	STP-SB-21	x	x	x	x	x	x	x
	STP-SB-22	x	x	x	x	x	x	x
	STP-SB-25							x
	STP-SB-26							x
	STP-SB-27							x
Sample Matrix	**Sample Location**	**EPH[2]**	**PAHs**	**VPH**	**VOCs**	**PCBs**	**Pesticides**	**Metals**
Headwall Piping Material		Priority 1[3]		Priority 2[3]		Priority 3[3]		
	STP-HW-01	x	x	x	x	x	x	x
	STP-HW-02	x	x	x	x	x	x	x
	STP-HW-03	x	x	x	x	x	x	x

Notes:
1 - Up to two samples will be collected from each subsurface soil boring location.
2 - EPH analysis includes petroleum fingerprint analysis.
3 - Priority for sample collection will depend on volume of material in headwall pipe

Abbreviations:
EPH - extractable petroleum hydrocarbons
VPH - volatile petroleum hydrocarbons
VOC - volatile organic compounds
PAHs - Polycyclic aromatic hydrocarbons
PCBs - Polychlorinated biphenyls

TABLE 3-2A
QAPP ADDENDUM 1

ANALYTICAL METHODS FOR SOIL
FORMER SEWAGE TREATMENT PLANT SITE
NAS SOUTH WEYMOUTH, WEYMOUTH, MASSACHUSETTS

Matrix	Parameter	Analysis Method	Reference
Soil/ Headwall Piping Material	VOCs	SW-846 Method 8260B	SW846
	PAHs	SW-846 Method 8270D SIM	SW846
	PCBs	SW-846 Method 8082A	SW846
	Pesticides	SW-846 Method 8081B	SW846
	VPH	MassDEP Revision 1.1, 2004	MassDEP
	EPH, including petroleum fingerprint analysis	MassDEP Revision 1.1, 2004	MassDEP
	TAL Metals	SW-846 Methods 6010C/6020A/7471B	SW846

NOTES:

PAH: polycyclic aromatic hydrocarbon
PCB: polychlorinated biphenyl
VOC: volatile organic compound
EPH: extractable petroleum hydrocarbons
VPH: volatile petroleum hydrocarbons

Method References:

- SW846 – Test Methods for Evaluating Solid Wastes. U. S. EPA Office of Solid Waste. Third Edition, including all promulgated revisions.
- MassDEP - Massachusetts Department of Environmental Protection

TABLE 3-3A
QAPP ADDENDUM 1

FIELD AND FIXED LABORATORY QUALITY CONTROL SAMPLE SUMMARY
FORMER SEWAGE TREATMENT PLANT SITE
NAS SOUTH WEYMOUTH, WEYMOUTH, MASSACHUSETTS

SAMPLE TYPE	ANALYSIS	FIELD SAMPLES	Trip Blanks(1)	RINSATE (EQUIPMENT) BLANKS(2)	FIELD DUPLICATES(3)	FIELD BLANKS(4)	TOTAL FIELD and FIELD QC	LAB QC(5)
Soil	VOCs	46	3	3	5	1	58	3
	VPH	46	3	3	5	1	58	3
	PAH	46	-	3	5	1	55	3
	EPH	46	-	3	5	1	55	3
	Pesticides	26	-	2	3	1	32	2
	PCBs	26	-	2	3	1	32	2
	Metals	29	-	2	3	1	35	2

NOTES:

(1) Collect 1 trip blank per 20 samples or per cooler shipped.
(2) Collect 1 rinsate blank per 20 field samples.
(3) Collect 1 duplicate per 10 field samples.
(4) Collect 1 field blank per water source (e.g. decontamination rinse water).
(5) Collect 1 Lab QC per 20 samples - Organics - Matrix Spike and a Matrix Spike Duplicate; Inorganics - Matrix Spike and Laboratory Duplicate. The Lab QC volume is not included in the Field and Field Quality Control Sample total.

TABLE 3-4A
QAPP ADDENDUM 1

ANALYSES, SAMPLE CONTAINER, PRESERVATIVE, AND HOLDING TIME REQUIREMENTS
FORMER SEWAGE TREATMENT PLANT SITE
NAS SOUTH WEYMOUTH, WEYMOUTH, MASSACHUSETTS

Sample Medium	Analysis	Sample Container[1]	Preservative	Holding Time
Soil/ Headwall Piping Material	VOCs (low)	2-40 mL vials	1 g NaHSO4 in 5 ml VOC-free reagent water, cool to 4°C	14 days
	VOCs (high)	1-40 mL vial	5 ml methanol, cool to 4°C	14 days
	VPH	1-40-mL VOA vials	1-5-mL MeOH	14 days (Analyze)
	PAH /EPH	1-8 oz wide mouth jar	Cool to 4°C	14 days (Extraction) / 40 days (Analysis)
	Pesticides/PCBs	1-4 oz wide mouth jar	Cool to 4°C	Pesticides:14 days (Extraction) / 40 days (Analysis) PCBs: none
	Metals	1-8 oz wide mouth jar	Cool to 4°C	6 Months (ICP metals), 28 days (mercury)
Aqueous (Blanks)	VOCs	3-40-mL VOA vials	HCl to pH <2, Cool to 4°C	14 days (Analyze)
	VPH	3-40-mL VOA vials	HCl to pH <2, Cool to 4°C	14days (Analyze)
	PAH	2-1 Liter amber glass bottle	Cool to 4°C	7 days (Extraction) / 40 days (Analyze)
	EPH	2-1 Liter amber glass bottle	5 ml of 1:1 HCl , Cool to 4°C	7 days (Extraction) / 40 days (Analyze)
	Pesticides/PCBs	2-1 Liter amber glass bottle	Cool to 4°C	Pesticide: 7 days (Extraction) / 40 days (Analyze) PCB: none
	Metals	1-500-mL polyethylene bottle	Nitric Acid to pH <2, Cool to 4°C	6 Months (ICP metals), 28 days (mercury)

Notes:
(1) Triple volume needed for organic laboratory QC, and double volume needed for metal laboratory QC, at a rate of one per 20 field samples. Also, actual volumes and bottle requirements needed for all analyses will be verified with the selected analytical laboratory prior to initiation of sampling event.

VOC volatile organic compound
PAH: polycyclic aromatic hydrocarbon
EPH: extractable petroleum hydrocarbons
VPH: volatile petroleum hydrocarbons
PCB: polychlorinated biphenyl

TABLE 3-6
QAPP ADDENDUM 1

KATAHDIN ANALYTICAL SERVICES QC SAMPLES*
FORMER SEWAGE TREATMENT PLANT SITE
NAS SOUTH WEYMOUTH, WEYMOUTH, MASSACHUSETTS

Matrix: Soil and Aqueous Field Blanks **Analytical Group: VOCs**		**Analytical Method/SOP Reference: SW-846 8260B/ CA-202**				
QC Sample:	**Frequency/ Number**	**Method/SOP QC Acceptance Limits**	**Corrective Action**	**Person(s) Responsible for Corrective Action**	**Data Quality Indicator (DQI)**	**Measurement Performance Criteria (MPC)**
Method Blank	One per preparation batch of twenty or fewer samples of similar matrix.	No target compounds > ½ LOQ (> LOQ for common laboratory contaminants) and > 1/10 the amount measured in any sample or 1/10 the PSL, whichever is greater.	Correct the problem. Report sample results that are <LOD or >10x the blank concentration. Re-prepare and reanalyze the method blank and all associated samples with results > LOD and < 10x the contaminated blank result.	Analyst, Laboratory Department Manager, and Data Validator	Bias/ Contamination	Same as Method/SOP QC Acceptance Limits.
Surrogate	Four per sample	%R must be within the laboratory's statistically-derived QC limits.	For QC and field samples, correct problem then re-prepare 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. Contact Client if samples cannot be reanalyzed within hold time.	Analyst, Laboratory Department Manager and Data Validator	Accuracy /Bias	Same as Method/SOP QC Acceptance Limits.
Laboratory Control Sample (LCS)	One per preparation batch of twenty or fewer samples of similar matrix.	%R must be within the laboratory's statistically-derived QC limits, allowing for the number of marginal exceedances presented in the DoD Quality Systems Manual (QSM) Version 4.1, Table G-1.	Correct problem, then re-prepare and reanalyze the LCS and all samples in the associated preparatory batch for failed analytes, if sufficient sample material is available. Contact Client if samples cannot be reanalyzed within hold time.	Analyst, Laboratory Department Manager, and Data Validator	Accuracy/ Bias	Same as Method/SOP QC Acceptance Limits.
Matrix Spike/ Matrix Spike Duplicate (MS/MSD) (not applicable for rinsate blanks)	One per sample delivery group (SDG) or every 20 samples.	%R should be within the laboratory's statistically derived QC limits. Water Precision: RPD should be ≤ 20%. Soil Precision: RPD should be ≤ 30%	Corrective actions will not be taken for samples when recoveries are outside limits if likely due to matrix, otherwise contact client.	Analyst, Laboratory Department Manager, and Data Validator	Precision/ Accuracy/ Bias	Same as Method/SOP QC Acceptance Limits.
Internal Standard	Three per sample- Pentafluorobenzene Chlorobenzene-d5 1,4-dichlorobezene-d4	Retention times for internal standards must be ± 30 seconds and the responses within -50% to +100% of the ICAL midpoint standard.	Inspect mass spectrometer or gas chromatograph for malfunctions; mandatory reanalysis of samples analyzed while system was malfunctioning.	Analyst, Laboratory Department Manager, and Data Validator	Accuracy/ Bias	Same as Method/SOP QC Acceptance Limits.

* Katahdin's statistically-derived QC limits referenced in this table refer to Katahdin's limits at the time of analysis. Katahdin's current limits are presented in Appendix C.

TABLE 3-6
QAPP ADDENDUM 1

KATAHDIN ANALYTICAL SERVICES QC SAMPLES*
FORMER SEWAGE TREATMENT PLANT SITE
NAS SOUTH WEYMOUTH, WEYMOUTH, MASSACHUSETTS

Matrix: Soil and Aqueous Field Blanks **Analytical Group: PAHs**		**Analytical Method/SOP Reference: SW-846 8270D SIM/ CA-213**				
QC Sample:	**Frequency/ Number**	**Method/SOP QC Acceptance Limits**	**Corrective Action**	**Person(s) Responsible for Corrective Action**	**Data Quality Indicator (DQI)**	**Measurement Performance Criteria (MPC)**
Method Blank	One per preparation batch of twenty or fewer samples of similar matrix.	No target compounds > ½ LOQ (> LOQ for common laboratory contaminants) and > 1/10 the amount measured in any sample or 1/10 the PSL, whichever is greater.	Correct the problem. Report sample results that are <LOD or >10x the blank concentration. Re-prepare and reanalyze the method blank and all associated samples with results > LOD and < 10x the contaminated blank result.	Analyst, Laboratory Department Manager and Data Validator	Bias/ contamination	Same as Method/SOP QC Acceptance Limits.
Surrogate	3 per sample	%R must be within the laboratory's statistically-derived QC limits.	For QC and field samples, correct problem then re-prepare 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. Contact Client if samples cannot be re-prepared within hold time.	Analyst, Laboratory Department Manager, and Data Validator	Accuracy/Bias	Same as Method/SOP QC Acceptance Limits.
LCS	One per preparation batch of twenty or fewer samples of similar matrix.	%R must be within the laboratory's statistically-derived QC limits, allowing for the number of marginal exceedances presented in DoD QSM Table G-1.	Correct problem, then re-prepare 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 F). Contact Client if samples cannot be re-prepared within hold time.	Analyst, Laboratory Department Manager, and Data Validator	Accuracy / Bias	Same as Method/SOP QC Acceptance Limits.
MS/MSD (not applicable for rinsate blanks)	One per SDG or every 20 samples.	%R should be within the laboratory's statistically-derived QC limits. Water Precision: RPD should be ≤ 30%. Soil Precision: RPD should be ≤ 50%	Corrective actions will not be taken for samples when recoveries are outside limits if likely due to matrix, otherwise contact client.	Analyst, Laboratory Department Manager, and Data Validator	Precision/ Accuracy/ Bias	Same as Method/SOP QC Acceptance Limits.

TABLE 3-6
QAPP ADDENDUM 1

KATAHDIN ANALYTICAL SERVICES QC SAMPLES*
FORMER SEWAGE TREATMENT PLANT SITE
NAS SOUTH WEYMOUTH, WEYMOUTH, MASSACHUSETTS

Matrix: Soil and Aqueous Field Blanks **Analytical Group: PAHs**		**Analytical Method/SOP Reference: SW-846 8270D SIM/ CA-213**				
QC Sample:	**Frequency/ Number**	**Method/SOP QC Acceptance Limits**	**Corrective Action**	**Person(s) Responsible for Corrective Action**	**Data Quality Indicator (DQI)**	**Measurement Performance Criteria (MPC)**
Internal Standard	Five per sample – Naphthalene-d8 Acenaphthene-d10 Phenanthrene-d10 Chrysene-d12 Perylene-d12	Retention times for internal standards must be ± 30 seconds and the responses within -50% to +100% of the ICAL midpoint.	Inspect mass spectrometer or gas chromatograph for malfunctions. Mandatory reanalysis of samples analyzed while system was malfunctioning.	Analyst, Laboratory Department Manager, and Data Validator	Accuracy/ Bias	Same as Method/SOP QC Acceptance Limits.

* Katahdin's statistically-derived QC limits referenced in this table refer to Katahdin's limits at the time of analysis. Katahdin's current limits are presented in Appendix C.

TABLE 3-6
QAPP ADDENDUM 1

KATAHDIN ANALYTICAL SERVICES QC SAMPLES*
FORMER SEWAGE TREATMENT PLANT SITE
NAS SOUTH WEYMOUTH, WEYMOUTH, MASSACHUSETTS

Matrix: Soil and Aqueous Field Blanks **Analytical Group: VPH**		**Analytical Method/SOP Reference: MADEP VPH / CA-312**				
QC Sample:	**Frequency/ Number**	**Method/SOP QC Acceptance Limits**	**Corrective Action**	**Person(s) Responsible for Corrective Action**	**Data Quality Indicator (DQI)**	**Measurement Performance Criteria (MPC)**
Method Blank	One per preparation batch of twenty or fewer samples of similar matrix.	No analytes detected > LOQ	Investigate source of contamination. Evaluate the samples and associated QC: i.e., if the blank results are above the LOQ, report samples results which are < LOQ and >10X the blank. Otherwise, re-prepare a blank and the remaining samples.	Analyst, Supervisor, QA Manager	Accuracy/Bias, Contamination	Same as Method/SOP QC Acceptance Limits.
Surrogates	2,5-Dibromotoluene	Water and soil: %R must be within 70-130%.	If the surrogate from one detector is low and outside of the acceptance limits and the surrogate from the other detector is within criteria, narrate, otherwise reanalyze; present both sets of data.	Analyst, Supervisor, QA Manager	Accuracy/Bias	Same as Method/SOP QC Acceptance Limits.
LCSLCSD	One per preparation batch of twenty or fewer samples of similar matrix.	Water and soil: %R must be within 70-130%. RPD should be ≤ 25%.	Evaluate the samples and associated QC: i.e. If an MS/MSD was performed and acceptable, narrate. If an LCS/LCSD was performed and only one of the set was unacceptable, narrate. If the surrogate recoveries in the LCS are low but are acceptable in the blank and samples, narrate. If the LCS recovery is high but the sample results are < LOQ, narrate. Otherwise, re-prepare a blank and the remaining samples.	Analyst, Supervisor, QA Manager	Accuracy/Bias	Same as Method/SOP QC Acceptance Limits.
MS/MSD (not applicable for rinsate blanks)	One per SDG or every 20 samples.	Water and soil: %R should be within 70-130%. RPD should be ≤ 50%.	Evaluate the samples and associated QC: i.e. If the LCS results are acceptable, narrate. If both the LCS and MS/MSD are unacceptable, re-prepare the samples and QC.	Analyst, Supervisor, QA Manager	Precision/ Accuracy/Bias	Same as Method/SOP QC Acceptance Limits..

* Katahdin's statistically-derived QC limits referenced in this table refer to Katahdin's limits at the time of analysis. Katahdin's current limits are presented in Appendix C.

TABLE 3-6
QAPP ADDENDUM 1

KATAHDIN ANALYTICAL SERVICES QC SAMPLES*
FORMER SEWAGE TREATMENT PLANT SITE
NAS SOUTH WEYMOUTH, WEYMOUTH, MASSACHUSETTS

Matrix: Soil and Aqueous Field Blanks **Analytical Group: EPH**		**Analytical Method/SOP Reference: MADEP EPH / CA-322**				
QC Sample:	**Frequency/ Number**	**Method/SOP QC Acceptance Limits**	**Corrective Action**	**Person(s) Responsible for Corrective Action**	**Data Quality Indicator (DQI)**	**Measurement Performance Criteria (MPC)**
Method Blank	One per preparation batch of twenty or fewer samples of similar matrix.	No analytes detected > LOQ	Investigate source of contamination. Evaluate the samples and associated QC: i.e., if the blank results are above the LOQ, report samples results which are < LOQ and >10X the blank. Otherwise, re-prepare a blank and the remaining samples.	Analyst, Supervisor, QA Manager	Accuracy/Bias, Contamination	Same as Method/SOP QC Acceptance Limits.
Surrogates	ortho-Terphenyl, 5-alpha-androstane, 2-Fluorobiphenyl, 1-Chloro octadecane 2-Bromonaphthalene	Water and soil: %R must be within 40-140% for all 5 surrogates.	If one fractionation surrogate is low and outside of the acceptance criteria and one is within the acceptance criteria, narrate, otherwise refractionate. If one aliphatic extraction surrogate is low and outside of the acceptance criteria but the other is within the acceptance critera, narrate otherwise reextract. If the aromatic extraction surrogate is outside of the acceptance limits, reextract.	Analyst, Supervisor, QA Manager	Accuracy/Bias	Same as Method/SOP QC Acceptance Limits.
LCS/LCSD	One per preparation batch of twenty or fewer samples of similar matrix.	Water and soil: %R must be within 40-140% recovery. RPD should be ≤ 25%	Evaluate the samples and associated QC: i.e. If an MS/MSD was performed and acceptable, narrate. If an LCS/LCSD was performed and only one of the set was unacceptable, narrate. If the surrogate recoveries in the LCS are low but are acceptable in the blank and samples, narrate. If the LCS recovery is high but the sample results are < LOQ, narrate. Otherwise, re-prepare a blank and the remaining samples.	Analyst, Supervisor, QA Manager	Accuracy/Bias	Same as Method/SOP QC Acceptance Limits.
MS/MSD (not applicable for rinsate blanks)	One per SDG or every 20 samples.	Water and soil: %R should be within 40-140%; RPD should be ≤ 40%	Evaluate the samples and associated QC: i.e. If the LCS is acceptable, narrate. If both the LCS and MS/MSD are unacceptable, re-prepare the samples and QC.	Analyst, Supervisor, QA Manager	Precision/ Accuracy/Bias	Same as Method/SOP QC Acceptance Limits.

* Katahdin's statistically-derived QC limits referenced in this table refer to Katahdin's limits at the time of analysis. Katahdin's current limits are presented in Appendix C.

TABLE 3-6
QAPP ADDENDUM 1

KATAHDIN ANALYTICAL SERVICES QC SAMPLES*
FORMER SEWAGE TREATMENT PLANT SITE
NAS SOUTH WEYMOUTH, WEYMOUTH, MASSACHUSETTS

Matrix: Soil and Aqueous Field Blanks **Analytical Group: Pesticides/PCBs**		**Analytical Method/SOP Reference: SW-846 8081B and 8082A/ CA-302 and CA-329**				
QC Sample:	**Frequency/ Number**	**Method/SOP QC Acceptance Limits**	**Corrective Action**	**Person(s) Responsible for Corrective Action**	**Data Quality Indicator (DQI)**	**Measurement Performance Criteria (MPC)**
Method Blank	One per preparation batch of twenty or fewer samples of similar matrix.	No target compounds > ½ LOQ and > 1/10 the amount measured in any sample or 1/10 the PSL, whichever is greater.	Correct the problem. Report sample results that are <LOD or >10x the blank concentration. Re-prepare and reanalyze the method blank and all associated samples with results > LOD and < 10x the contaminated blank result.	Analyst, Laboratory Department Manager and Data Validator	Bias/ Contamination	Same as Method/SOP QC Acceptance Limits.
Surrogates	Pesticides: Two per sample – Tetrachloro-m-xylene Decachlorobiphenyl PCBs: One per sample - Decachlorobiphenyl.	%R must be within the laboratory's statistically derived QC limits.	For QC and field samples, correct problem then re-prepare 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. Contact Client if samples cannot be re-prepared within hold time.	Analyst, Laboratory Department Manager, and Data Validator	Accuracy/Bias	Same as Method/SOP QC Acceptance Limits.
LCS	One per preparation batch of twenty or fewer samples of similar matrix.	%R must be within the laboratory's statistically-derived QC limits.	Correct problem, then re-prepare 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 F). Contact Client if samples cannot be re-prepared within hold time.	Analyst, Laboratory Department Manager, and Data Validator	Accuracy/ Bias	Same as Method/SOP QC Acceptance Limits.
MS/MSD (not applicable for rinsate blanks)	One per SDG or every 20 samples.	%R should be within the laboratory's statistically-derived QC limits. Water Precision: RPD should be ≤ 30%. Soil Precision: RPD should be ≤ 50%	Corrective actions will not be taken for samples when recoveries are outside limits if likely due to matrix, otherwise contact client.	Analyst, Laboratory Department Manager, and Data Validator	Precision/ Accuracy/ Bias	Same as Method/SOP QC Acceptance Limits.
Second Column Confirmation	All positive results must be confirmed.	RPD between primary and second column must be ≤ 40%.	No corrective action is applicable. Apply "J" flag to results and narrate.	Analyst, Laboratory Department Manager, and Data Validator	Precision	Same as Method/SOP QC Acceptance Limits.

* Katahdin's statistically-derived QC limits referenced in this table refer to Katahdin's limits at the time of analysis. Katahdin's current limits are presented in Appendix C.

TABLE 3-6
QAPP ADDENDUM 1

KATAHDIN ANALYTICAL SERVICES QC SAMPLES*
FORMER SEWAGE TREATMENT PLANT SITE
NAS SOUTH WEYMOUTH, WEYMOUTH, MASSACHUSETTS

Matrix: Soil and Aqueous Field Blanks **Analytical Group: Metals (ICP-MS)**		**Analytical Method/SOP Reference: SW846 6020A/ CA-627**				
QC Sample:	**Frequency/ Number**	**Method/SOP QC Acceptance Limits**	**Corrective Action**	**Person(s) Responsible for Corrective Action**	**Data Quality Indicator (DQI)**	**Measurement Performance Criteria (MPC)**
Method Blank	One per digestion batch of 20 or fewer samples of similar matrix.	No target metals > ½ LOQ and > 1/10 the amount measured in any sample or 1/10 the PSL, whichever is greater. For negative blanks, absolute value < LOD.	Correct the problem. Report sample results that are <LOD or >10x the blank concentration. Re-prepare and reanalyze the method blank and all associated samples with results > LOD and < 10x the contaminated blank result.	Analyst, Laboratory Department Manager and Data Validator	Bias/ Contamination	Same as Method/SOP QC Acceptance Limits.
Interference Check Sample (ICS)	Beginning of analytical run	ICS-A: Absolute value of concentration for all non-spiked analytes (except verified trace impurities) must be < LOD. ICS-AB: %R must be within 80-120%.	Terminate analysis; locate and correct problem; reanalyze ICS; reanalyze all samples.	Analyst, Laboratory Department Manager, and Data Validator	Accuracy/Bias/ Contamination	ICS-A: Absolute value of concentration for all non-spiked analytes (except verified trace impurities) must be < LOQ. ICS-AB: %R must be within 80-120%.
LCS	One per digestion batch of 20 or fewer samples of similar matrix.	Water and Soil: %R must be within 80-120%, allowing for the marginal exceedances presented in DoD QSM Table G-1.	Redigest and reanalyze all associated samples for affected analyte.	Analyst, Laboratory Department Manager, and Data Validator	Accuracy/Bias/ Contamination	Same as Method/SOP QC Acceptance Limits.
Matrix Spike (not applicable for rinsate blanks)	One per SDG or every 20 samples.	%R should be within 80-120%if sample < 4x spike added.	Flag results for affected analytes for all associated samples with "N".	Analyst, Laboratory Department Manager, and Data Validator	Accuracy/Bias	%R should be within 75-125% if sample < 4x spike added.
Post-digestion Spike (not applicable for rinsate blanks)	Project-specific frequency: When MS recovery fails or analyte concentration in all samples < 50x LOD	%R should be within 75-125%.	Run associated samples by method of standard addition or flag results.	Analyst, Laboratory Department Manager, and Data Validator	Accuracy/Bias	Same as Method/SOP QC Acceptance Limits.
Laboratory Duplicate (not applicable for rinsate blanks)	One per SDG or every 20 samples.	Project-specific criteria: If values are ≥ 5x LOQ, RPD should be ≤ 20%. If values are < 5x LOQ, Absolute Difference should be ≤ LOQ.	Flag results for affected analytes for all associated samples.	Analyst, Laboratory Department Manager, and Data Validator	Precision	Soils: If values are ≥ 5x LOQ, RPD should be ≤ 35%; if values are < 5x LOQ, Absolute Difference should be ≤ 2x LOQ.
ICP Serial	One per preparation batch	If original sample result is at	Flag results for affected			Same as Method/SOP QC Acceptance

TABLE 3-6
QAPP ADDENDUM 1

KATAHDIN ANALYTICAL SERVICES QC SAMPLES*
FORMER SEWAGE TREATMENT PLANT SITE
NAS SOUTH WEYMOUTH, WEYMOUTH, MASSACHUSETTS

Matrix: Soil and Aqueous Field Blanks **Analytical Group: Metals (ICP-MS)**		**Analytical Method/SOP Reference: SW846 6020A/ CA-627**				
QC Sample:	**Frequency/ Number**	**Method/SOP QC Acceptance Limits**	**Corrective Action**	**Person(s) Responsible for Corrective Action**	**Data Quality Indicator (DQI)**	**Measurement Performance Criteria (MPC)**
Dilution (not applicable for rinsate blanks)	of twenty or fewer samples of similar matrix.	least 50x LOQ, 5-fold dilution must agree within ± 10% of the original result.	analytes for all associated samples with "E".	Analyst, Laboratory Department Manager, and Data Validator	Accuracy/Bias	Limits.
Internal Standard	Appropriate internal standard required for all analytes in all samples. Mass of internal standard must be <50 amu different from that of analyte.	For each sample, internal standard intensity must be within 30-120% of that of initial calibration standard.	Reanalyze affected samples.	Analyst, Supervisor, QA Manager	Accuracy/Bias	For each sample, internal standard intensity must be ≥ 70% of that of initial calibration standard.

* Katahdin's statistically-derived QC limits referenced in this table refer to Katahdin's limits at the time of analysis. Katahdin's current limits are presented in Appendix C.

TABLE 3-6
QAPP ADDENDUM 1

KATAHDIN ANALYTICAL SERVICES QC SAMPLES*
FORMER SEWAGE TREATMENT PLANT SITE
NAS SOUTH WEYMOUTH, WEYMOUTH, MASSACHUSETTS

Matrix: Soil and Aqueous Field Blanks **Analytical Group: Metals (Mercury)**		**Analytical Method/SOP Reference: SW846 7470A, 7471B/ CA-611, CA-615**				
QC Sample:	**Frequency/ Number**	**Method/SOP QC Acceptance Limits**	**Corrective Action**	**Person(s) Responsible for Corrective Action**	**Data Quality Indicator (DQI)**	**Measurement Performance Criteria (MPC)**
Method Blank	One per digestion batch of 20 or fewer samples of similar matrix.	No mercury > ½ LOQ and > 1/10 the amount measured in any sample or 1/10 the PSL, whichever is greater. For negative blanks, absolute value < LOD.	Correct the problem. Report sample results that are <LOD or >10x the blank concentration. Re-prepare and reanalyze the method blank and all associated samples with results > LOD and < 10x the contaminated blank result.	Analyst, Laboratory Department Manager and Data Validator	Bias/contamination	Same as Method/SOP QC Acceptance Limits.
LCS	One per digestion batch of 20 or fewer samples of similar matrix.	Water and Soil: %R must be within 80-120%.	Re-digest and reanalyze all associated samples for affected analyte.	Analyst, Laboratory Department Manager, and Data Validator	Accuracy/Bias/ Contamination	Same as Method/SOP QC Acceptance Limits.
MS (not applicable for rinsate blanks)	One per sample delivery group (SDG) or every 20 samples.	%R should be within 80-120% if sample < 4x spike added. RPD should be ≤ 20%.	Flag results for affected analytes for all associated samples with "N".	Analyst, Laboratory Department Manager, and Data Validator	Accuracy/Bias	%R should be within 75-125% if sample < 4x spike added.
Laboratory Duplicate (not applicable for rinsate blanks)	One per sample delivery group (SDG) or every 20 samples.	Project-specific criteria: If values are ≥ 5x LOQ, RPD should be ≤ 20%. If if values are < 5x LOQ, Absolute Difference should be ≤ LOQ.	Flag results for affected analytes for all associated samples.	Analyst, Laboratory Department Manager, and Data Validator	Precision	Waters: If values are ≥ 5x LOQ, RPD should be ≤ 20%; if values are < 5x LOQ, Absolute Difference should be ≤ LOQ. Soils: If values are ≥ 5x LOQ, RPD should be ≤ 35%; if values are < 5x LOQ, Absolute Difference should be ≤ 2x LOQ.

* Katahdin's statistically-derived QC limits referenced in this table refer to Katahdin's limits at the time of analysis. Katahdin's current limits are presented in Appendix C.

TABLE 4-1A
QAPP ADDENDUM 1

PROJECT DOCUMENTATION AND RECORDS
FORMER SEWAGE TREATMENT PLANT SITE
NAS SOUTH WEYMOUTH, WEYMOUTH, MASSACHUSETTS

Sample Collection and Other Field Records	Fixed Laboratory Records	Data Assessment Records
Field Logbooks	Sample Receipt, Custody and Tracking Records	Field Sampling Audit Check Lists
Boring Logs	Standards Traceability Logs	Fixed Laboratory Check Lists
Sample Log Sheets – Solid Phase	Equipment Calibration Logs	Audit Report and Quality Notices
Telephone Logs	Sample Prep Logs	Telephone Logs
Field Modification Records	Sample Analysis Logs	Data Validation Reports
Field Instrument Calibration Logs	Equipment Maintenance and Testing Logs	Telephone Logs
Chain-Of Custody Records	Corrective Action Forms	
Air Bills	Data Results Forms	
Custody Seals	Reported Results for Standards, QC Checks, and QC Samples	
	Instrument Print-outs for Samples and Standards	
	Data Verification Check List	
	Sample Disposal Records	
	Telephone Logs	
	Records required by laboratory's specific quality assurance programs	

TABLE 4-2A
QAPP ADDENDUM 1

LABORATORY DATA PACKAGE ELEMENTS
FORMER SEWAGE TREATMENT PLANT SITE
NAS SOUTH WEYMOUTH, WEYMOUTH, MASSACHUSETTS

DATA PACKAGE ELEMENTS	VOCs	VPH/EPH	Metals	PAHs	Pesticides/ PCBs
♦ **NARRATIVE (Org. Narrative, Inorg. Cover Page)**	X	X	X	X	X
♦ **EPA SHIPPING/RECEIVING DOCUMENTS AND INTERNAL LABORATORY COC RECORDS:**					
- Airbills	X	X	X	X	X
- Chain-of-Custody Records/Forms (Traffic Report)	X	X	X	X	X
- Sample Log-In Sheet	X	X	X	X	X
- Miscellaneous Shipping/Receiving Records	X	X	X	X	X
- Internal Lab. Sample Transfer Records and Tracking Sheets	X	X	X	X	X
♦ **SAMPLE DATA:**					
- Tabulated Summary Form for Field Sample Results (Org. and Inorg. Form I; VPH and EPH Exhibit 1)	X	X	X	X	X
- Reconstructed Total Ion Chromatogram (RIC) for each sample	X	X		X	X
- Raw spectra of target compound and background subtracted spectrum of target compound for each sample	X			X	
- Manual worksheets	X	X	X	X	X
- Sample preparation/extraction/digestion log (Inorg. Form XII) and logbook pages	X	X	X	X	X
- Sample analysis run log (Inorg. Form XIII) and logbook pages	X	X	X	X	X
- ICP Raw Data			X		
- Mercury Raw Data			X		
- Other Analytical Raw Data	X	X	X	X	X
♦ **STANDARDS DATA:**					
- Initial Calibration Tabulated Summary Form (Org. Form VI)	X	X		X	X
- Initial Calibration Verification Tabulated Summary Form (Laboratory-specific Org. Form, Inorg. Form IIA)	X	X	X	X	X
- Continuing Calibration Verification Tabulated Summary Form (Org. Form VII, Inorg. Form IIA)	X	X	X	X	X
- Reconstructed Ion Chromatograms and Quantitation Reports for all GC/MS standards	X			X	
- Method Detection Limits Tabulated Summary Form (Inorg. Form IX)			X		

TABLE 4-2A
QAPP ADDENDUM 1

LABORATORY DATA PACKAGE ELEMENTS
FORMER SEWAGE TREATMENT PLANT SITE
NAS SOUTH WEYMOUTH, WEYMOUTH, MASSACHUSETTS

DATA PACKAGE ELEMENTS	VOCs	VPH/EPH	Metals	PAHs	Pesticides/ PCBs
- ICP Linear Ranges Tabulated Summary Form (Inorg. Form XI)			X		
- Standards preparation logbook pages	X	X	X	X	X
♦ **QC DATA:**					
- Tuning and Mass Calibration Tabulated Summary Form (Org. Form V)	X			X	
- ICP-MS Tune Tabulated summary Form (Inorg. Form XIV)			X		
- ICP-MS Internal Standard Relative Intensity Summary Form (Inorg. Form XV)			X		
- Surrogate Percent Recovery Tabulated Summary Form (Org. Form II)	X	X		X	X
- MS/MSD Recovery Tabulated Summary Form (Org. Form III)	X	X		X	X
- Method Blank Tabulated Summary Form (Inorg. Form III)			X		
- Internal Standard Area and RT Tabulated Summary Form (Org. Form VIII)	X			X	
- Pesticide and Aroclor Analytical Sequence Summary Form (Org. Form VIII)		X			X
- Identification Summary for Single and Multiple component Analytes Tabulated Summary Form (Org. Form X)					X
- QC Raw Data – RICs, Chromatograms, Quan Reports, Integration Reports, Mass Spectra, etc.	X			X	X
- ICP Interference Check Sample Tabulated Summary Form (Inorg. Form IV)					
- Spike Sample and Post-Digestion Spike Sample Recovery Tabulated Summary Forms (Inorg. Forms VA and VB)			X		
- Duplicates Tabulated Summary Form (Inorg. Form VI)			X		
- Internal Laboratory Control Sample Tabulated Summary Form (Inorg. Form VII)			X		
- ICP Serial Dilutions Tabulated Summary Form (Inorg. Form VIII)			X		
- QC Raw Data – ICP and Mercury computer printouts, etc.			X		
- QC sample preparation logbook pages	X	X	X	X	X
♦ **MISCELLANEOUS DATA:**		X			
- Original preparation and analysis forms or copies of preparation and analysis logbook pages	X	X	X	X	X
- Screening records	X	X	X	X	X
- All instrument output, including strip charts from screening activities	X	X	X	X	X

TABLE 4-2A
QAPP ADDENDUM 1

LABORATORY DATA PACKAGE ELEMENTS
FORMER SEWAGE TREATMENT PLANT SITE
NAS SOUTH WEYMOUTH, WEYMOUTH, MASSACHUSETTS

DATA PACKAGE ELEMENTS	VOCs	VPH/EPH	Metals	PAHs	Pesticides/ PCBs
- Preparation Logs Raw Data	X	X	X	X	X
- Other Records (ex. Telephone Communication Log)	X	X	X	X	X

Notes:
VOCs = Volatile organic compounds
Metals = Target Analyte List Metals
PAH = Polycyclic aromatic Hydrocarbons
PCB = Polychlorinated biphenyls
( ) = Form Number
Form References:
Org. and Inorg. Forms – USEPA Contract Laboratory Program (CLP) Statement of Work (SOW) for Organic Analytes, SOM01.2 (June 2007), and USEPA CLP SOW for Inorganic Analytes, ISM01.2 (January 2010); laboratory may use previous versions of CLP SOW forms.
VPH and EPH Exhibit 1 – MADEP VPH Method (May 2004, Revision 1.1), Appendix C; and MADEP EPH Method (May 2004, Revision 1.1), Appendix C

TABLE 5-1
QAPP ADDENDUM 1

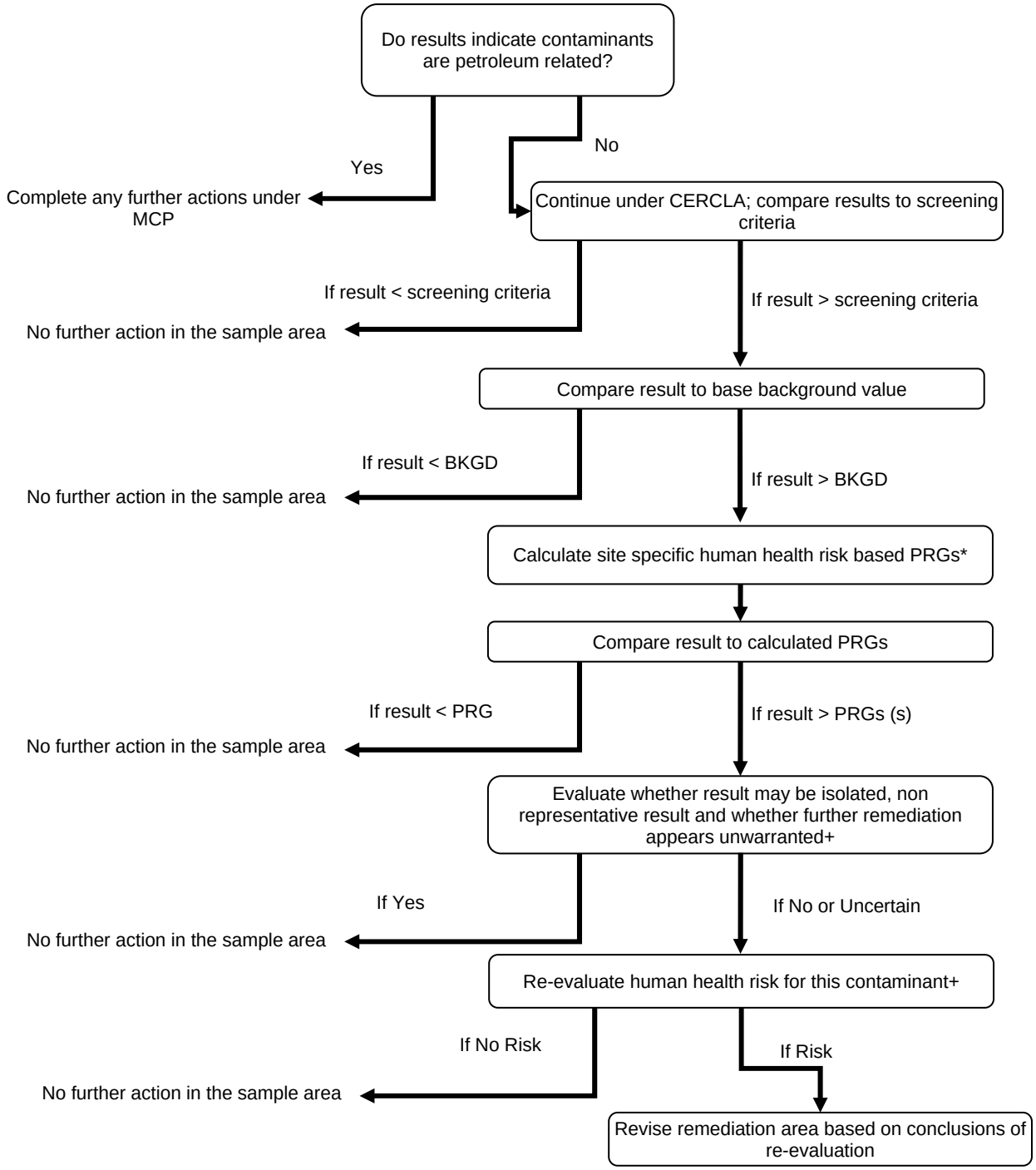
ANALYTICAL DATA VALIDATION SUMMARY TABLE
FORMER SEWAGE TREATMENT PLANT SITE
NAS SOUTH WEYMOUTH, WEYMOUTH, MASSACHUSETTS

Step IIa / IIb	**Matrix**	**Analytical Group**	**Validation Criteria**	**Data Validator** (title and organizational affiliation)
IIa and IIb	Soil/ Headwall Piping Material	VOCs, VPH, EPH, PAHs	Tier II data validation. Project-specific criteria for VOCs by SW-846 8260B, PAHs by SW-846 8270D SIM, VPH by MADEP-VPH-04-1.1, and EPH by MADEP-EPH-04-1.1, are listed in Tables 2-4A and 3-3A and analytical laboratory documentation. Region I USEPA-NE Data Validation Functional Guidelines for Evaluating Environmental Analyses, Part II, December 1996 (USEPA, 1996) will be applied using these criteria.	Tetra Tech, Project Chemist (L. Guzman) and staff chemists
IIa and IIb	Soil/ Headwall Piping Material	Pesticides	Tier II data validation. Project-specific criteria for pesticides by SW-846 8081B are listed in Tables 2-4A and 3-3A and analytical laboratory documentation. Region I EPA-NE Data Validation Functional Guidelines for Evaluating Environmental Analyses, Part III, February 2004 (USEPA, 2004) will be applied using these criteria.	
IIa and IIb	Soil/ Headwall Piping Material	PCBs	Tier II data validation. Project-specific criteria for PCBs by SW-846 8082A are listed in Tables 2-4A and 3-3A and analytical laboratory documentation. Region I EPA-NE Data Validation Functional Guidelines for Evaluating Environmental Analyses, Part III, February 2004 (USEPA, 2004) will be applied using these criteria.	
IIa and IIb	Soil/ Headwall Piping Material	Metals	Tier II data validation. Project-specific criteria for ICP metals by SW-846 6010B and 6020A, and for mercury by SW-846 7470A and 7471B are listed in Tables 2-4A and 3-3A and analytical laboratory documentation. Region I EPA-NE Data Validation Functional Guidelines for Evaluating Environmental Analyses, Part IV, November 2008 (U.S. EPA, 2008) will be applied using these criteria.	Tetra Tech, Project Chemist (L. Guzman) and staff chemists

FIGURES

FIGURE 2-7A

DECISION DIAGRAM FOR ANALYTES WITH NO SITE PRGs
FORMER SEWAGE TREATMENT PLANT SITE
NAS SOUTH WEYMOUTH, WEYMOUTH, MASSACHUSETTS

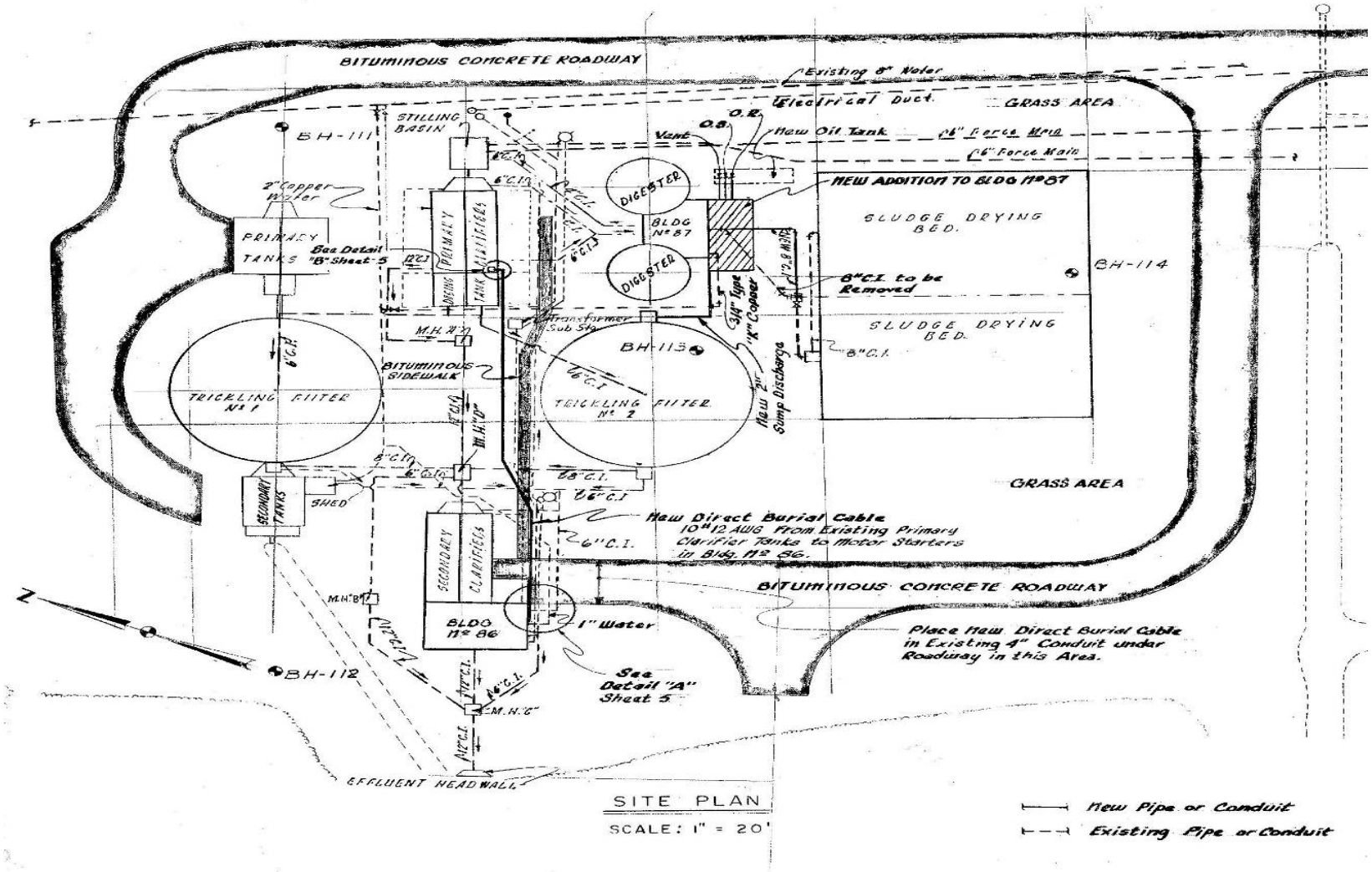


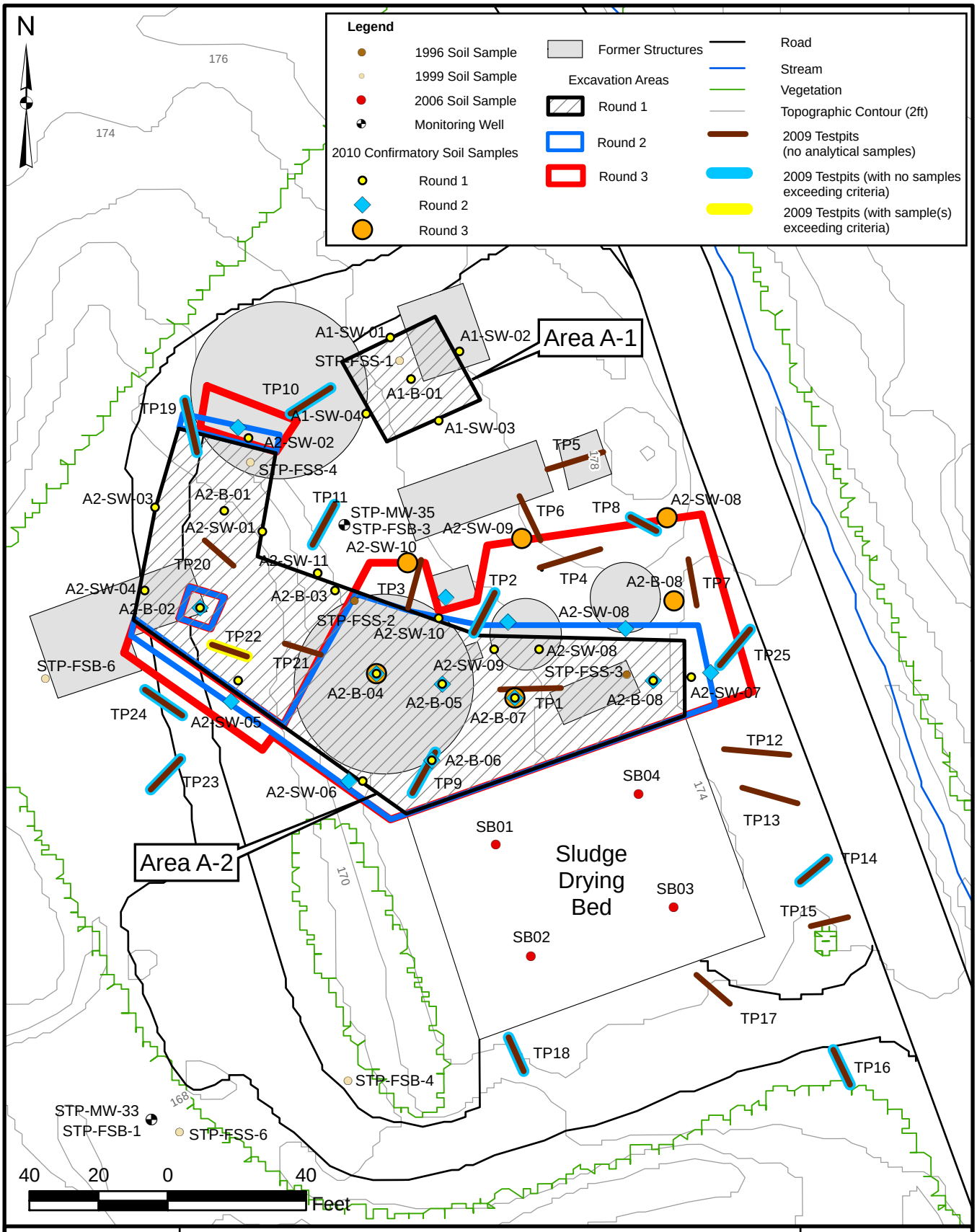
* = Calculate PRGs by same methods and for same receptors used in the FS.
\+ = Final decisions on representativeness of results and need for re-evaluation of risk will be made in conjunction with EPA and MADEP.

FIGURE 2-10

AS-BUILT DRAWING, FORMER SEWAGE TREATMENT PLANT SITE

NAVAL AIR STATION SOUTH WEYMOUTH, WEYMOUTH, MASSACHUSETTS

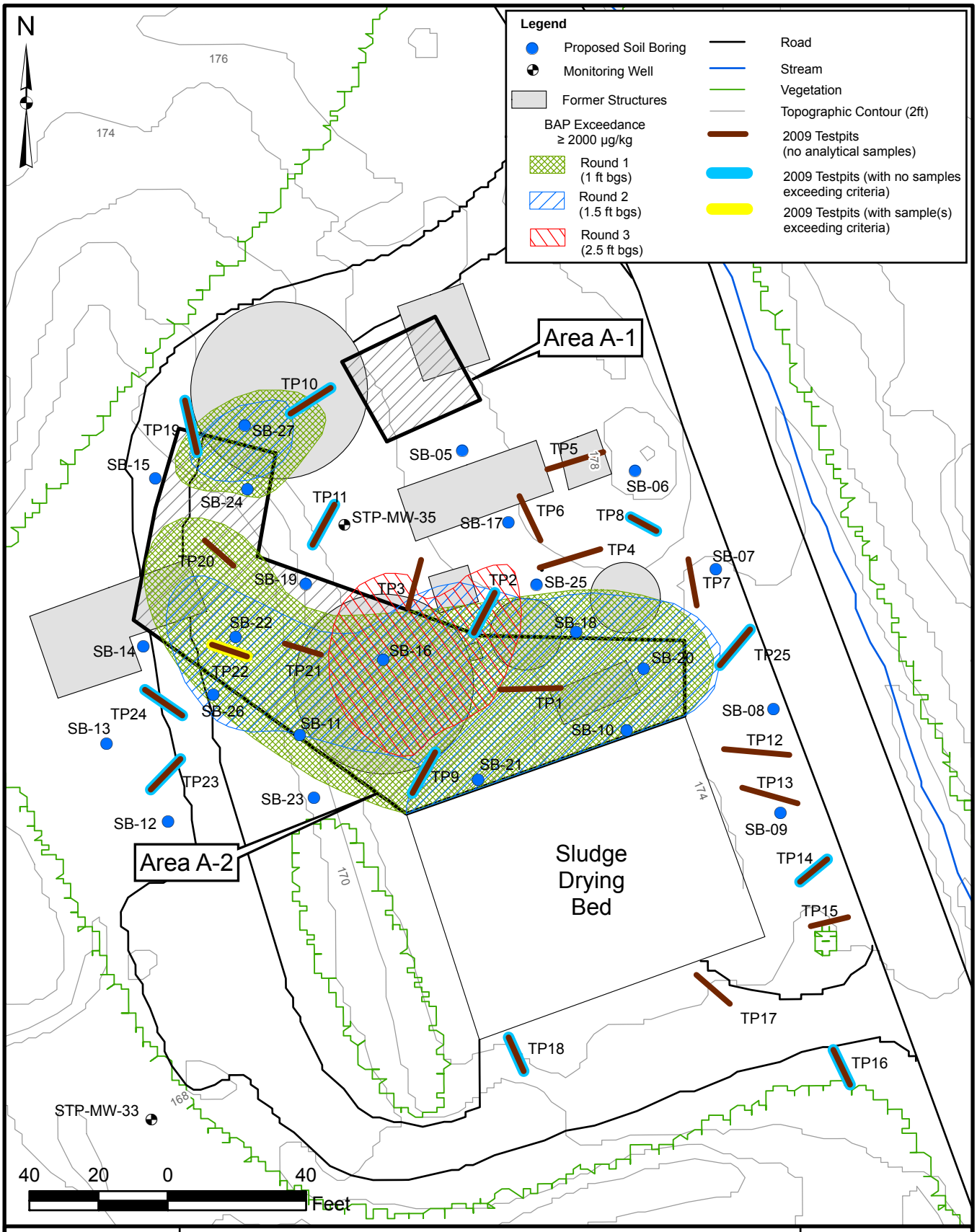




Tetra Tech NUS, Inc.

REMEDIAL ACTION LOCATIONS
QAPP ADDENDUM
FORMER SEWAGE TREATMENT PLANT
NAVAL AIR STATION SOUTH WEYMOUTH
WEYMOUTH, MASSACHUSETTS

SCALE	
AS NOTED	
FILE	
\..\STP_REM_AREA.MXD	
REV	DATE
0	03/07/11
FIGURE NUMBER	
FIGURE 2-11	



Tetra Tech NUS, Inc.

PRIOR INVESTIGATION DATA AND SAMPLE DEPTHS
QAPP ADDENDUM
FORMER SEWAGE TREATMENT PLANT
NAVAL AIR STATION SOUTH WEYMOUTH
WEYMOUTH, MASSACHUSETTS

SCALE	
AS NOTED	
FILE	
\..\STP_BAP_EXTENT_NO_CONF_SAMP.MXD	
REV	DATE
0	03/07/11
FIGURE NUMBER	
FIGURE 2-12	

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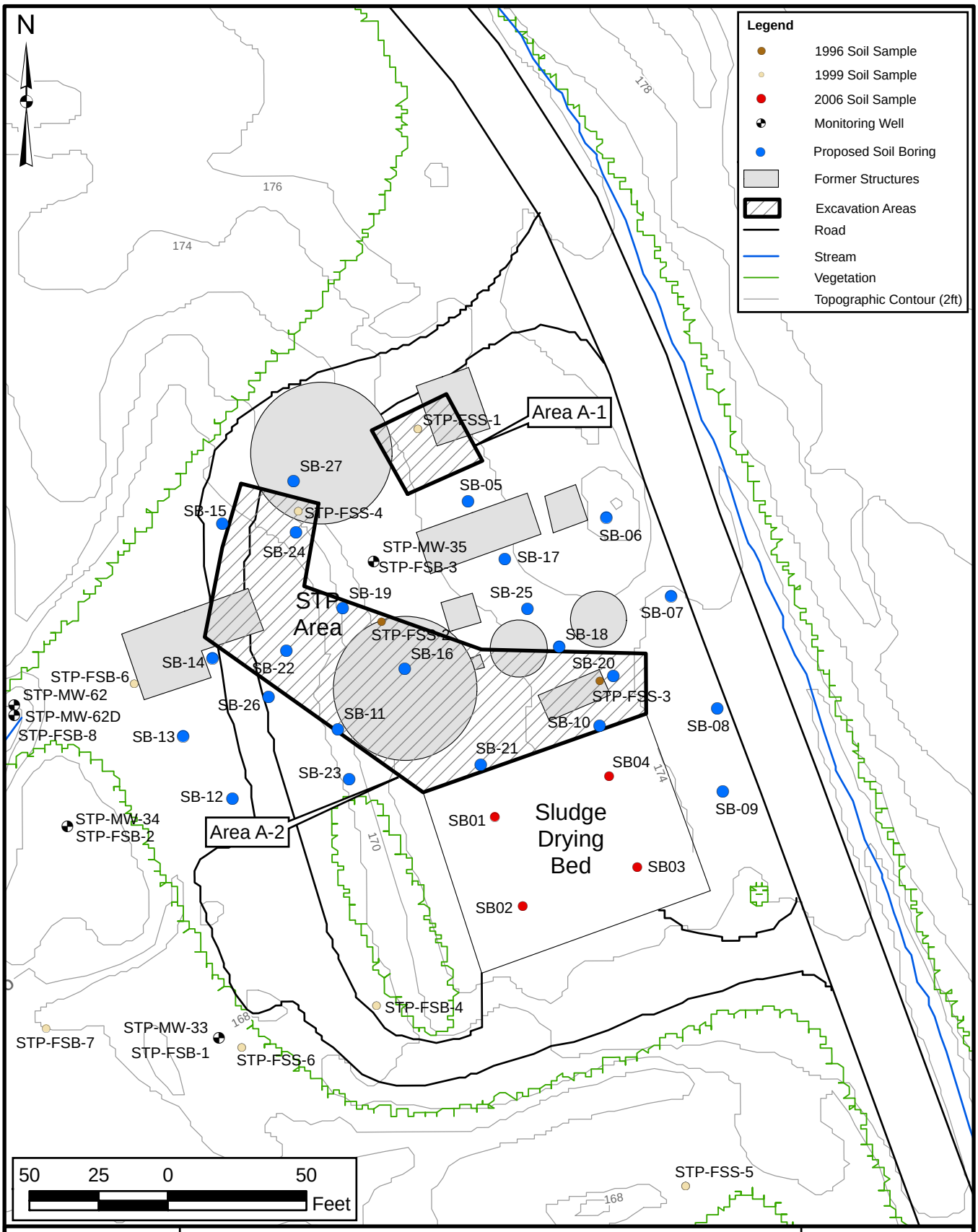

Tetra Tech NUS, Inc.

PROPOSED BORING LOCATIONS
QAPP ADDENDUM
FORMER SEWAGE TREATMENT PLANT
NAVAL AIR STATION SOUTH WEYMOUTH
WEYMOUTH, MASSACHUSETTS

SCALE	
AS NOTED	
FILE \..\STP_PROP_BOR_REM_AREA.MXD	
REV	DATE
0	03/04/11
FIGURE NUMBER	
FIGURE 3-1A	

REFERENCES

REFERENCES

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APPENDIX A

SELECTED STANDARD OPERATING PROCEDURES

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1.0 PURPOSE

The purpose of this document is to specify a consistent procedure for the quality assurance review of electronic and hard copy databases. This SOP outlines the requirements for establishment of a Database Record File, Quality Assurance review procedures, and documentation of the Quality Assurance Review Process.

2.0 SCOPE

The methods described in this Standard Operating Procedure (SOP) shall be used consistently for all projects managed by Tetra Tech NUS (TtNUS).

3.0 GLOSSARY

Chain-of-Custody Form - A Chain-of-Custody Form is a printed form that accompanies a sample or a group of samples from the time of sample collection to the laboratory. The Chain-of-Custody Form is retained with the samples during transfer of samples from one custodian to another. The Chain-of-Custody Form is a controlled document that becomes part of the permanent project file. Chain-of-Custody and field documentation requirements are addressed in SOP SA-6.1.

Electronic Database - A database provided on a compact laser disk (CD). Such electronic databases will generally be prepared using public domain software such as DBase, RBase, Oracle, Visual FoxPro, Microsoft Access, Paradox, etc.

Hardcopy Database - A printed copy of a database prepared using the software discussed under the definition of an electronic database.

Form I - A printed copy of the analytical results for each sample.

Sample Tracking Summary - A printed record of sample information including the date the samples were collected, the number of samples collected, the sample matrix, the laboratory to which the samples were shipped, the associated analytical requirements for the samples, the date the analytical data were received from the laboratory, and the date that validation of the sample data was completed.

4.0 RESPONSIBILITIES

Database Records Custodian - It shall be the responsibility of the Database Records Custodian to update and file the Sample Tracking Summaries for all active projects on a weekly basis. It shall be the responsibility of the Database Records Custodian to ensure that the most recent copies of the Sample Tracking Summaries are placed in the Database Records file. It shall be the responsibility of the Database Records Custodian to ensure that a copy of all validation deliverables is provided to the Project Manager (for placement in the project file). It shall be the responsibility of the Database Records Custodian to ensure that photocopies of all validation deliverables and historical data and reports (as applicable) are placed in the Database Records file.

Data Validation Coordinator - It shall be the responsibility of the Data Validation Coordinator (or designee) to ensure that the Sample Tracking Summaries are maintained by the Database Records Custodian. It shall be the responsibility of the Data Validation Coordinator (or designee) to ensure that photocopies of all data validation deliverables are placed in the applicable Database Records file by the Database Records Custodian.

Earth Sciences Department Manager - It shall be the responsibility of the Earth Sciences Department Manager (or equivalent) to ensure that all field personnel are familiar with the requirements of this Standard Operating Procedure (specifically Section 5.5).

FOL - It shall be the responsibility of the FOL (FOL) of each project to ensure that all field technicians or sampling personnel are thoroughly familiar with this SOP, specifically regarding provision of the Chain-of-Custody Forms to the Database Records Custodian. Other responsibilities of the FOL are described in Sections 5.4 and 5.5.

Management Information Systems (MIS) Manager - It shall be the responsibility of the MIS Manager to ensure that copies of original electronic deliverables (CDs) are placed in both the project files and the Database Records File. It shall be the responsibility of the MIS Manager (or designee) to verify the completeness of the database (presence of all samples) in both electronic and hardcopy form in the Database Records File. It shall be the responsibility of the MIS Manager to ensure that Quality Assurance Reviews are completed and are attested to by Quality Assurance Reviewers. It shall be the responsibility of the MIS Manager to ensure that records of the Quality Assurance review process are placed in the Database Records File. It shall be the responsibility of the MIS Manager to ensure that both electronic and hardcopy forms of the final database are placed in both the project and the Database Record File. It shall be the responsibility of the MIS Manager to ensure that data validation qualifiers are entered in the database.

Furthermore, it shall be the responsibility of the MIS Manager to participate in project planning at the request of the Project Manager, specifically with respect to the generation of level of effort and schedule estimates. To support the project planning effort, the MIS Manager shall provide a copy of the MIS Request From included as Attachment A to the project manager. It shall be the responsibility of the MIS Manager to generate level of effort and budget estimates at the time database support is requested if a budget does not exist at the time of the request. The MIS Request Form shall be provided to the Project Manager at the time of any such requests. It shall be the responsibility of the MIS Manager to notify the Project Manager of any anticipated level of effort overruns or schedule noncompliances as soon as such problems arise along with full justification for any deviations from the budget estimates (provided they were generated by the MIS Manager). It shall be the responsibility of the MIS Manager to document any changes to the scope of work dictated by the Project Manager, along with an estimate of the impact of the change on the level of effort and the schedule.

Program/Department Managers - It shall be the responsibility of the Department and/or Program Managers (or designees) to inform their respective department's Project Managers of the existence and requirements of this SOP.

Project Manager - It shall be the responsibility of each Project Manager to determine the applicability of this SOP based on: (1) program-specific requirements, and (2) project size and objectives. It shall be the responsibility of the Project Manager (or designee) to ensure that the FOL is familiar with the requirements regarding Chain-of-Custody Form provision to the Database Records Custodian. It shall be the responsibility of the Project Manager (or designee) to determine which, if any, historical data are relevant and to ensure that such data (including all relevant information such as originating entity, sample locations, sampling dates, etc.) are provided to the Database Records Custodian for inclusion in the Database Records File. It shall be the responsibility of the Project Manager to obtain project planning input regarding the level of effort and schedule from the MIS Manager. It shall be the responsibility of the Project Manager to complete the database checklist (Attachment A) to support the level of effort and schedule estimate and to facilitate database preparation and subroutine execution.

Risk Assessment Department Manager - It shall be the responsibility of the Risk Assessment Department Manager to monitor compliance with this Standard Operating Procedure, to modify this SOP as necessary, and to take corrective action if necessary. Monitoring of the process shall be completed on a quarterly basis.

Quality Assurance Reviewers - It shall be the responsibility of the Quality Assurance Reviewers to verify the completeness of the sample results via review of the Chain-of-Custody Forms and Sample Tracking Summaries. It shall be the responsibility of the Quality Assurance Reviewers to ensure the correctness of the database via direct comparison of the hardcopy printout of the database and the hardcopy summaries of the original analytical data (e.g., Form Is provided in data validation deliverables). Correctness includes the presence of all relevant sample information (all sample information fields), agreement of the laboratory and database analytical results, and the presence of data validation qualifiers.

Quality Manager - It shall be the responsibility of the Quality Manager to monitor compliance with this Standard Operating Procedure via routine audits.

5.0 PROCEDURES

5.1 Introduction

Verification of the accuracy and completeness of an electronic database can only be accomplished via comparison of a hardcopy of the database with hardcopy of all relevant sample information. The primary purposes of this SOP are to ensure that 1) all necessary hardcopy information is readily available to Quality Assurance Reviewers; 2) ensure that the Quality Assurance review is completed in a consistent and comprehensive manner, and; 3) ensure that documentation of the Quality Assurance review process is maintained in the project file.

5.2 File Establishment

A Database Record file shall be established for a specific project at the discretion of the Project Manager. Initiation of the filing procedure will commence upon receipt of the first set of Chain-of-Custody documents from a FOL or sampling technician. The Database Record Custodian shall establish a project-specific file for placement in the Database Record File. Each file in the Database Record File shall consist of standard components placed in the file as the project progresses. Each file shall be clearly labeled with the project number, which shall be placed on the front of the file drawer and on each and every hanging file folder relevant to the project. The following constitute the minimum components of a completed file:

- Electronic Deliverables
- Sample Tracking Forms
- Chain-of-Custody Forms
- Data Validation Letters
- Quality Assurance Records

5.3 Electronic Deliverables

The format of electronic deliverables shall be specified in the laboratory procurement specification and shall be provided by the laboratory. The integrity of all original electronic data deliverables shall be maintained. This shall be accomplished via the generation of copies of each electronic deliverable provided by the laboratory. The original electronic deliverable shall be provided to the project manager for inclusion in the project file. A copy of the original electronic deliverable shall be placed in the Database Record File. The second copy shall be maintained by the MIS Manager (or designee) to be used as a working copy.

5.4 Sample Tracking Forms

Updated versions of the sample tracking form for each relevant project shall be maintained by the Database Record Custodian. The Sample Tracking Forms shall be updated any time additional Chain-of-Custody Forms are received from a FOL or sampling technician, or at any time that data are received from a laboratory, or at any time that validation of a given data package (sample delivery group) is completed. The Data Validation Coordinator shall inform the Database Record Custodian of the receipt of any data packages from the laboratory and of completion of validation of a given data package to facilitate updating of the Sample Tracking Form. The Database Record Custodian shall place a revised copy of the Sample Tracking Form in the Database Record File anytime it has been updated. Copies of the updated Sample Tracking Form shall also be provided to the project manager to apprise the project manager of sample package receipt, completion of validation, etc.

5.5 Chain-of-Custody Forms

The Chain-of-Custody Forms for all sampling efforts will be used as the basis for (1) updating the Sample Tracking Form, and (2) confirming that all required samples and associated analyses have been completed. It shall be the responsibility of the FOL (or sample technician) to provide a photocopy of all Chain-of-Custody Forms to the Database Record Custodian immediately upon completion of a sampling effort. The Database Record Custodian shall then place the copies of the Chain-of-Custody Form(s) in the Database Record File. Upon receipt of a sample data package from an analytical laboratory, the Data Validation Coordinator shall provide a copy of the laboratory Chain-of-Custody Form to the Database Record Custodian. The Database Record Custodian shall use this copy to update the Sample Tracking Summary and shall place the copy of the laboratory-provided Chain-of-Custody Form in the Database Record File. The photocopy of the laboratory-provided Chain-of Custody Form shall be stapled to the previously filed field copy. Upon receipt of all analytical data, two copies of the Chain-of-Custody will therefore be in the file. Review of the Chain-of-Custody Forms will therefore be a simple mechanism to determine if all data have been received. Chain-of-Custody is addressed in SOP SA-6.1.

5.6 Data Validation Letters

All data validation deliverables (or raw data summaries if validation is not conducted) shall be provided for inclusion in both the Database Record File and the project file. If USEPA regional- or client-specific requirements are such that Form Is (or similar analytical results) need not be provided with the validation deliverable, copies of such results must be appended to the deliverable. It is preferable, although not essential that the validation qualifiers be hand-written directly on the data summary forms. The data validation deliverables (and attendant analytical summaries) will provide the basis for direct comparison of the database printout and the raw data and qualifiers.

5.7 Historical Data

At the direction of the Project Manager, historical data may also be included in a project-specific analytical database. In the event that historical data are germane to the project, hardcopy of the historical data must be included in the Database Record File. Historical data may be maintained in the form of final reports or as raw data. The information contained in the historical data file must be sufficient to identify its origin, its collection date, the sample location, the matrix, and any and all other pertinent information. All available analytical data, Chain-of-Custody Forms, boring logs, well construction logs, sample location maps, shall be photocopied by the Project Manager (or designee) and placed in one or more 3-ring binders. All information shall be organized chronologically by matrix. It shall be the responsibility of the Project Manager (or designee) to ensure that all inconsistencies between analytical data, Chain-of-Custody Forms, boring logs, sample log sheets, and field logbooks are identified and corrected. The Project Manager (or designee) shall decide which nomenclature is appropriate and edit, initial and date all relevant forms. Data entry may only be performed on information that has undergone the aforementioned

editing process, thereby having a direct correlation between hardcopy information and what will become the electronic database.

6.0 RECORDS

Records regarding database preparation and quality assurance review include all those identified in the previous section. Upon completion of the database task, records from the file will be forwarded to the Project Manager for inclusion in the project file, or will be placed in bankers boxes (or equivalent) for storage. The final records for storage shall include the following minimum information on placards placed on both the top and end of the storage box:

Database Record File
PROJECT NUMBER: ____
SITE NAME: _____
DATE FILED: __/__/__
SUMMARY OF CONTENTS ENCLOSED
BOX _ OF _

Project- or program-specific record keeping requirements shall take precedence over the record keeping requirements of this SOP.

ATTACHMENT A

MIS REQUEST FORM

Tetra Tech NUS, Inc.

Project Name: _____ Request Date: _____
CTO: _____ Date Data Available for Production: _____
Project Manager: _____ Request in Support of: _____
Requestor: _____ Database Lead: _____
Program/Client: _____ GIS Lead: _____
State/EPA Region: _____ Statistics Lead: _____
Risk Lead: _____
Site Name(s) (Area, OU, etc.): _____
Sampling Date(s): _____
Matrix: ☐ GW ☐ SO ☐ SD ☐ SW ☐ Other: _____

Labels: ☐ Labels needed for an upcoming sampling event _____ Total # of Samples
_____ Estimated Hours
_____ Due Date
_____ Complete ETS Charge No.
_____ FOL
Additional Instructions: _____

Data Entry:
☐ Chemical data needs to be entered from hardcopy _____ Estimated # of Samples
☐ Chemical data needs to be formated electronically
☐ Field analytical data needs to be entered from hardcopy
☐ Geologic data needs to be entered from hardcopy
☐ Hydrology data needs to be entered from hardcopy
_____ Estimated Hours
_____ Due Date
_____ Complete ETS Charge No.
Additional Instructions: _____

Tables:
☐ Full Data Printout
☐ Summary of Positive Hits
☐ Occurance and Distribution ☐ with criteria
☐ Sampling Analytical Summary
☐ Other: _____
_____ Estimated Hours
_____ Due Date
_____ Complete ETS Charge No.
Additional Instructions: _____

GIS:
☐ General Facility Location
☐ Site Location
☐ Potentiometric Contours/Groundwater Flow
☐ Sample Location Proposed
☐ Sample Location Existing
☐ Tag Map Single Round
☐ Tag Map Multiple Round
☐ Isoconcentrations
☐ Chart Map
☐ 3D Visualization
☐ EGIS CD
☐ Other: _____
_____ Estimated Hours
_____ Due Date
_____ Complete ETS Charge No.
Additional Instructions: _____

Statistics: ☐ Yes
_____ Estimated Hours
_____ Due Date
_____ Complete ETS Charge No.
Additional Instructions: _____

Geostatistics: ☐ Yes
_____ Estimated Hours
_____ Due Date
_____ Complete ETS Charge No.
Additional Instructions: _____

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1.0 PURPOSE

The purpose of this Standard Operating Procedure (SOP) is to specify a consistent sample nomenclature system that will facilitate subsequent data management in a cost-effective manner. The sample nomenclature system has been devised such that the following objectives can be attained:

- Sorting of data by matrix
- Sorting of data by depth
- Maintenance of consistency (field, laboratory, and database sample numbers)
- Accommodation of all project-specific requirements
- Accommodation of laboratory sample number length constraints (maximum of 20 characters)

2.0 SCOPE

The methods described in this SOP shall be used consistently for all projects requiring electronic data. Other contract- or project-specific sample nomenclature requirements may also be applicable.

3.0 GLOSSARY

None.

4.0 RESPONSIBILITIES AND PERSONNEL QUALIFICATIONS

Program Manager - It shall be the responsibility of the Project Manager (or designee) to inform contract-specific Project Managers (PMs) of the existence and requirements of this SOP.

Project Manager - It shall be the responsibility of the PM to determine the applicability of this SOP based on: (1) program-specific requirements and (2) project size and objectives. It shall be the responsibility of the PM (or designee) to ensure that sample nomenclature requirements are thoroughly specified in the relevant project planning document (e.g., sampling and analysis plan) and are consistent with this SOP if relevant. It shall be the responsibility of the PM to ensure that the FOL is familiar with the sample nomenclature system.

Field Operations Leader (FOL) - It shall be the responsibility of the FOL to ensure that all field technicians or sampling personnel are thoroughly familiar with this SOP and the project-specific sample nomenclature system. It shall be the responsibility of the FOL to ensure that the sample nomenclature system is used during all project-specific sampling efforts.

General personnel qualifications for sample nomenclature activities in the field include the following:

- Occupational Safety and Health Administration (OSHA) 40-hour and applicable refresher training.
- Capability of performing field work under the expected physical and environmental (i.e., weather) conditions.
- Familiarity with appropriate procedures for field documentation, handling, packaging, and shipping.

5.0 PROCEDURES

5.1 INTRODUCTION

The sample identification (ID) system can consist of as few as eight but not more than 20 distinct alpha-numeric characters. The sample ID will be provided to the laboratory on the sample labels and chain-of-custody forms. The basic sample ID provided to the laboratory has three segments and shall be as follows, where "A" indicates "alpha," and "N" indicates "numeric":

A or N 3 or 4 Characters	**AAA 2 or 3 Characters**	**A or N 3 to 6 Characters**
Site Identifier	Sample Type	Sample Location

Additional segments may be added as needed. For example:

(1) Soil and sediment sample ID

A or N 3 or 4 Characters	**AAA 2 or 3 Characters**	**A or N 3 to 6 Characters**	**NNNN 4 Characters**
Site identifier	Sample type	Sample location	Sample depth

(2) Aqueous (groundwater or surface water) sample ID

A or N 3 or 4 Characters	**AAA 2 or 3 Characters**	**A or N 3 to 6 Characters**	**NN 2 Characters**	**-A 1 Character**
Site identifier	Sample type	Sample location	Round number	Filtered sample only

(3) Biota sample ID

A or N 3 or 4 Characters	**AAA 2 or 3 Characters**	**A or N 3 to 6 Characters**	**AA 2 Characters**	**NNN 3 Characters**
Site identifier	Sample type	Sample location	Species identifier	Sample group number

5.2 SAMPLE IDENTIFICATION FIELD REQUIREMENTS

The various fields in the sample ID include but are not limited to the following:

- Site identifier
- Sample type
- Sample location
- Sample depth
- Sampling round number
- Filtered
- Species identifier
- Sample group number

The site identifier must be a three- or four-character field (numeric characters, alpha characters, or a mixture of alpha and numeric characters may be used). A site number is necessary because many facilities/sites have multiple individual sites, Solid Waste Management Units (SWMUs), Operable Units (OUs), etc. Several examples are presented in Section 5.3 of this SOP.

The sample type must be a two- or three-character alpha field. Suggested codes are provided in Section 5.3 of this SOP.

The sample location must be at least a three-character field but may have up to six characters (alpha, numeric, or a mixture). The six characters may be useful in identifying a monitoring well to be sampled or describing a grid location.

The sample depth field is used to note the depth below ground surface (bgs) at which a soil or sediment sample is collected. The first two numbers of the four-number code specify the top interval, and the third and fourth specify the bottom interval in feet bgs of the sample. If the sample depth is equal to or greater than 100, then only the top interval would be represented and the sampling depth would be truncated to three characters. The depths will be noted in whole numbers only; further detail, if needed, will be recorded on the sample log sheet or boring log, in the logbook, etc.

A two-digit round number will be used to track the number of aqueous samples collected from a particular aqueous sample location. The first sample collected from a location will be assigned the round identifier 01, the second 02, etc. This applies to both existing and proposed monitoring wells and surface water locations.

Aqueous samples that are field filtered (dissolved analysis) will be identified with an "-F" in the last field segment. No entry in this segment signifies an unfiltered (total) sample.

The species identifier must be a two-character alpha field. Several suggested codes are provided in Section 5.3 of this SOP.

The three-digit sample group number will be used to track the number of biota sample groups (a particular group size may be determined by sample technique, media type, the number of individual caught, weight issues, time, etc.) by species and location. The first sample group of a particular species collected from a given location will be assigned the sample group number 001, and the second sample group of the same species collected from the same location will be assigned the sample group number 002.

5.3 EXAMPLE SAMPLE FIELD DESIGNATIONS

Examples of each of the fields are as follows:

Site identifier - Examples of site numbers/designations are as follows:

A01 - Area of Concern (AOC) 1
125 - SWMU 125
000 - Base- or facility-wide sample (e.g., upgradient well)
BBG - Base background

The examples cited are only suggestions. Each PM (or designee) must designate appropriate (and consistent) site designations for their individual project.

Sample type - Examples of sample types are as follows:

AH - Ash Sample

AS - Air Sample
BM - Building Material Sample
BSB - Biota Sample Full Body
BSF - Biota Sample Fillet
CP - Composite Sample
CS - Chip Sample
DS - Drum Sample
DU - Dust Sample
FP - Free Product
IDW - Investigation-Derived Waste Sample
LT - Leachate Sample
MW - Monitoring Well Groundwater Sample
OF - Outfall Sample
RW - Residential Well Sample
SB - Soil Boring Sample
SD - Sediment Sample
SC - Scrape Sample
SG - Soil Gas Sample
SL - Sludge Sample
SP - Seep Sample
SS - Surface Soil Sample
ST - Storm Sewer Water Sample
SW - Surface Water Sample
TP - Test Pit Sample
TW - Temporary Well Sample
WC - Well Construction Material Sample
WP - Wipe Sample
WS - Waste/Solid Sample
WW - Wastewater Sample

Sample location - Examples of the location field are as follows:

001 - Monitoring well 1
N32E92 - Grid location 32 North and 92 East
D096 - Investigation-derived waste drum number 96

Species identifier - Examples of species identifier are as follows:

BC - Blue Crab
GB - Blue Gill
CO - Corn
SB - Soybean

5.4 EXAMPLES OF SAMPLE NOMENCLATURE

The first round monitoring well groundwater sample collected from existing monitoring well 001 at SWMU 16 for a filtered sample would be designated as 016MW00101-F.

The second round monitoring well groundwater sample collected from existing monitoring well C20P2 at Site 23 for an unfiltered sample would be designated as 023MWC20P202.

The second surface water sample collected from point 01 at SWMU 130 for an unfiltered sample would be designated as 130SW00102.

A surface soil sample collected from grid location 32 North and 92 East at Site 32 at the 0- to 2-foot interval would be designated as 032SSN32E920002.

A subsurface soil sample from soil boring 03 at SWMU 32 at an interval of 4 to 5 feet bgs would be designated as 032SB0030405.

A sediment sample collected at SWMU 19 from 0 to 6 inches at location 14 would be designated as 019SD0140001. The sample data sheet would reflect the precise depth at which this sample was collected.

During biota sampling for full-body analysis, the first time a minnow trap was checked at grid location A25 of SWMU 1415, three small blue gills were captured, collected, and designated with the sample ID of 1415BSBA25BG001. The second time blue gill were collected at the same location (grid location A25 at SWMU 1415), the sample ID would be 1415BSBA25BG002.

Note: No dash (-) or spacing is used between the segments with the exception of the filtered segment. The "F" used for a filtered aqueous sample is preceded by a dash (-F).

5.5 FIELD QA/QC SAMPLE NOMENCLATURE

Field Quality Assurance (QA)/Quality Control (QC) samples are designated using a different coding system. The QC code will consist of a three- to four-segment alpha-numeric code that identifies the sample QC type, the date the sample was collected, and the number of this type of QC sample collected on that date.

AA	NNNNNN	NN	-F
QC type	Date	Sequence number (per day)	Filtered (aqueous only, if needed)

The QC types are identified as:

TB = Trip Blank
RB = Rinsate Blank (Equipment Blank)
FD = Field Duplicate
AB = Ambient Conditions Blank
WB = Source Water Blank

The sampling time recorded on the chain-of-custody form, labels, and tags for duplicate samples will be 0000 so that the samples are "blind" to the laboratory. Notes detailing the sample number, time, date, and type will be recorded on the routine sample log sheets and will document the location of the duplicate sample (sample log sheets are not provided to the laboratory). Documentation for all other QC types (TB, RB, AB, and WB) will be recorded on the QC Sample Log Sheet (see SOP SA-6.3, Field Documentation).

5.6 EXAMPLES OF FIELD QA/QC SAMPLE NOMENCLATURE

The first duplicate of the day for a filtered groundwater sample collected on June 3, 2000, would be designated as FD06030001-F.

The third duplicate of the day taken of a subsurface soil sample collected on November 17, 2003, would be designated as FD11170303.

The first trip blank associated with samples collected on October 12, 2000, would be designated as TB10120001.

The only rinsate blank collected on November 17, 2001, would be designated as RB11170101.

6.0 DEVIATIONS

Any deviation from this SOP must be addressed in detail in the site-specific planning documents.

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1.0 PURPOSE

Utilities such as electric service lines, natural or propane gas lines, water and sewage lines, telecommunications, and steam lines are very often in the immediate vicinity of work locations. Contact with underground or overhead utilities can have serious consequences including employee injury/fatality, property and equipment damage, substantial financial impacts, and loss of utility service to users.

The purpose of this procedure is to provide minimum requirements and technical guidelines regarding the appropriate procedures to be followed when performing subsurface and overhead utility locating services. It is the policy of Tetra Tech NUS, Inc. (TtNUS) to provide a safe and healthful work environment for the protection of our employees. The purpose of this Standard Operating Procedure (SOP) is to aid in achieving the objectives of this policy, to present the acceptable procedures pertaining to utility locating and excavation clearance activities, and to present requirements and restrictions relevant to these types of activities. This SOP must be reviewed by any employee potentially involved with underground or overhead utility locating and avoidance activities.

2.0 SCOPE

This procedure applies to all TtNUS field activities where there may be potential contact with underground or overhead utilities. This procedure provides a description of the principles of operation, instrumentation, applicability, and implementability of typical methods used to determine the presence and avoidance of contact with utility services. This procedure is intended to assist with work planning and scheduling, resource planning, field implementation, and subcontractor procurement. Utility locating and excavation clearance requires site-specific information prior to the initiation of any such activities on a specific project. This SOP is not intended to provide a detailed description of methodology and instrument operation. Specialized expertise during both planning and execution of several of the methods presented may also be required.

3.0 GLOSSARY

Electromagnetic Induction (EMI) Survey - A geophysical exploration method whereby electromagnetic fields are induced in the ground and the resultant secondary electromagnetic fields are detected as a measure of ground conductivity.

Magnetometer – A device used for precise and sensitive measurements of magnetic fields.

Magnetic Survey – A geophysical survey method that depends on detection of magnetic anomalies caused by the presence of buried ferromagnetic objects.

Metal Detection – A geophysical survey method that is based on electromagnetic coupling caused by underground conductive objects.

Vertical Gradiometer – A magnetometer equipped with two sensors that are vertically separated by a fixed distance. It is best suited to map near surface features and is less susceptible to deep geologic features.

Ground Penetrating Radar – Ground Penetrating Radar (GPR) involves specialized radar equipment whereby a signal is sent into the ground via a transmitter. Some portion of the signal will be reflected from the subsurface material, which is then recorded with a receiver and electronically converted into a graphic picture.

4.0 RESPONSIBILITIES

Project Manager (PM)/Task Order Manager (TOM) - Responsible for ensuring that all field activities are conducted in accordance with this procedure.

Site Manager (SM)/Field Operations Leader (FOL) - Responsible for the onsite verification that all field activities are performed in compliance with approved SOPs or as otherwise directed by the approved project plan(s).

Site Health & Safety Officer (SHSO) – Responsible to provide technical assistance and verify full compliance with this SOP. The SHSO is also responsible for reporting any deficiencies to the Corporate Health and Safety Manager (HSM) and to the PM/TOM.

Health & Safety Manager (HSM) – Responsible for preparing, implementing, and modifying corporate health and safety policy and this SOP.

Site Personnel – Responsible for performing their work activities in accordance with this SOP and the TtNUS Health and Safety Policy.

5.0 PROCEDURES

This procedure addresses the requirements and technical procedures that must be performed to minimize the potential for contact with underground and overhead utility services. These procedures are addressed individually from a buried and overhead standpoint.

5.1 Buried Utilities

Buried utilities present a heightened concern because their location is not typically obvious by visual observation, and it is common that their presence and/or location is unknown or incorrectly known on client properties. This procedure must be followed prior to beginning any subsurface probing or excavation that might potentially be in the vicinity of underground utility services. In addition, the Utility Clearance Form (Attachment 3) must be completed for every location or cluster of locations where intrusive activities will occur.

Where the positive identification and de-energizing of underground utilities cannot be obtained and confirmed using the following steps, the PM/TOM is responsible for arranging for the procurement of a qualified, experienced, utility locating subcontractor who will accomplish the utility location and demarcation duties specified herein.

1. A comprehensive review must be made of any available property maps, blue lines, or as-builts prior to site activities. Interviews with local personnel familiar with the area should be performed to provide additional information concerning the location of potential underground utilities. Information regarding utility locations shall be added to project maps upon completion of this exercise.

2., A visual site inspection must be performed to compare the site plan information to actual field conditions. Any findings must be documented and the site plan/maps revised. The area(s) of proposed excavation or other subsurface activities must be marked at the site in white paint or pin flags to identify those locations of the proposed intrusive activities. The site inspection should focus on locating surface indications of potential underground utilities. Items of interest include the presence of nearby area lights, telephone service, drainage grates, fire hydrants, electrical service vaults/panels, asphalt/concrete scares and patches, and topographical depressions. Note the location of any emergency shut off switches. Any additional information regarding utility

locations shall be added to project maps upon completion of this exercise and returned to the PM/TOM.

3. If the planned work is to be conducted on private property (e.g., military installations, manufacturing facilities, etc.) the FOL must identify and contact appropriate facility personnel (e.g., public works or facility engineering) before any intrusive work begins to inquire about (and comply with) property owner requirements. It is important to note that private property owners may require several days to several weeks advance notice prior to locating utilities.

4. If the work location is on public property, the state agency that performs utility clearances must be notified (see Attachment 1). State "one-call" services must be notified prior to commencing fieldwork per their requirements. Most one-call services require, by law, 48- to 72-hour advance notice prior to beginning any excavation. Such services typically assign a "ticket" number to the particular site. This ticket number must be recorded for future reference and is valid for a specific period of time, but may be extended by contacting the service again. The utility service will notify utility representatives who then mark their respective lines within the specified time frame. It should be noted that most military installations own their own utilities but may lease service and maintenance from area providers. Given this situation, "one call" systems may still be required to provide location services on military installations.

5. Utilities must be identified and their locations plainly marked using pin flags, spray paint, or other accepted means. The location of all utilities must be noted on a field sketch for future inclusion on project maps. Utility locations are to be identified using the following industry-standard color code scheme, unless the property owner or utility locator service uses a different color code:

white	excavation/subsurface investigation location
red	electrical
yellow	gas, oil, steam
orange	telephone, communications
blue	water, irrigation, slurry
green	sewer, drain

6. Where utility locations are not confirmed with a high degree of confidence through drawings, schematics, location services, etc., the work area must be thoroughly investigated prior to beginning the excavation. In these situations, utilities must be identified using safe and effective methods such as passive and intrusive surveys, or the use of non-conductive hand tools. Also, in situations where such hand tools are used, they should always be used in conjunction with suitable detection equipment, such as the items described in Section 6.0 of this SOP. Each method has advantages and disadvantages including complexity, applicability, and price. It also should be noted that in some states, initial excavation is required by hand to a specified depth.

7. At each location where trenching or excavating will occur using a backhoe or other heavy equipment, and where utility identifications and locations cannot be confirmed prior to groundbreaking, the soil must be probed using a device such as a tile probe which is made of non-conductive material such as fiberglass. If these efforts are not successful in clearing the excavation area of suspect utilities, hand shoveling must be performed for the perimeter of the intended excavation.

8. All utilities uncovered or undermined during excavation must be structurally supported to prevent potential damage. Unless necessary as an emergency corrective measure, TtNUS shall not make any repairs or modifications to existing utility lines without prior permission of the utility owner, property owner, and Corporate HSM. All repairs require that the line be locked-out/tagged-out prior to work.

5.2 Overhead Power Lines

If it is necessary to work within the minimum clearance distance of an overhead power line, the overhead line must be de-energized and grounded, or re-routed by the utility company or a registered electrician. If protective measures such as guarding, isolating, or insulating are provided, these precautions must be adequate to prevent employees from contacting such lines directly with any part of their body or indirectly though conductive materials, tools, or equipment.

The following table provides the required minimum clearances for working in proximity to overhead power lines.

Nominal Voltage	Minimum Clearance
0 -50 kV	10 feet, or one mast length; whichever is greater
50+ kV	10 feet plus 4 inches for every 10 kV over 50 kV or 1.5 mast lengths; whichever is greater

6.0 UNDERGROUND LOCATING TECHNIQUES

A variety of supplemental utility locating approaches are available and can be applied when additional assurance is needed. The selection of the appropriate method(s) to employ is site-specific and should be tailored to the anticipated conditions, site and project constraints, and personnel capabilities.

6.1 Geophysical Methods

Geophysical methods include electromagnetic induction, magnetics, and ground penetrating radar. Additional details concerning the design and implementation of electromagnetic induction, magnetics, and ground penetrating radar surveys can be found in one or more of the TtNUS SOPs included in the References (Section 8.0).

Electromagnetic Induction

Electromagnetic Induction (EMI) line locators operate either by locating a background signal or by locating a signal introduced into the utility line using a transmitter. A utility line acts like a radio antenna, producing electrons, which can be picked up with a radiofrequency receiver. Electrical current carrying conductors have a 60HZ signal associated with them. This signal occurs in all power lines regardless of voltage. Utilities in close proximity to power lines or used as grounds may also have a 60HZ signal, which can be picked up with an EM receiver. A typical example of this type of geophysical equipment is an EM-61.

EMI locators specifically designed for utility locating use a special signal that is either indirectly induced onto a utility line by placing the transmitter above the line or directly induced using an induction clamp. The clamp induces a signal on the specific utility and is the preferred method of tracing since there is little chance of the resulting signals being interfered with. A good example of this type of equipment is the Schonstedt® MAC-51B locator. The MAC-51B performs inductively traced surveys, simple magnetic locating, and traced nonmetallic surveys.

When access can be gained inside a conduit to be traced, a flexible insulated trace wire can be used. This is very useful for non-metallic conduits but is limited by the availability of gaining access inside the pipe.

Magnetics

Magnetic locators operate by detecting the relative amounts of buried ferrous metal. They are incapable of locating or identifying nonferrous utility lines but can be very useful for locating underground storage tanks (UST's), steel utility lines, and buried electrical lines. A typical example of this type of equipment is the Schonstedt® GA-52Cx locator. The GA-52Cx is capable of locating 4-inch steel pipe up to 8 feet deep.

Non-ferrous lines are often located by using a typical plumbing tool (snake) fed through the line. A signal is then introduced to the snake that is then traced.

Ground Penetrating Radar

Ground Penetrating Radar (GPR) involves specialized radar equipment whereby a signal is sent into the ground via a transmitter. Some portion of the signal will be reflected from the subsurface material, which is then recorded with a receiver and electronically converted into a graphic picture. In general, an object which is harder than the surrounding soil will reflect a stronger signal. Utilities, tunnels, UST's, and footings will reflect a stronger signal than the surrounding soil. Although this surface detection method may determine the location of a utility, this method does not specifically identify utilities (i.e., water vs. gas, electrical vs. telephone); hence, verification may be necessary using other methods. This method is somewhat limited when used in areas with clay soil types or with a high water table.

6.2 Passive Detection Surveys

Acoustic Surveys

Acoustic location methods are generally most applicable to waterlines or gas lines. A highly sensitive Acoustic Receiver listens for background sounds of water flowing (at joints, leaks, etc.) or to sounds introduced into the water main using a transducer. Acoustics may also be applicable to determine the location of plastic gas lines.

Thermal Imaging

Thermal (i.e., infrared) imaging is a passive method for detecting the heat emitted by an object. Electronics in the infrared camera convert subtle heat differentials into a visual image on the viewfinder or a monitor. The operator does not look for an exact temperature; rather they look for heat anomalies (either elevated or suppressed temperatures) characteristic of a potential utility line.

The thermal fingerprint of underground utilities results from differences in temperature between the atmosphere and the fluid present in a pipe or the heat generated by electrical resistance. In addition, infrared scanners may be capable of detecting differences in the compaction, temperature and moisture content of underground utility trenches. High-performance thermal imagery can detect temperature differences to hundredths of a degree.

6.3 Intrusive Detection Surveys

Vacuum Excavation

Vacuum excavation is used to physically expose utility services. The process involves removing the surface material over approximately a 1' x 1' area at the site location. The air-vacuum process proceeds with the simultaneous action of compressed air-jets to loosen soil and vacuum extraction of the resulting

debris. This process ensures the integrity of the utility line during the excavation process, as no hammers, blades, or heavy mechanical equipment comes into contact with the utility line, eliminating the risk of damage to utilities. The process continues until the utility is uncovered. Vacuum excavation can be used at the proposed site location to excavate below the "utility window" which is usually 8 feet.

Hand Excavation

When the identification and location of underground utilities cannot be positively confirmed through document reviews and/or other methods, borings and excavations may be cleared via the use of non-conductive hand tools. This should always be done in conjunction with the use of detection equipment. This would be required for all locations where there is a potential to impact buried utilities. The minimum hand-excavation depth that must be reached is to be determined considering the geographical location of the work site. This approach recognizes that the placement of buried utilities is influenced by frost line depths that vary by geographical region. Attachment 2 presents frost line depths for the regions of the contiguous United States. At a minimum, hand excavation depths must be at least to the frost line depth (see Attachment 2) plus two (2) feet, but never less than 4 feet below ground surface (bgs). For hand excavation, the hole created must be reamed large enough to be at least the diameter of the drill rig auger or bit prior to drilling. For soil gas surveys, the survey probe shall be placed as close as possible to the cleared hand excavation. It is important to note that a post-hole digger must not be used in this type of hand excavation activity.

Tile Probe Surveys

For some soil types, site conditions, and excavation requirements, non-conductive tile probes may be used. A tile probe is a "T"-handled rod of varying lengths that can be pushed into the soil to determine if any obstructions exist at that location. Tile probes constructed of fiberglass or other nonconductive material are readily-available from numerous vendors. Tile probes must be performed to the same depth requirements as previously specified. As with other types of hand excavating activities, the use of a non-conductive tile probe, should always be in conjunction with suitable utility locating detection equipment.

7.0 INTRUSIVE ACTIVITIES SUMMARY

The following list summarizes the activities that must be performed prior to beginning subsurface activities:

1. Map and mark all subsurface locations and excavation boundaries using white paint or markers specified by the client or property owner.

2. Notify the property owner and/or client that the locations are marked. At this point, drawings of locations or excavation boundaries shall be provided to the property owner and/or client so they may initiate (if applicable) utility clearance.

   Note: Drawings with confirmed locations should be provided to the property owner and/or client as soon as possible to reduce potential time delays.

3. Notify "One Call" service. If possible, arrange for an appointment to show the One Call representative the surface locations or excavation boundaries in person. This will provide a better location designation to the utilities they represent. You should have additional drawings should you need to provide plot plans to the One Call service.

4. Implement supplemental utility detection techniques as necessary and appropriate to conform utility locations or the absence thereof.

5. Complete Attachment 3, Utility Clearance Form. This form should be completed for each excavation location. In situations where multiple subsurface locations exist within the close proximity of one another, one form may be used for multiple locations provided those locations are noted on the Utility Clearance Form. Upon completion, the Utility Clearance Form and revised/annotated utility location map becomes part of the project file.

8.0 REFERENCES

OSHA Letter of Interpretation, Mr. Joseph Caldwell, Attachment 4
OSHA 29 CFR 1926(b)(2)
OSHA 29 CFR 1926(b)(3)
TtNUS Utility Locating and Clearance Policy
TtNUS SOP GH-3.1; Resistivity and Electromagnetic Induction
TtNUS SOP GH-3.2; Magnetic and Metal Detection Surveys
TtNUS SOP GH-3.4; Ground-penetrating Radar Surveys

ATTACHMENT 1
LISTING OF UNDERGROUND UTILITY CLEARANCE RESOURCES

American Public Works Association
2345 Grand Boulevard, Suite 500, Kansas City, MO 64108-2625
Phone (816) 472-6100 • Fax (816) 472-1610
Web www.apwa.net • E-mail apwa@apwa.net

ONE-CALL SYSTEMS INTERNATIONAL CONDENSED DIRECTORY

Alabama
Alabama One-Call
1-800-292-8525

Alaska
Locate Call Center of Alaska, Inc.
1-800-478-3121

Arizona
Arizona Blue Stake
1-800-782-5348

Arkansas
Arkansas One Call System, Inc.
1-800-482-8998

California
Underground Service Alert North
1-800-227-2600
Underground Service Alert of Southern California
1-800-227-2600

Colorado
Utility Notification Center of Colorado
1-800-922-1987

Connecticut
Call Before You Dig
1-800-922-4455

Delaware
Miss Utility of Delmarva
1-800-282-8555

Florida
Sunshine State One-Call of Florida, Inc.
1-800-432-4770

Georgia
Underground Protection Center, Inc.
1-800-282-7411

Hawaii
Underground Service Alert North
1-800-227-2600

Idaho
Dig Line Inc.
1-800-342-1585
Kootenai County One-Call
1-800-428-4950
Shoshone - Benewah One-Call
1-800-398-3285

Illinois
JULIE, Inc.
1-800-892-0123
Digger (Chicago Utility Alert Network)
312-744-7000

Indiana
Indiana Underground Plant Protection Service
1-800-382-5544

Iowa
Iowa One-Call
1-800-292-8989

Kansas
Kansas One-Call System, Inc.
1-800-344-7233

Kentucky
Kentucky Underground Protection Inc.
1-800-752-6007

Louisiana
Louisiana One Call System, Inc.
1-800-272-3020

Maine
Dig Safe System, Inc.
1-888-344-7233

Maryland
Miss Utility
1-800-257-7777
Miss Utility of Delmarva
1-800-282-8555

Massachusetts
Dig Safe System, Inc.
1-888-344-7233

Michigan
Miss Dig System, Inc.
1-800-482-7171

Minnesota
Gopher State One Call
1-800-252-1166

Mississippi
Mississippi One-Call System, Inc
1-800-227-6477

Missouri
Missouri One-Call System, Inc.
1-800-344-7483

Montana
Utilities Underground Protection Center
1-800-424-5555
Montana One Call Center
1-800-551-8344

Nebraska
Diggers Hotline of Nebraska
1-800-331-5666

Nevada
Underground Service Alert North
1-800-227-2600

New Hampshire
Dig Safe System, Inc.
1-888-344-7233

New Jersey
New Jersey One Call
1-800-272-1000

New Mexico
New Mexico One Call System, Inc.
1-800-321-2537
Las Cruces- Dona Ana Blue Stakes
1-888-526-0400

New York
Dig Safely New York
1-800-962-7962
New York City- Long Island One Call Center
1-800-272-4480

North Carolina
The North Carolina One-Call Center, Inc.
1-800-632-4949

North Dakota
North Dakota One-Call
1-800-795-0555

Ohio
Ohio Utilities Protection Service
1-800-362-2764
Oil & Gas Producers Underground Protect'n Svc
1-800-925-0988

Oklahoma
Call Okie
1-800-522-6543

Oregon
Oregon Utility Notification Center/One Call Concepts
1-800-332-2344

Pennsylvania
Pennsylvania One Call System, Inc.
1-800-242-1776

Rhode Island
Dig Safe System, Inc.
1-888-344-7233

South Carolina
Palmetto Utility Protection Service Inc.
1-888-721-7877

South Dakota
South Dakota One Call
1-800-781-7474

Tennessee
Tennessee One-Call System, Inc.
1-800-351-1111

ATTACHMENT 1 (Continued)

Texas
Texas One Call System
1-800-245-4545
Texas Excavation Safety System, Inc.
1-800-344-8377
Lone Star Notification Center
1-800-669-8344

Utah
Blue Stakes of Utah
1-800-662-4111

Vermont
Dig Safe System, Inc.
1-888-344-7233

Virginia
Miss Utility of Virginia
1-800-552-7001
Miss Utility (Northern Virginia)
1-800-257-7777

Washington
Utilities Underground Location Center
1-800-424-5555
Northwest Utility Notification Center
1-800-553-4344
Inland Empire Utility Coordinating Council
509-456-8000

West Virginia
Miss Utility of West Virginia, Inc.
1-800-245-4848

Wisconsin
Diggers Hotline, Inc.
1-800-242-8511

Wyoming
Wyoming One-Call System, Inc.
1-800-348-1030
Call Before You Dig of Wyoming
1-800-849-2476

District of Columbia
Miss Utility
1-800-257-7777

Alberta
Alberta One-Call Corporation
1-800-242-3447

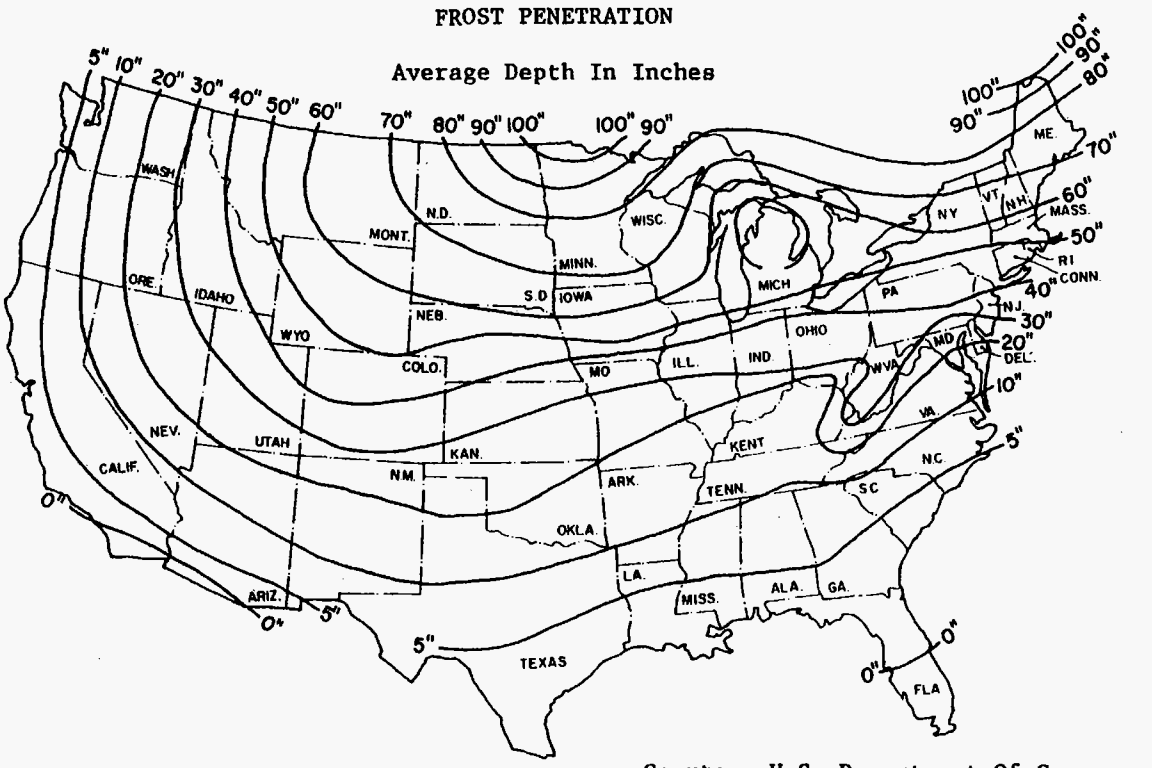
British Columbia
BC One Call
1-800-474-6886

Ontario
Ontario One-Call System
1-800-400-2255

Quebec
Info-Excavation
1-800-663-9228

ATTACHMENT 2

FROST LINE PENETRATION DEPTHS BY GEOGRAPHIC LOCATION



Courtesy U.S. Department Of Commerce

ATTACHMENT 3
UTILITY CLEARANCE FORM

Client: _____ Project Name: _____

Project No.: _____ Completed By: _____

Location Name: _____ Work Date: _____

Excavation Method/Overhead Equipment: _____

1. Underground Utilities — Circle One

a)	Review of existing maps?	yes	no	N/A
b)	Interview local personnel?	yes	no	N/A
c)	Site visit and inspection?	yes	no	N/A
d)	Excavation areas marked in the field?	yes	no	N/A
e)	Utilities located in the field?	yes	no	N/A
f)	Located utilities marked/added to site maps?	yes	no	N/A
g)	Client contact notified Name _____ Telephone: _____ Date: _____	yes	no	N/A
g)	State One-Call agency called? Caller: _____ Ticket Number: _____ Date: _____	yes	no	N/A
h)	Geophysical survey performed? Survey performed by: _____ Method: _____ Date: _____	yes	no	N/A
i)	Hand excavation performed (with concurrent use of utility detection device)? Completed by: _____ Total depth: _____ feet Date: _____	yes	no	N/A
j)	Trench/excavation probed? Probing completed by: _____ Depth/frequency: _____ Date: _____	yes	no	N/A

2. Overhead Utilities — Present Absent

a)	Determination of nominal voltage	yes	no	N/A
b)	Marked on site maps	yes	no	N/A
c)	Necessary to lockout/insulate/re-route	yes	no	N/A
d)	Document procedures used to lockout/insulate/re-route	yes	no	N/A
e)	Minimum acceptable clearance (SOP Section 5.2): _____			

3. Notes:

_____

_____

_____

Approval:

_____ _____

Site Manager/Field Operations Leader Date

c: PM/Project File
Program File

ATTACHMENT 4
OSHA LETTER OF INTERPRETATION

Mr. Joseph Caldwell
Consultant
Governmental Liaison
Pipeline Safety Regulations
211 Wilson Boulevard
Suite 700
Arlington, Virginia 22201

Re: Use of hydro-vacuum or non-conductive hand tools to locate underground utilities.

Dear Mr. Caldwell:

In a letter dated July 7, 2003, we responded to your inquiry of September 18, 2002, regarding the use of hydro-vacuum equipment to locate underground utilities by excavation. After our letter to you was posted on the OSHA website, we received numerous inquiries that make it apparent that aspects of our July 7 letter are being misunderstood. In addition, a number of industry stakeholders, including the National Utility Contractors Association (NUCA), have provided new information regarding equipment that is available for this work.

To clarify these issues, we are withdrawing our July 7 letter and issuing this replacement response to your inquiry.

Question: *Section 1926.651 contains several requirements that relate to the safety of employees engaged in excavation work. Specifically, paragraphs (b)(2) and (b)(3) relate in part to the safety of the means used to locate underground utility installations that, if damaged during an uncovering operation, could pose serious hazards to employees.*

Under these provisions, what constitutes an acceptable method of uncovering underground utility lines, and further, would the use of hydro-vacuum excavation be acceptable under the standard?

Answer

Background

Two sections of 29 CFR 1926 Subpart P (Excavations), 1926.651(Specific excavation requirements), govern methods for uncovering underground utility installations. Specifically, paragraph (b)(2) states:

> When utility companies or owners cannot respond to a request to locate underground utility installations within 24 hours * * * or cannot establish the exact location of these installations, the employer may proceed, provided the employer does so with caution, and provided detection equipment or other acceptable means to locate utility installations are used. (emphasis added).

Paragraph (b)(3) provides:

ATTACHMENT 4 (Continued)

> When excavation operations approach the estimated location of underground installations, the exact location of the installations shall be determined by safe and acceptable means. (emphasis added).

Therefore, "acceptable means" must be used where the location of the underground utilities have not been identified by the utility companies and detection equipment is not used.

Subpart P does not contain a definition of either "other acceptable means" or "safe and acceptable means." The preambles to both the proposed rule and the final rule discussed the rationale behind the wording at issue. For example, the preamble to the proposed rule, 52 Fed. Reg. 12301 (April 15, 1987), noted that a 1972 version of this standard contained language that specified "careful probing or hand digging" as the means to uncover utilities. The preamble then noted that an amendment to the 1972 standard later deleted that language "to allow other, *equally effective means* of locating such installations." The preamble continued that in the 1987 proposed rule, OSHA again proposed using language in section (b)(3) that would provide another example of an acceptable method of uncovering utilities that could be used *where the utilities have not been marked and detection equipment is not being used* – "probing with hand-held tools." This method was rejected in the final version of 29 CFR 1926. As OSHA explained in the preamble to the final rule, 54 Fed. Reg. 45916 (October 31, 1989):

> OSHA received two comments * * * and input from ACCSH [OSHA's Advisory Committee on Construction Safety and Health] * * * on this provision. All commenters recommended dropping 'such as probing with hand-held tools' from the proposed provision, because this could create a hazard to employees by damaging the installation or its insulation.

In other words, the commenters objected to the use of hand tools being used unless detection equipment was used in conjunction with them. OSHA then concluded its discussion relative to this provision by agreeing with the commentators and ultimately not including any examples of "acceptable means" in the final provision.

Non-conductive hand tools are permitted

This raises the question of whether the standard permits the use of hand tools alone -- without also using detection equipment. NUCA and other industry stakeholders have recently informed us that non-conductive hand tools that are appropriate to be used to locate underground utilities are now commonly available.

Such tools, such as a "shooter" (which has a non-conductive handle and a snub nose) and non-conductive or insulated probes were not discussed in the rulemaking. Since they were not considered at that time, they were not part of the class of equipment that was thought to be unsafe for this purpose. Therefore, we conclude that the use of these types of hand tools, when used with appropriate caution, is an "acceptable means" for locating underground utilities.

ATTACHMENT 4 (Continued)

Hydro-vacuum excavation

It is our understanding that some hydro-vacuum excavation equipment can be adjusted to use a minimum amount of water and suction pressure. When appropriately adjusted so that the equipment will not damage underground utilities (especially utilities that are particularly vulnerable to damage, such as electrical lines), use of such equipment would be considered a "acceptable means" of locating underground utilities. However, if the equipment cannot be sufficiently adjusted, then this method would not be acceptable under the standard.

Other technologies

We are not suggesting that these are the only devices that would be "acceptable means" under the standard. Industry stakeholders have informed us that there are other types of special excavation equipment designed for safely locating utilities as well.

We apologize for any confusion our July 7 letter may have caused. If you have further concerns or questions, please feel free to contact us again by fax at: U.S. Department of Labor, OSHA, Directorate of Construction, Office of Construction Standards and Compliance Assistance, fax # 202-693-1689. You can also contact us by mail at the above office, Room N3468, 200 Constitution Avenue, N.W., Washington, D.C. 20210, although there will be a delay in our receiving correspondence by mail.

Sincerely,

Russell B. Swanson, Director
Directorate of Construction

NOTE: OSHA requirements are set by statute, standards and regulations. Our interpretation letters explain these requirements and how they apply to particular circumstances, but they cannot create additional employer obligations. This letter constitutes OSHA=s interpretation of the requirements discussed. Note that our enforcement guidance may be affected by changes to OSHA rules. Also, from time to time we update our guidance in response to new information. To keep apprised of such developments, you can consult OSHA's website at http://www.osha.gov.

TETRA TECH	STANDARD OPERATING PROCEDURES	Number SA-1.3	Page 1 of 31
		Effective Date 04/072008	Revision 9
		Applicability Tetra Tech NUS, Inc.	
		Prepared Earth Sciences Department	
Subject SOIL SAMPLING		Approved Tom Johnston	

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1.0 PURPOSE

This Standard Operating Procedure (SOP) describes the procedures to be used to collect surface, near-surface, and subsurface soil samples. Additionally, it describes the methods for sampling of test pits and trenches to determine subsurface soil and rock conditions and for recovery of small-volume or bulk samples from pits.

2.0 SCOPE

This document applies to the collection of surface, near-surface, and subsurface soil samples exposed through hand digging, hand augering, drilling, or machine excavating at hazardous substance sites for laboratory testing, onsite visual examination, and onsite testing.

3.0 GLOSSARY

Composite Sample - A composite sample is a combination of more than one grab sample from various locations and/or depths and times that is homogenized and treated as one sample. This type of sample is usually collected when determination of an average waste concentration for a specific area is required. Composite samples shall not be collected for volatile organics analysis.

Confined Space - As stipulated in 29 Code of Federal Regulations (CFR) 1910.146, a confined space means a space that: (1) is large enough and so configured that an employee can bodily enter and perform assigned work; (2) has limited or restricted means for entry or exit (e.g., tanks, vessels, silos, storage bins, hoppers, vaults, pits, and excavations); and (3) is not designed for continuous employee occupancy. TtNUS considers all confined space as permit-required confined spaces.

Grab Sample - One sample collected at one location and at one specific time.

Hand Auger - A sampling device used to extract soil from the ground.

Representativeness – A qualitative description of the degree to which an individual sample accurately reflects population characteristics or parameter variations at a sampling point. It is therefore an important characteristic not only of assessment and quantification of environmental threats posed by the site, but also for providing information for engineering design and construction. Proper sample location selection and proper sample collection methods are important to ensure that a truly representative sample has been collected.

Sample for Non-Volatile Analyses - Includes all chemical parameters other than volatile organics (e.g., semivolatiles, pesticides/PCBs, metals, etc.) and those engineering parameters that do not require undisturbed soil for their analysis.

Split-Barrel Sampler - A steel tube, split in half lengthwise, with the halves held together by threaded collars at either end of the tube. Also called a split-spoon sampler, this device can be driven into resistant materials using a drive weight mounted in the drilling string. A standard split-barrel sampler is typically available in two common lengths, providing either 20-inch or 26-inch longitudinal clearance for obtaining 18-inch or 24-inch-long samples, respectively. These split-barrel samplers commonly range in size from 2 to 3.5 inches OD. The larger sizes are commonly used when a larger volume of sample material is required (see Attachment B).

Test Pit and Trench - Open, shallow excavations, typically rectangular (if a test pit) or longitudinal (if a trench), excavated to determine shallow subsurface conditions for engineering, geological, and soil chemistry exploration and/or sampling purposes. These pits are excavated manually or by machine (e.g., backhoe, clamshell, trencher, excavator, or bulldozer).

Thin-Walled Tube Sampler - A thin-walled metal tube (also called a Shelby tube) used to recover relatively undisturbed soil samples. These tubes are available in various sizes, ranging from 2 to 5 inches outside diameter (OD) and from 18 to 54 inches in length.

4.0 RESPONSIBILITIES AND PERSONNEL QUALIFICATIONS

Project Manager - The Project Manager is responsible for determining the sampling objectives, selecting proposed sampling locations, and selecting field procedures used in the collection of soil samples. Additionally, in consultation with other project personnel (geologist, hydrogeologist, etc.), the Project Manager establishes the need for test pits or trenches and determines their approximate locations and dimensions.

Site Safety Officer (SSO) - The SSO (or a qualified designee) is responsible for providing the technical support necessary to implement the project Health and Safety Plan. This will include (but not be limited to) performing air quality monitoring during sampling, boring, and excavation activities and to ensure that workers and offsite (downwind) individuals are not exposed to hazardous levels of airborne contaminants. The SSO/designee may also be required to advise the FOL on other safety-related matters regarding boring, excavation, and sampling, such as mitigative measures to address potential hazards from unstable trench walls, puncturing of drums or other hazardous objects, etc.

Field Operations Leader (FOL) - This individual is primarily responsible for the execution of the planning document containing the Sampling and Analysis Plan (SAP). This is accomplished through management of a field sampling team for the proper acquisition of samples. He or she is responsible for the supervision of onsite analyses; ensuring proper instrument calibration, care, and maintenance; sample collection and handling; the completion and accuracy of all field documentation; and making sure that custody of all samples obtained is maintained according to proper procedures. When appropriate and as directed by the FOL, such responsibilities may be performed by other qualified personnel (e.g., field technicians) where credentials and time permit. The FOL is responsible for finalizing the locations for collection of surface, near-surface, and subsurface (hand and machine borings, test pits/trenches) soil samples. He/she is ultimately responsible for the sampling and backfilling of boreholes, test pits, and trenches and for adherence to Occupational Safety and Health Administration (OSHA) regulations during these operations through self acquisition or through the management of a field team of samplers.

Project Geologist/Sampler - The project geologist/sampler is responsible for the proper acquisition of samples in accordance with this SOP and/or other project-specific documents. In addition, this individual is responsible for the completion of all required paperwork (e.g., sample log sheets, field notebook, boring logs, test pit logs, container labels, custody seals, and chain-of-custody forms) associated with the collection of those samples.

Competent Person - A Competent Person, as defined in 29 CFR 1929.650 of Subpart P - Excavations, means one who is capable of identifying existing and predictable hazards in the surroundings, or working conditions that are unsanitary, hazardous, or dangerous to employees, and who has authorization to take prompt corrective measures to eliminate them.

General personnel qualifications for groundwater sample collection and onsite water quality testing include the following:

- Occupational Safety and Health Administration (OSHA) 40-hour and applicable refresher training.
- Capability of performing field work under the expected physical and environmental (i.e., weather) conditions.

- Familiarity with appropriate procedures for sample documentation, handling, packaging, and shipping.

5.0 HEALTH AND SAFETY

Health and safety precautions are identified for individual sample collection procedures throughout this SOP. In addition to those precautions, the following general hazards may be incurred during sampling activities:

- Knee injuries from kneeling on hard or uneven surfaces
- Slips, trips, and falls
- Cuts and lacerations
- Traffic hazards associated with sampling in parking areas, along roadways and highways.

Methods of avoiding these hazards are provided below.

Knee injuries – If kneeling is required during soil sampling, this could result in knee injuries from stones/foreign objects and general damage due to stress on the joints. To minimize this hazard:

- Clear any foreign objects from the work area.
- Wear hard-sided knee pads.
- Stretch ligaments, tendons and muscles before, during and after. Take breaks as frequently as necessary.
- Report pre-existing conditions to the SSO if you feel this activity will aggravate an existing condition.

Slips, Trips, and Falls – These hazards exist while traversing varying terrains carrying equipment to sample locations. To minimize these hazards:

- Pre-survey sampling locations. Eliminate, barricade, or otherwise mark physical hazards leading to the locations.
- Carry small loads that do not restrict the field of vision.
- Travel the safest and clearest route (not necessarily the shortest).

Cuts and Lacerations - To prevent cuts and lacerations associated with soil sampling, the following provisions are required:

- Always cut away from yourself and others when cutting tubing or rope. This will prevent injury to yourself and others if the knife slips.
- Do not place items to be cut in your hand or on your knee.
- Change blades as necessary to maintain a sharp cutting edge. Many accidents result from struggling with dull cutting attachments.

- Whenever practical, wear cut-resistant gloves (e.g., leather or heavy cotton work gloves) at least on the hand not using the knife.
- Keep cutting surfaces clean and smooth.
- Secure items to be cut – do not hold them against the opposing hand, a leg, or other body part.
- When transporting glassware, keep it in a hard-sided container such as a cooler so that if there is a fall, you will be less likely to get cut by broken glass.
- DO NOT throw broken sample jars or glass ampoules into garbage bags. Place broken glass and glass ampoules in hard-sided containers such as a cardboard box or directly into a dumpster. DO NOT reach into garbage bags to retrieve any item accidentally thrown away. Empty the contents onto a flat surface to avoid punctures and lacerations from reaching where you cannot see.

Vehicular and Foot Traffic Hazards – When sampling along the roadway or near traffic patterns, follow the following precautions:

- Motorists may be distracted by onsite activities – ASSUME THEY DO NOT SEE YOU OR MEMBERS OF YOUR FIELD CREW.
- DO NOT place obstructions (such as vehicles) along the sides of the road that may cause site personnel to move into the flow of traffic to avoid your activities or equipment or that will create a blind spot.
- **Provide a required free space of travel**. Maintain at least 6 feet of space between you and moving traffic. Where this is not possible, use flaggers and/or signs to warn oncoming traffic of activities near or within the travel lanes.
- Face Traffic. Whenever feasible, if you must move within the 6 feet of the required free space or into traffic, attempt to face moving traffic at all times. Always leave yourself an escape route.
- Wear high-visibility vests to increase visual recognition by motorists.
- Do not rely on the vehicle operator's visibility, judgment, or ability. Make eye contact with the driver. Carefully and deliberately use hand signals so they will not startle or confuse motorists or be mistaken for a flagger's direction before moving into traffic.
- Your movements may startle a motorist and cause an accident, so move deliberately. Do not make sudden movements that might confuse a motorist.

6.0 PROCEDURES

The following procedures address surface and subsurface sampling.

CAUTION

Each situation must be evaluated individually to determine the applicability and necessity for obtaining a utility clearance ticket/dig permit. Common sense dictates, prior to digging or boring with power equipment, no matter what the depth, or digging by hand in a manner that could damage unprotected underground utilities, that a dig permit is required. See SOP HS-1.0, Utility Locating and Excavation Clearance, for additional clarification. If you do not know or are unsure as to whether a ticket is necessary – **Get the Ticket**.

6.1 Overview

Soil sampling is an important adjunct to groundwater monitoring. Sampling of the soil horizons above the groundwater table can detect contaminants before they migrate to the water table, and can establish the amount of contamination absorbed or adsorbed on aquifer solids that have the potential of contributing to groundwater contamination.

Soil types can vary considerably on a hazardous waste site. These variations, along with vegetation, can affect the rate of contaminant migration through the soil. It is important, therefore, that a detailed record be maintained during sampling operations, particularly noting sampling locations, depths, and such characteristics as grain size, color, and odor. Subsurface conditions are often stable on a daily basis and may demonstrate only slight seasonal variation especially with respect to temperature, available oxygen and light penetration. Changes in any of these conditions can radically alter the rate of chemical reactions or the associated microbiological community, thus further altering specific site conditions. Certain vegetation species can create degradation products that can alter contaminant concentrations in soil. This is why vegetation types and extent of degradation of this foliage must be recorded. To prevent degradation, samples must be kept at their at-depth temperature or lower, protected from direct light, sealed tightly in approved glass containers, and be analyzed as soon as possible after collection. In addition, to the extent possible, vegetation should be removed from the sample.

The physical properties of the soil, its grain size, cohesiveness, associated moisture, and such factors as depth to bedrock and water table, will limit the depth from which samples can be collected and the method required to collect them. It is the intent of this document to present the most commonly employed soil sampling methods used at hazardous waste sites.

6.2 Soil Sample Collection

6.2.1 Procedure for Preserving and Collecting Soil Samples for Volatile Organic Compound Analysis

Samples collected using traditional methods such as collection in a jar with no preservation have been known to yield non-representative samples due to loss of volatile organic compounds (VOCs). To prevent such losses, preservation of samples with methanol or sodium bisulfate may be used to minimize volatilization and biodegradation. This preservation may be performed either in the field or laboratory, depending on the sampling methodology employed. Because of the large number of sampling methods and associated equipment required, careful coordination between field and laboratory personnel is needed.

Soil samples to be preserved by the laboratory are currently being collected using Method SW-846, 5035. For samples preserved in the field, laboratories are currently performing low-level analyses (sodium bisulfate preservation) and high- to medium-level analyses (methanol preservation) depending on the needs of the end user.

The following procedures outline the necessary steps for collecting soil samples to be preserved at the laboratory, and for collecting soil samples to be preserved in the field with methanol or sodium bisulfate.

6.2.1.1 Soil Samples to be Preserved at the Laboratory

Soil samples collected for volatile organic analysis that are to be preserved at the laboratory shall be obtained using a hermetically sealed sample vial such as an EnCore™ sampler. Each sample shall be

obtained using a reusable sampling handle (T-handle) that can be provided with the EnCore™ sampler when requested and purchased. Collect the sample in the following manner for each EnCore™ sampler:

1. Scene Safety - Evaluate the area where sampling will occur. Ensure that the area is safe from physical, chemical, and natural hazards. Clear or barricade those hazards that have been identified.

2. Wear the appropriate personal protective equipment (PPE). This will include, at a minimum, safety glasses and nitrile surgeon's gloves. If you must kneel on the ground or place equipment on the surface being sampled, cover the ground surface with plastic to minimize surface contamination of your equipment and clothing. Wear knee pads to protect your knees from kneeling on hard or uneven surfaces.

3. Load the Encore™ sampler into the T-handle with the plunger fully depressed.

4. Expose the area to be sampled using a hand trowel or similar device to remove surface debris.

5. Press the T-handle against the freshly exposed soil surface, forcing soil into the sampler. The plunger will be forced upward as the cavity fills with soil.

6. When the sampler is full, rotate the plunger and lock it into place. If the plunger does not lock, the sampler is not full. This method ensures there is no headspace. Soft soil may require several plunges or forcing soil against a hard surface such as a sample trowel to ensure that headspace is eliminated.

7. Use a paper towel to remove soil from the side of the sampler so a tight seal can be made between the sample cap and the rubber O-ring.

8. With soil slightly piled above the rim of the sampler, force the cap on until the catches hook the side of the sampler.

9. Remove any surface soil from the outside of the sampler and place in the foil bag provided with the sampler. Good work hygiene practices and diligent decontamination procedures prevents the spread of contamination even on the outside of the containers.

10. Label the bag with appropriate information in accordance with SOP SA-6.3.

11. Place the full sampler inside a lined cooler with ice and cool to 4˚C ± 2 ˚C. Make sure any required trip blanks and temperature blanks are also in the cooler. Secure custody of the cooler in accordance with SOP SA-6.3.

12. Typically, collect three Encore™ samplers at each location. Consult the SAP or laboratory to determine the required number of Encore™ samplers to be collected.

13. The T-handle shall be decontaminated before moving to the next interval or location using a soap and water wash and rinse, and where applicable, the selected solvent as defined in the project planning documents.

Using this type of sampling device eliminates the need for field preservation and the shipping restrictions associated with preservatives. A complete set of instructions is included with each Encore™ sampler.

After the Encore™samples are collected, they should be placed on ice immediately and delivered to the laboratory within 48 hours (following the chain-of-custody and documentation procedures outlined in SOP SA-6.1). Samples must be preserved by the laboratory within 48 hours of sample collection.

6.2.1.2 Soil Samples to be Preserved in the Field

Soil samples preserved in the field may be prepared for analyses using both the low-level (sodium bisulfate preservation) and high- to medium-level (methanol preservation) methods.

Safety Reminder

When using chemicals in the field to preserve samples, the FOL and/or SSO must ensure that Materials Safety Data Sheets (MSDSs) have been provided with the chemicals to be used. They also must ensure that these chemicals have been added to the Chemical Inventory List contained within Section 5.0, Hazard Communication, of your Health and Safety Guidance Manual (HSGM). Lastly, but most importantly, the FOL and/or SSO must review the hazards with personnel using these chemicals and ensure that provisions are available for recommended PPE and emergency measures (e.g., eyewash, etc.).

Methanol Preservation (High to Medium Level):

Bottles may be pre-spiked with methanol in the laboratory or prepared in the field. Soil samples to be preserved in the field with methanol shall utilize 40 to 60 mL glass vials with septum-lined lids. Each sample bottle shall be filled with 25 mL of demonstrated analyte-free purge-and-trap grade methanol. The preferred method for adding methanol to the sample bottle is by removing the lid and using a pipette or scaled syringe to add the methanol directly to the bottle.

CAUTION

NEVER attempt to pipette by mouth

In situations where personnel are required to spike the septum using a hypodermic needle, the following provisions for handling sharps must be in place:

- Training of personnel regarding methods for handling of sharps
- Hard-sided containers for the disposal of sharps
- Provisions for treatment in cases where persons have received a puncture wound

Soil shall be collected with the use of a decontaminated (or disposable), small-diameter coring device such as a disposable tube/plunger-type syringe with the tip cut off. The outside diameter of the coring device must be smaller than the inside diameter of the sample bottle neck.

A small electronic balance or manual scale will be necessary for measuring the volume of soil to be added to the methanol-preserved sample bottle. Calibration of the scale shall be performed prior to use and intermittently throughout the day according to the manufacturer's requirements.

The sample should be collected as follows:

1. Weigh the unused syringe and plunger to the nearest 0.01 gram.

2. Pull the plunger back and insert the syringe into the soil to be sampled.

3. Collect 8 to 12 grams of soil by pushing the syringe barrel into the soil.

4. Weigh the sample and adjust until obtaining the required amount of sample.

5. Record the sample weight to the nearest 0.01 gram in the field logbook and/or on the sample log sheet.

6. Extrude the weighed soil sample into the methanol-preserved sample bottle taking care not to contact the sample container with the syringe.

7. If dirty, wipe soil particles from the threads of the bottle and cap. Cap the bottle tightly.

8. After capping the bottle, swirl the sample (do not shake) in the methanol and break up the soil such that all of the soil is covered with methanol.

9. Place the sample on ice immediately and prepare for shipment to the laboratory as described in SOP SA-6.1.

Sodium Bisulfate Preservation (Low Level):

> ***CAUTION***
> Care should be taken when adding the soil to the sodium bisulfate solution. A chemical reaction of soil containing carbonates (limestone) may cause the sample to effervesce or the vial to possibly explode. To avoid this hazard or hazards of this type, a small sample aliquot should be subjected to the sample preservative. If it effervesces in an open air environment, utilize an alternative method such as Encore™ or 2-ounce jar.

Bottles may be prepared in the laboratory or in the field with sodium bisulfate solution. Samples to be preserved in the field using the sodium bisulfate method are to be prepared and collected as follows:

1. Add 1 gram of sodium bisulfate to 5 mL of laboratory-grade deionized water in a 40 to 60 mL glass vial with septum-lined lid.

2. Collect the soil sample and record the sample weight to the nearest 0.01 gram in the field logbook or on the sample log sheet as described for methanol preservation

3. Add the weighed sample to the sample vial.

4. Collect duplicate samples using the methanol preservation method on a one-for-one sample basis because it is necessary for the laboratory to perform both low-level and medium-level analyses.

5. Place the samples on ice immediately and prepare for shipment to the laboratory as described in SOP SA-6.1.

> ***NOTE***
> If lower detection limits are necessary, an option to field preserving with sodium bisulfate may be to collect EnCore™ samplers at a given sample location. Consult the planning documents to determine whether this is required. If it is, collect samples in accordance with the Encore™ sampling procedure above and then send all samplers to the laboratory to perform the required preservation and analyses.

6.2.2 Procedure for Collecting Soil Samples for Non-Volatile Analyses

Samples collected for non-volatile analyses may be collected as either grab or composite samples as follows:

1. With a stainless steel trowel or other approved tool, transfer a portion of soil to be sampled to a stainless steel bowl or disposable inert plastic tray.

2. Remove roots, vegetation, sticks, and stones larger than the size of a green pea.

3. Thoroughly mix the soil in the bowl or tray to obtain as uniform a texture and color as practicable. The soil type, moisture content, amount of vegetation, and other factors may affect the amount of time required to obtain a properly mixed sample. In some cases, it may be impossible to obtain a uniform sample appearance. Use the field logbook to describe any significant difficulties encountered in obtaining a uniform mixture.

4. Transfer the mixed soil to the appropriate sample containers and close the containers.

5. Label the sample containers in accordance with SOP SA-6.3.

6. Place the containers in a cooler of ice as soon after collection as possible.

7. Prepare the sample shipment and ship the samples in accordance with SOP SA-6.1.

> ***NOTE***
> Cooling may not be required for some samples depending on the scheduled analyses. Consult the planning documents if in doubt regarding correct sample preservation conditions. When in doubt – Cool to 4˚C.

> ***NOTE***
> Head space is permitted in soil sample containers for non-volatile analyses to allow for sample expansion.

6.2.3 Procedure for Collecting Undisturbed Soil Samples

> ***NOTE***
> Use of thin-walled undisturbed tube samplers is restricted by the consistency of the soil to be sampled. Often, very loose and/or wet samples cannot be retrieved by the samplers, and soil with a consistency in excess of very stiff cannot be penetrated by the sampler. Devices such as Dennison or Pitcher core samplers can be used to obtain undisturbed samples of stiff soil. Using these devices normally increases sampling costs, and therefore their use should be weighed against the need for acquiring an undisturbed sample. These devices are not discussed in this SOP because they are not commonly used.

When it is necessary to acquire undisturbed samples of soil for purposes of engineering parameter analysis (e.g., permeability), a thin-walled, seamless tube sampler (Shelby tube) shall be employed using the following collection procedure:

1. In preparation for sampling utilizing a drill rig, field personnel must complete the following activities:

   - Ensure that all subsurface drilling activities are preceded by a utility clearance for the area to be investigated. This includes activities described in SOP HS-1.0, Utility Location and Excavation Clearance, as well as any location-specific procedures that may apply.

REMEMBER
If you are digging near a marked utility (within the diameter of an underground utility that has been marked plus 18 inches), you must first locate the utility through vacuum extraction or hand digging to ensure that your activities will not damage the utility.

- Complete an Equipment Inspection Checklist for the drill rig or direct-push technology (DPT) rig. This checklist will be provided in the HASP.
- Review the Safe Work Permit prior to conducting the activity.
- Review the activity to be conducted.

2. Remove all surface debris (e.g., vegetation, roots, twigs, etc.) from the specific sampling location and drill and/or clean out the borehole to the desired sampling depth. Be careful to minimize potential disturbance of the material to be sampled. In saturated material, withdraw the drill bit slowly to prevent loosening of the soil around the borehole and to maintain the water level in the hole at or above groundwater level.

CAUTION
The use of bottom-discharge bits or jetting through an open-tube sampler to clean out the borehole shall not be allowed. Only the use of side-discharge bits is permitted.

3. Determine whether a stationary piston-type sampler is required to limit sample disturbance and aid in retaining the sample. Either the hydraulically operated or control rod activated-type of stationary piston sampler may be used.

4. Prior to inserting the tube sampler into the borehole, check to ensure that the sampler head contains a check valve. The check valve is necessary to keep water in the rods from pushing the sample out the tube sampler during sample withdrawal. In addition, the check valve maintains a positive suction within the tube to help retain the sample.

5. A stainless steel tube sampler is typically used to minimize chemical reaction between the sample and the sampling tube.

6. With the sampling tube resting on the bottom of the hole and the water level in the boring at groundwater level or above, push the tube into the soil with a continuous and rapid motion, without impacting or twisting. If the soil is too hard to penetrate by pushing alone, careful hammering may be used by minimizing drop distance (tapping) of the hammer. Before pulling the tube, turn it at least one revolution to shear the sample off at the bottom. In no case shall the tube be pushed farther than the length provided for the soil sample. Allow about 3 inches in the tube for cuttings and sludge.

7. Upon removal of the sampling tube from the hole, measure the length of sample in the tube and also the length penetrated.

8. Remove disturbed material in the upper end of the tube and measure the length of sample again.

9. After removing at least 1 inch of soil from the lower end, place enough packing material (clean inert material such as paper or cloth) tightly in each end of the Shelby tube and then pour melted wax into each end to make at least a ½-inch wax plug and then add more packing material to fill the voids at both ends.

10. Place plastic caps on the ends, tape the caps in place, and dip the ends in wax to prevent loss of soil.

11. Affix label(s) to the tube as required and record sample number, depth, penetration, and recovery length on the label.

12. Mark the "up" direction on the side and upper end of the tube with indelible ink.

13. Complete a chain-of-custody form (see SOP SA-6.3) and other required forms (including Attachment A of this SOP).

14. Ship samples protected with suitable resilient packing material to reduce shock, vibration, and disturbance.

CAUTION

To preserve sample integrity do not allow tubes to freeze, and store the samples vertically with the same orientation they had in the ground, (i.e., top of sample is up) in a cool place out of the sun at all times.

CAUTION

A primary concern in the preparation of the wax plugs is the potential for the heat source and melted wax to cause a fire and/or burns. Follow the directions below to prevent injury or fire.

Electrical Heating

Using hot plates to melt the wax is acceptable. In an outdoor setting, make sure a Ground Fault Circuit Interrupter (GFCI) is employed within the electrical circuit. If a portable generator is used, ensure that the generator is an adequate distance from the sampling operation (at least 50 feet). Ensure that the extension cord is rated for the intended load and for outdoor use and is free from recognizable damage. Ensure flammable preservatives are not employed or stored near the hot plate. Although a Hot Work Permit is not required, scene safety evaluation by site personnel of the above elements is. As always, if a fire potential exists, the provisions for extinguishing must be immediately accessible as well as any provisions for first aid measures.

Open Flame

If an open flame is used, the following provisions are necessary:

- Complete a Hot Work Permit and any local permit required for elevated temperature applications. The Hot Work Permit, provided in your HASP, will aid the FOL and/or the SSO in ensuring that fire protection provisions (extinguishers, fire watches, etc.) are in place as well as ensuring that local requirements have been addressed.

- Ensure that water is available to address any wax splashes or contact. If possible, immerse the contacted area. Where this is not possible, run water over the area and apply cold compresses. The need for medical attention or first aid shall be determined on site under the direction of the SSO.

6.3 Surface Soil Sampling

The simplest, most direct method of collecting surface soil samples for subsequent analysis is by use of a stainless steel shovel, hand auger, soil corer, or stainless steel or disposable plastic trowel.

> ***NOTE***
> Multiple depth intervals are used to describe surface soil. Sometimes surface soil is defined as soil from 0 to 2 inches below ground surface (bgs), and sometimes it is defined as soil from other depths such as 0 to 2 feet bgs. Ensure that the definition of surface soil depth is clear before collecting surface soil samples.
>
> For the purposes of instruction, the terms "surface soil" and "near-surface soil" are used in this SOP as follows:
>
> - Surface soil - 0 to 6 inches bgs
> - Near-surface soil - 6 to 18 inches bgs
>
> If these intervals are defined differently in the planning documents, substitute the appropriate depth ranges.

In general, the following equipment is necessary for obtaining surface soil samples:

- Stainless steel or pre-cleaned disposable trowel.
- Stainless steel hand auger, soil corer, or shovel.
- Real-time air monitoring instrument (e.g., PID, FID) as directed in project planning document.
- Required PPE.
  - Nitrile surgeon's or latex gloves may be used, layered as necessary.
  - Safety glasses
  - Other – Items identified on the Safe Work Permit may be required based on location-specific requirements such as hearing protection, steel-toed work boots, and a hard hat when working near a drill rig. These provisions will be listed in the HASP or directed by the FOL and/or SSO.

> ***Safety Reminder***
> The use of latex products may elicit an allergic reaction in some people. Should this occur, remove the latex gloves, treat for an allergic reaction, and seek medical attention as necessary.

- Required paperwork (see SOP SA-6.3 and Attachment A of this SOP)
- Required decontamination equipment
- Required sample container(s)
- Wooden stakes or pin flags

- Sealable polyethylene bags (e.g., Ziploc® baggies)
- Heavy duty cooler
- Ice
- Chain-of-custody records and custody seals

When acquiring surface soil samples, use the following procedure:

1. Place padding or use knee pads when kneeling near the sample location. If necessary, place plastic sheeting to provide a clean surface for sample equipment to avoid possible cross- contamination.
2. Carefully remove vegetation, roots, twigs, litter, etc. to expose an adequate soil surface area to accommodate sample volume requirements.
3. Using a precleaned syringe or EnCore™ samplers, follow the procedure in Section 6.2.1 for collecting surface soil samples for volatile analysis. Surface soil samples for volatile organic analysis should be collected deeper than 6 inches bgs because shallower material has usually lost most of the volatiles through evaporation. Ensure that the appropriate surface soil depth is being analyzed in accordance with the planning document.
4. Using decontaminated sampling tools, thoroughly mix in place a sufficient amount of soil to fill the remaining sample containers. See Section 6.5 of this procedure for hand auger instruction, as needed.
5. Transfer the sample into those containers utilizing a stainless steel trowel.
6. Cap and securely tighten all sample containers.
7. Affix a sample label to each container. Be sure to fill out each label carefully and clearly, addressing all the categories described in SOP SA-6.3.
8. Proceed with the handling and processing of each sample container as described in SOP SA-6.2.
9. Site restoration – Whenever removing sample materials, always restore the surface. It is our intent to leave the area better than we found it. Do NOT create trip hazards in areas when pedestrian traffic may exist.

6.4 Near-Surface Soil Sampling

Collection of samples from near the surface (depth of 6 to 18 inches) can be accomplished with tools such as shovels, hand auger, soil corers, and stainless steel or pre-cleaned disposable trowels and the equipment listed under Section 6.5 of this procedure.

To obtain near-surface soil samples, the following protocol shall be used:

1. With a clean shovel, make a series of vertical cuts in the soil to the depth required to form a square approximately 1 foot by 1 foot.
2. Lever out the formed plug and scrape the bottom of the freshly dug hole with a decontaminated stainless steel or pre-cleaned disposable trowel to remove any loose soil.

3. Follow steps 1 through 9 of Section 6.3.

6.5 Subsurface Soil Sampling With a Hand Auger

A hand augering system generally consists of a variety of stainless steel bucket bits (approximately 6.5 inches long and 2, 2.75, 3.25, and 4 inches in diameter), series of extension rods (available in 2-, 3-, 4- and 5-inch lengths), and a T-handle connected to extension rods and to the auger bucket. A larger-diameter bucket bit is commonly used to bore a hole to the desired sampling depth and then it is withdrawn. The larger-diameter bit is then replaced with a smaller-diameter bit, lowered down the hole, and slowly turned into the soil to the completion depth (approximately 6 inches). The apparatus is then withdrawn and the soil sample collected.

The hand auger can be used in a wide variety of soil conditions. It can be used to sample soil either from the surface, or to depths in excess of 12 feet. However, the presence of subsurface rocks and landfill material and collapse of the borehole normally limit sampling depth.

To accomplish soil sampling using a hand augering system, the following equipment is required:

- Complete hand auger assembly (variety of bucket bit sizes)
- Stainless steel mixing bowls
- The equipment listed in Section 6.3
- Miscellaneous hand tools as required to assemble and disassemble the hand auger units

CAUTION

Potential hazards associated with hand augering include:

- Muscle strain and sprain due to over twisting and/or over compromising yourself.
- Equipment failure due to excessive stress on the T-handle or rods through twisting. Failure of any of these components will result in a sudden release and potential injury due to that failure.

As in all situations, any intrusive activities that could damage underground utilities shall be proceeded by a Dig/Excavation permit/ticket. Call the Utility Locating service in the area or your Project Health and Safety Officer for more information. When in doubt – **Get the Ticket!**

To obtain soil samples using a hand auger, use the following procedure:

1. Wearing designated PPE, attach a properly decontaminated bucket bit to a clean extension rod and attach the T-handle to the extension rod.
2. Clear the area to be sampled of any surface debris (vegetation, twigs, rocks, litter, etc.).
3. Twist the bucket into the ground while pushing vertically downward on the auger. The cutting shoes fill the bucket as it is advanced into the ground.
4. As the auger bucket fills with soil, periodically remove any unneeded soil.

5. Add rod extensions as necessary to extend the reach of the auger. Also, note (in a field notebook, boring log, and/or on a standardized data sheet) any changes in the color, texture or odor of the soil as a function of depth. The project-specific planning document (SAP, HASP, etc.) describe requirements for scanning the soil with a real-time air monitoring instrument (e.g., PID, FID, etc.) and recording the measurements.

6. After reaching the desired depth (e.g., the top of the interval to be sampled), slowly and carefully withdraw the apparatus from the borehole to prevent or minimize movement of soil from shallower intervals to the bottom of the hole.

7. Remove the soiled bucket bit from the rod extension and replace it with another properly decontaminated bucket bit. The bucket bit used for sampling is to be smaller in diameter than the bucket bit employed to initiate the borehole.

8. Carefully lower the apparatus down the borehole. Care must be taken to avoid scraping the borehole sides.

9. Slowly turn the apparatus until the bucket bit is advanced approximately 6 inches.

10. Discard the top of the core (approximately 1 inch), which represents any loose material collected by the bucket bit before penetrating the sample material.

11. Using a precleaned syringe or EnCore™ samplers, follow the procedure in Section 6.2.1 for collecting a soil sample for volatile compound analysis directly from the bucket bit.
12. Utilizing a properly decontaminated stainless steel trowel or dedicated disposable trowel, remove the remaining sample material from the bucket bit and place into a properly decontaminated stainless steel mixing bowl.

13. Homogenize the sample material as thoroughly as practicable then fill the remaining sample containers. Refer to Section 6.2.2.

14. Follow steps 4 through 7 listed in Section 6.3.

6.5.1 Sampling Using Stainless Steel Soil Corers

A soil corer is a stainless steel tube equipped with a cutting shoe and sample window in the side. The soil corer is advanced into the soil by applying downward pressure (body weight). The soil is unloaded by then forcing a ram towards the cutting shoe, which results in the discharge of the soil core through a window in the sleeve.

Use, application, and sample protocol is the same as for hand augering provided above, but without necessarily rotating the corer while advancing it.

SAFETY REMINDER

Hand augering and soil corer sampling can be physically demanding based on the type of geology and subsurface encumbrances encountered. Soil coring has some added hazards such the corer collapsing under your weight. To reduce the potential for muscle strain and damage, the following measures will be incorporated:

- Stretch and limber your muscles before heavy exertion. This hazard becomes more predominant in the early morning hours (prior to muscles becoming limber) and later in the day (as a result of fatigue).

- Job rotation – Share the duties so that repetitive actions do not result in fatigue and injury.

- Increase break frequencies as needed, especially as ambient conditions of heat and/or cold stress may dictate.

- Do not force the hand tools or use cheater pipes or similar devices to bypass an obstruction. Move to another location near the sampling point. Exerting additional forces on the sampling devices can result in damage and/or failure that could potentially injure someone in the immediate vicinity.

- Do not over compromise yourself when applying force to the soil corer or hand auger. If there is a sudden release, it could result in a fall or muscle injury due to strain.

6.6 Subsurface Soil Sampling with a Split-Barrel Sampler

A split-barrel (split-spoon) sampler consists of a heavy carbon steel or stainless steel sampling tube that can be split into two equal halves to reveal the soil sample (see Attachment B). A drive head is attached to the upper end of the tube and serves as a point of attachment for the drill rod. A removable tapered nosepiece/drive shoe attaches to the lower end of the tube and facilitates cutting. A basket-like sample retainer can be fitted to the lower end of the split tube to hold loose, dry soil samples in the tube when the sampler is removed from the drill hole. This split-barrel sampler is made to be attached to a drill rod and forced into the ground by means of a 140-pound or larger casing driver.

Safety Reminder

It is intended through the Equipment Inspection for Drill Rigs form provided in the HASP that the hammer and hemp rope, where applicable, associated with this activity will be inspected (no physical damage is obvious), properly attached to the hammer (suitable knots or sufficient mechanical devices), and is in overall good condition.

Split-barrel samplers are used to collect soil samples from a wide variety of soil types and from depths greater than those attainable with other soil sampling equipment.

The following equipment is used for obtaining split-barrel samples:

- Drilling equipment (provided by subcontractor).
- Split-barrel samplers (2-inch OD, 1-3/8-inch ID, either 20 inches or 26 inches long); Larger OD samplers are available if a larger volume of sample is needed.
- Drive weight assembly, 140-pound weight, driving head, and guide permitting free fall of 30 inches.
- Stainless steel mixing bowls.
- Equipment listed in Section 6.3.

The following steps shall be followed to obtain split-barrel samples (Steps 1 through 4 are typically performed by the drilling subcontractor):

1. Attach the split-barrel sampler to the sampling rods.

2. Lower the sampler into the borehole inside the hollow stem auger bits.

3. Advance the split-barrel sampler by hammering the length (typically 18 or 24 inches) of the split-barrel sampler into the soil using 140-pound or larger hammer.

4. When the desired depth is achieved, extract the drill rods and sampler from the augers and/or borehole.

5. Detach the sampler from the drill rods.

6. Place the sampler securely in a vise so it can be opened using pipe wrenches.

> ***CAUTION***
> Pipe wrenches are used to separate the split spoon into several components. The driller's helper should not apply excessive force through the use of cheater pipes or push or pull in the direction where, if the wrench slips, hands or fingers will be trapped against an immovable object.

7. Remove the drive head and nosepiece with the wrenches, and open the sampler to reveal the soil sample.

8. Immediately scan the sample core with a real-time air monitoring instrument (e.g., FID, PID, etc.) (as project-specific planning documents dictate). Carefully separate (or cut) the soil core, with a decontaminated stainless steel knife or trowel, at about 6-inch intervals while scanning the center of the core for elevated readings. Also scan stained soil, soil lenses, and anomalies (if present), and record readings.

9. If elevated vapor readings were observed, collect the sample scheduled for volatile analysis from the center of the core where elevated readings occurred. If no elevated readings where encountered, the sample material should be collected from the core's center (this area represents the least disturbed area with minimal atmospheric contact) (refer to Section 6.2.1).

10. Using the same trowel, remove remaining sample material from the split-barrel sampler (except for the small portion of disturbed soil usually found at the top of the core sample) and place the soil into a decontaminated stainless steel mixing bowl.

11. Homogenize the sample material as thoroughly as practicable then fill the remaining sample containers (refer to Section 6.2.2).

12. Follow steps 4 through 7 in Section 6.3.

6.7 Subsurface Soil Sampling Using Direct-Push Technology

Subsurface soil samples can be collected to depths of 40+ feet using DPT. DPT equipment, responsibilities, and procedures are described in SOP SA-2.5.

6.8 Excavation and Sampling of Test Pits and Trenches

6.8.1 Applicability

This subsection presents routine test pit or trench excavation techniques and specialized techniques that are applicable under certain conditions.

CAUTION

During the excavation of trenches or pits at hazardous waste sites, several health and safety concerns arise from the method of excavation. No personnel shall enter any test pit or excavation over 4 feet deep except as a last resort, and then only under direct supervision of a Competent Person (as defined in 29 CFR 1929.650 of Subpart P - Excavations). Whenever possible, all required chemical and lithological samples should be collected using the excavator bucket or other remote sampling apparatus. If entrance is required, all test pits or excavations must be stabilized by bracing the pit sides using specifically designed wooden, steel, or aluminum support structures or through sloping and benching. Personnel entering the excavation may be exposed to toxic or explosive gases and oxygen-deficient environments; therefore, monitoring will be conducted by the Competent Person to determine if it is safe to enter. Any entry into a trench greater than 4 feet deep will constitute a Confined Space Entry and must be conducted in conformance with OSHA standard 29 CFR 1910.146. In all cases involving entry, substantial air monitoring, before entry, appropriate respiratory gear and protective clothing determination, and rescue provisions are mandatory. There must be at least three people present at the immediate site before entry by one of the field team members. This minimum number of people will increase based on the potential hazards or complexity of the work to be performed. The reader shall refer to OSHA regulations 29 CFR 1926.650, 29 CFR 1910.120, 29 CFR 1910.134, and 29 CFR 1910.146. High-hazard entries such as this will be supported by members of the Health Sciences Group professionally trained in these activities.

Excavations are generally not practical where a depth of more than about 15 to 20-feet is desired, and they are usually limited to a few feet below the water table. In some cases, a pumping system may be required to control water levels within the pit, providing that pumped water can be adequately stored or disposed. If soil data at depths greater than 15-feet are required, the data are usually obtained through test borings instead of test pits.

In addition, hazardous wastes may be brought to the surface by excavation equipment. This material, whether removed from the site or returned to the subsurface, must be properly handled according to any and all applicable federal, state, and local regulations.

6.8.2 Test Pit and Trench Excavation

Test pits or trench excavations are constructed with the intent that they will provide an open view of subsurface lithology and/or disposal conditions that a boring will not provide. These procedures describe the methods for excavating and logging test pits and trenches installed to determine subsurface soil and rock conditions. Test pit operations shall be logged and documented (see Attachment C).

Test pits and trenches may be excavated by hand or power equipment to permit detailed descriptions of the nature and contamination of the in-situ materials. The size of the excavation will depend primarily on the following:

- The purpose and extent of the exploration

- The space required for efficient excavation
- The chemicals of concern
- The economics and efficiency of available equipment

Test pits normally have a cross section that is 4 to 10 feet square; test trenches are usually 3 to 6 feet wide and may be extended for any length required to reveal conditions along a specific line. The following table provides guidelines for design consideration based on equipment efficiencies.

Equipment	Typical Widths, in Feet
Trenching machine	0.25 to 1.0
Backhoe/Track Hoe	2 to 6

The lateral limits of excavation of trenches and the position of test pits shall be carefully marked on area base maps. If precise positioning is required to indicate the location of highly hazardous materials, nearby utilities, or dangerous conditions, the limits of the excavation shall be surveyed. Also, if precise determination of the depth of buried materials is needed for design or environmental assessment purposes, the elevation of the ground surface at the test pit or trench location shall also be determined by survey. If the test pit/trench will not be surveyed immediately, it shall be backfilled and its position identified with stakes placed in the ground at the margin of the excavation for later surveying.

The construction of test pits and trenches shall be planned and designed in advance as much as possible. However, the following field conditions may necessitate revisions to the initial plans:

- Subsurface utilities
- Surface and subsurface encumbrances
- Vehicle and pedestrian traffic patterns
- Purpose for excavation (e.g., the excavation of potential ordnance items)

The final depth and construction method shall be collectively determined by the FOL and designated Competent Person. The actual layout of each test pit, temporary staging area, and spoils pile may further be predicated based on site conditions and wind direction at the time the test pit is excavated. Prior to excavation, the area may be surveyed by magnetometer or metal detector or other passive methods specified in SOP HS1.0, Utility Location and Excavation Clearance, to identify the presence of underground utilities or drums. Where possible, the excavator should be positioned upwind and preferably within an enclosed cab.

No personnel shall enter any test pit or excavation except as a last resort, and then only under direct supervision of a Competent Person. If entrance is required, OSHA requirements must be met (e.g., walls must be braced with wooden or steel braces, ladders must be placed for every 25 feet of lateral travel and extended 3 feet above ground surface). A temporary guard rail or vehicle stop must be placed along the surface of the hole before entry in situations where the excavation may be approached by traffic. Spoils will be stockpiled no closer than 2 feet from the sidewall of the excavation. The excavation equipment operator shall be careful not to undercut sidewalls and will, where necessary, bench back to increase stability. The top cover, when considered clean, will be placed separately from the subsurface materials to permit clean cover. It is emphasized that the project data needs should be structured such that required samples can be collected without requiring entrance into the excavation. For example,

samples of leachate, groundwater, or sidewall soil can be collected with telescoping poles or similar equipment.

Dewatering and watering may be required to ensure the stability of the side walls, to prevent the bottom of the pit from heaving, and to keep the excavation stable. This is an important consideration for excavations in cohesionless material below the groundwater table and for excavations left open greater than a day. Liquids removed as a result of dewatering operations must be handled as potentially contaminated materials. Procedures for the collection and disposal of such materials should be discussed in the site-specific project plans.

Where possible excavations and test pits shall be opened and closed within the same working day. Where this is not possible, the following engineering controls shall be put in place to control access:

- Trench covers/street plates
- Fences encompassing the entire excavation intended to control access
- Warning signs warning personnel of the hazards
- Amber flashing lights to demarcate boundaries of the excavation at night

Excavations left open will have emergency means to exit should someone accidentally enter.

6.8.3 Sampling in Test Pits and Trenches

6.8.3.1 General

Log test pits and trenches as they are excavated in accordance with the Test Pit Log presented in Attachment C. These records include plan and profile sketches of the test pit/trench showing materials encountered, their depth and distribution in the pit/trench, and sample locations. These records also include safety and sample screening information.

Entry of test pits by personnel is extremely dangerous, shall be avoided unless absolutely necessary, and can occur only after all applicable health and safety and OSHA requirements have been met as stated above. These provisions will be reiterated as appropriate in the project-specific HASP.

The final depth and type of samples obtained from each test pit will be determined at the time the test pit is excavated. Sufficient samples are usually obtained and analyzed to quantify contaminant distribution as a function of depth for each test pit. Additional samples of each waste phase and any fluids encountered in each test pit may also be collected.

In some cases, samples of soil may be extracted from the test pit for reasons other than waste sampling and chemical analysis, for instance, to obtain geotechnical information. Such information includes soil types, stratigraphy, strength, etc., and could therefore entail the collection of disturbed (grab or bulk) or relatively undisturbed (hand-carved or pushed/driven) samples that can be tested for geotechnical properties. The purposes of such explorations are very similar to those of shallow exploratory or test borings, but often test pits offer a faster, more cost-effective method of sampling than installing borings.

6.8.3.2 Sampling Equipment

The following equipment is needed for obtaining samples for chemical or geotechnical analysis from test pits and trenches:

- Backhoe or other excavating machinery.
- Shovels, picks, hand augers, and stainless steel trowels/disposable trowels.
- Sample container - bucket with locking lid for large samples; appropriate bottle ware for chemical or geotechnical analysis samples.
- Polyethylene bags for enclosing sample containers; buckets.
- Remote sampler consisting of 10-foot sections of steel conduit (1-inch-diameter), hose clamps, and right angle adapter for conduit (see Attachment D).

6.8.3.3 Sampling Methods

The methods discussed in this section refer to test pit sampling from grade level. If test pit entry is required, see Section 6.8.3.4.

- Excavate the trench or pit in several 0.5- to 1.0-foot depth increments. Where soil types support the use of a sand bar cutting plate, use of this device is recommended to avoid potentially snagging utilities with the excavator teeth. It is recommended that soil probes or similar devices be employed where buried items or utilities may be encountered. This permits the trench floor to be probed prior to the next cut.
- After each increment:
  - the operator shall wait while the sampler inspects the test pit from grade level
  - the sampler shall probe the next interval where this is considered necessary. Practical depth increments for lithological evaluations may range from 2 to 4 feet i or where lithological changes are noted.
- The backhoe operator, who will have the best view of the test pit, shall immediately cease digging if:
  - Any fluid phase, including groundwater seepage, is encountered in the test pit
  - Any drums, other potential waste containers, obstructions, or utility lines are encountered
  - Distinct changes of material being excavated are encountered

This action is necessary to permit proper sampling of the test pit and to prevent a breach of safety protocol. Depending on the conditions encountered, it may be required to excavate more slowly and carefully with the backhoe.

For obtaining test pit samples from grade level, the following procedure shall be followed:

- Use the backhoe to remove loose material from the excavation walls and floor to the greatest extent possible.
- Secure the walls of the pit, if necessary. (There is seldom any need to enter a pit or trench that would justify the expense of shoring the walls. All observations and samples should be taken from the ground surface.)

- Samples of the test pit material are to be obtained either directly from the backhoe bucket or from the material after it has been deposited on the ground, as follows:

  a. The sampler or FOL shall direct the backhoe operator to remove material from the selected depth or location within the test pit/trench.

  b. The backhoe operator shall bring the bucket over to a designated location on the sidewall a sufficient distance from the pit (at least 5 feet) to allow the sampler to work around the bucket.

  c. After the bucket has been set on the ground, the backhoe operator shall either disengage the controls or shut the machine down.

  d. When signaled by the operator that it is safe to do, the sampler will approach the bucket.

  e. The soil shall be monitored with a photoionization or flame ionization detector (PID or FID) as directed in the project -specific planning documents.

  f. The sampler shall collect the sample from the center of the bucket or pile in accordance with surface soil sampling procedures of Section 6.3 or 6.4, as applicable. Collecting samples from the center of a pile or bucket eliminates cross-contamination from the bucket or other depth intervals.

- If a composite sample is desired, several depths or locations within the pit/trench will be selected, and the bucket will be filled from each area. It is preferable to send individual sample bottles filled from each bucket to the laboratory for compositing under the more controlled laboratory conditions. However, if compositing in the field is required, each sample container shall be filled from materials that have been transferred into a mixing bucket and homogenized. Note that homogenization/compositing is not applicable for samples to be subjected to volatile organic analysis.

> ***CAUTION***
> Care must be exercised when using the remote sampler described in the next step because of potential instability of trench walls. In situations where someone must move closer than 2 feet to the excavation edge, a board or platform should be used to displace the sampler's weight to minimize the chance of collapse of the excavation edge. Fall protection should also be employed when working near the edges or trenches greater than 6 feet deep. An immediate means to extract people who have fallen into the trench will be immediately available. These means may include ladders or rope anchor points.

- Using the remote sampler shown in Attachment D, samples can be taken at the desired depth from the sidewall or bottom of the pit as follows:

  a. Scrape the face of the pit/trench using a long-handled shovel or hoe to remove the smeared zone that has contacted the backhoe bucket.

  b. Collect the sample directly into the sample jar, by scraping with the jar edge, eliminating the need for sample handling equipment and minimizing the likelihood of cross-contamination.

  c. Cap the sample jar, remove it from the remote sampler assembly, and package the sample for shipment in accordance with SOP SA-6.3.

- Complete documentation as described in SOP SA-6.3 and Attachment C of this SOP.

6.8.3.4 In-Pit Sampling

Under rare conditions, personnel may be required to enter the test pit/trench. This is necessary only when soil conditions preclude obtaining suitable samples from the backhoe bucket (e.g., excessive mixing of soil or wastes within the test pit/trench) or when samples from relatively small discrete zones within the test pit are required. This approach may also be necessary to sample any seepage occurring at discrete levels or zones in the test pit that are not accessible with remote samplers.

In general, personnel shall sample and log pits and trenches from the ground surface, except as provided for by the following criteria:

- There are no practical alternative means of obtaining such data.
- The SSO and Competent Person determine that such action can be accomplished without breaching site safety protocol. This determination will be based on actual monitoring of the pit/trench after it is dug (including, at a minimum, measurements of oxygen concentration, flammable gases, and toxic compounds, in that order). Action levels will be provided in project-specific planning documents.
- A company-designated Competent Person determines that the pit/trench is stable trough soil classification evaluation/inspections or is made stable (by cutting/grading the sidewalls or using shoring) prior to entrance of any personnel. OSHA requirements shall be strictly observed.

If these conditions are satisfied, only one person may enter the pit/trench. On potentially hazardous waste sites, this individual shall be dressed in selected PPE as required by the conditions in the pit. He/she shall be affixed to a harness and lifeline and continuously monitored while in the pit.

A second and possible third individual shall be fully dressed in protective clothing including a self-contained breathing device and on standby during all pit entry operations to support self rescue or assisted self rescue. The individual entering the pit shall remain therein for as brief a period as practical, commensurate with performance of his/her work. After removing the smeared zone, samples shall be obtained with a decontaminated trowel or spoon.

6.8.3.5 Geotechnical Sampling

In addition to the equipment described in Section 6.8.3.2, the following equipment is needed for geotechnical sampling:

- Soil sampling equipment, similar to that used in shallow drilled boring (i.e., thin-walled tube samplers), that can be pushed or driven into the floor of the test pit.
- Suitable driving (e,g., sledge hammer) or pushing (e.g., backhoe bucket) equipment used to advance the sampler into the soil.
- Knives, spatulas, and other suitable devices for trimming hand-carved samples.
- Suitable containers (bags, jars, tubes, boxes, etc.), labels, wax, etc. for holding and safely transporting collected soil samples.
- Geotechnical equipment (pocket penetrometer, torvane, etc.) for field testing collected soil samples for classification and strength properties.

Disturbed grab or bulk geotechnical soil samples may be collected for most soil in the same manner as comparable soil samples for chemical analysis. These collected samples may be stored in jars or plastic-lined sacks (larger samples), which will preserve their moisture content. Smaller samples of this type are usually tested for their index properties to aid in soil identification and classification: larger bulk samples are usually required to perform compaction tests.

Relatively undisturbed samples are usually extracted in cohesive soil using thin-walled tube samplers, and such samples are then tested in a geotechnical laboratory for their strength, permeability, and/or compressibility. The techniques for extracting and preserving such samples are similar to those used in performing Shelby tube sampling in borings, except that the sampler is advanced by hand or backhoe, rather than by a drill rig. Also, the sampler may be extracted from the test pit by excavation around the tube when it is difficult to pull it out of the ground. If this excavation requires entry of the test pit, the requirements described in Section 6.8.3.4 shall be followed. The thin-walled tube sampler shall be pushed or driven vertically into the floor or steps excavated in the test pit at the desired sampling elevations. Extracting tube samples horizontally from the walls of the test pit is not appropriate because the sample will not have the correct orientation.

A sledge hammer or backhoe may be used to drive or push the tube into the ground. Place a piece of wood over the top of the sampler or sampling tube to prevent damage during driving/pushing of the sample. Pushing the sampler with a constant thrust is always preferable to driving it with repeated blows, thus minimizing disturbance to the sample. When using a sledge hammer, it is recommended that the sampler be stabilized using a rope/strap wrench or pipe wrench to remove the person's hands holding the sampler from the strike zone. If the sample cannot be extracted by rotating it at least two revolutions (to shear off the sample at the bottom), hook the sampler to the excavator or backhoe and extract. This means an alternative head will be used as a connection point or that multiple choke hitches will be applied to extract the sampler. If this fails and the excavator can dig deeper without potentially impacting subsurface utilities, excavate the sampler. If this fails or if the excavator cannot be used due to subsurface utilities, hand-excavate to remove the soil from around the sides of the sampler. If hand-excavation requires entry into the test pit, the requirements in Section 6.8.3.4 must be followed. Prepare the sample as described in Steps 9 through 13 in Section 6.2.3, and label, pack and transport the sample in the required manner, as described in SOPs SA-6.3 and SA-6.1.

6.8.4 Backfilling of Trenches and Test Pits

All test pits and excavations must be either backfilled, covered, or otherwise protected at the end of each day. No excavations shall remain open during non-working hours unless adequately covered or otherwise protected.

Before backfilling, the onsite crew may photograph, if required by the project-specific work plan, all significant features exposed by the test pit and trench and shall include in the photograph a scale to show dimensions. Photographs of test pits shall be marked to include site number, test pit number, depth, description of feature, and date of photograph. In addition, a geologic description of each photograph shall be entered in the site logbook. All photographs shall be indexed and maintained as part of the project file for future reference.

After inspection, backfill material shall be returned to the pit under the direction of the FOL. Backfill should be returned to the trench or test pit in 6-inch to 1-foot lifts and compacted with the bucket. Remote controlled tampers or rollers may be lowered into the trench and operated from top side. This procedure will continue to the grade surface. It is recommended that the trench be tracked or rolled in. During excavation, clean soil from the top 2 feet may have been separated to be used to cover the last segments. Where these materials are not clean, it is recommended that clean fill be used for the top cover.

If a low-permeability layer is penetrated (resulting in groundwater flow from an upper contaminated flow zone into a lower uncontaminated flow zone), backfill material must represent original conditions or be impermeable. Backfill could consist of a soil-bentonite mix prepared in a proportion specified by the FOL (representing a permeability equal to or less than original conditions). Backfill can be covered by "clean" soil and graded to the original land contour. Revegetation of the disturbed area may also be required.

6.9 Records

The appropriate sample log sheet (see Attachment A of this SOP) must be completed by the site geologist/sampler for all samples collected. All soil sampling locations should be documented by tying in the location of two or more nearby permanent landmarks (building, telephone pole, fence, etc.) or obtaining GPS coordinates; and shall be noted on the appropriate sample log sheet, site map, or field notebook. Surveying may also be necessary, depending on the project requirements.

Test pit logs (see Attachment C of this SOP) shall contain a sketch of pit conditions. If the project-specific work plan requires photographs, at least one photograph with a scale for comparison shall be taken of each pit. Included in the photograph shall be a card showing the test pit number. Boreholes, test pits, and trenches shall be logged by the field geologist in accordance with SOP GH-1.5.

Other data to be recorded in the field logbook include the following:

- Name and location of job
- Date of boring and excavation
- Approximate surface elevation
- Total depth of boring and excavation
- Dimensions of pit
- Method of sample acquisition
- Type and size of samples
- Soil and rock descriptions
- Photographs if required
- Groundwater levels
- PID/FID/LEL/O_2 meter readings
- Other pertinent information, such as waste material encountered

In addition, site-specific documentation to be maintained by the SSO and/or Competent Person will be required including:

- Calibration logs
- Excavation inspection checklists

- Soil type classification

7.0 REFERENCES

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ATTACHMENT A
SOIL & SEDIMENT SAMPLE LOG SHEET

Tetra Tech NUS, Inc.

SOIL & SEDIMENT SAMPLE LOG SHEET

Page___ of ___

Project Site Name: _____
Project No.: _____

[] Surface Soil
[] Subsurface Soil
[] Sediment
[] Other: _____
[] QA Sample Type: _____

Sample ID No.: _____
Sample Location: _____
Sampled By: _____
C.O.C. No.: _____

Type of Sample:
[] Low Concentration
[] High Concentration

GRAB SAMPLE DATA:

Date:	Depth	Color	Description (Sand, Silt, Clay, Moisture, etc.)
Time:			
Method:			
Monitor Reading (ppm):			

COMPOSITE SAMPLE DATA:

Date:	Time	Depth	Color	Description (Sand, Silt, Clay, Moisture, etc.)
Method:				
Monitor Readings (Range in ppm):				

SAMPLE COLLECTION INFORMATION:

Analysis	Container Requirements	Collected	Other

OBSERVATIONS / NOTES:

MAP:

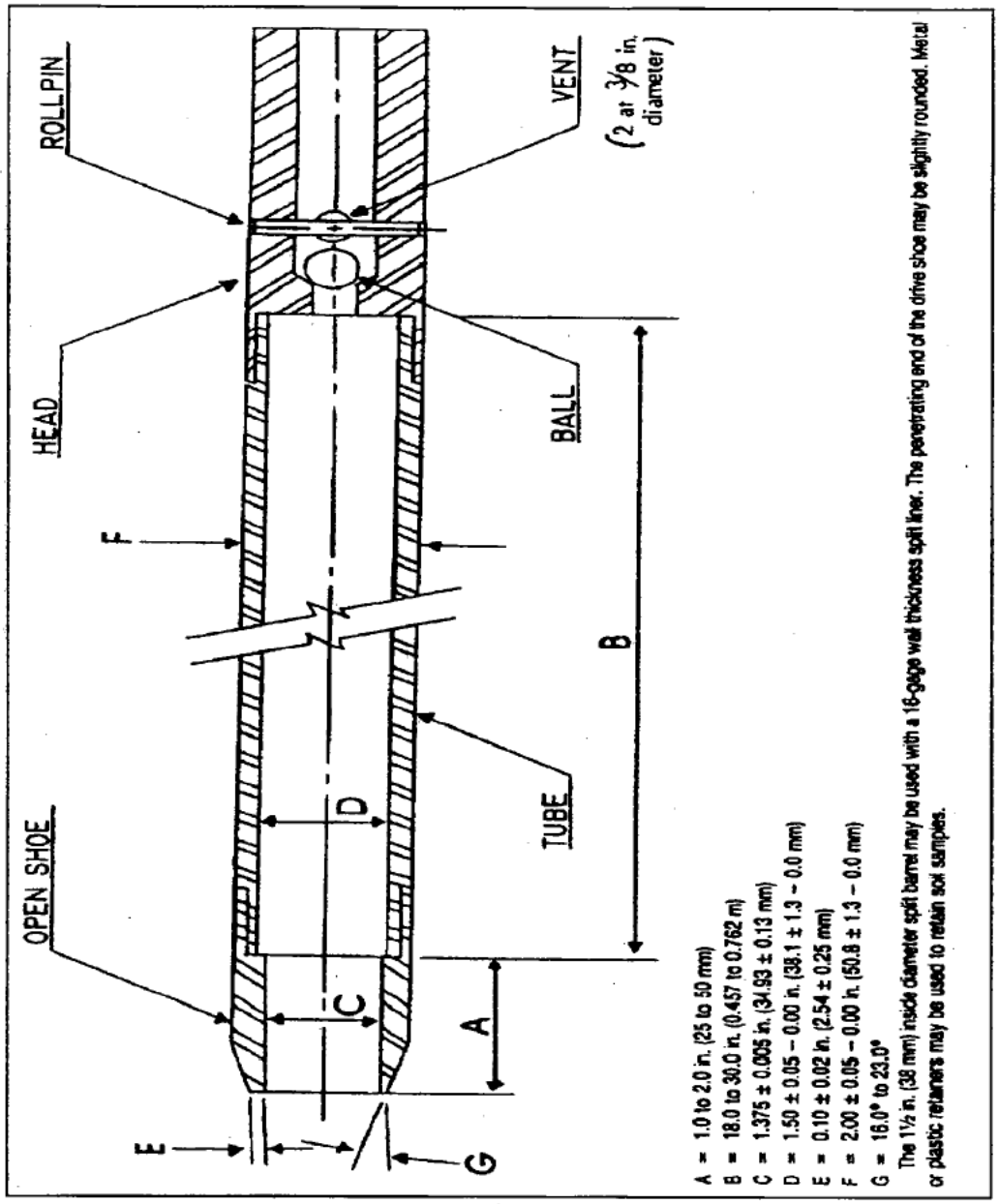
Circle if Applicable:

MS/MSD

Duplicate ID No.:

Signature(s):

ATTACHMENT B
SPLIT-SPOON SAMPLER



A = 1.0 to 2.0 in. (25 to 50 mm)
B = 18.0 to 30.0 in. (0.457 to 0.762 m)
C = 1.375 ± 0.005 in. (34.93 ± 0.13 mm)
D = 1.50 ± 0.05 – 0.00 in. (38.1 ± 1.3 – 0.0 mm)
E = 0.10 ± 0.02 in. (2.54 ± 0.25 mm)
F = 2.00 ± 0.05 – 0.00 in. (50.8 ± 1.3 – 0.0 mm)
G = 16.0° to 23.0°

The 1½ in. (38 mm) inside diameter split barrel may be used with a 16-gage wall thickness split liner. The penetrating end of the drive shoe may be slightly rounded. Metal or plastic retainers may be used to retain soil samples.

ATTACHMENT C
TEST PIT LOG

Tetra Tech NUS, Inc.

TEST PIT LOG

Page ___ of ___

PROJECT NAME: _____ TEST PIT No.: _____
PROJECT NUMBER: _____ DATE: _____
LOCATION: _____ GEOLOGIST: _____

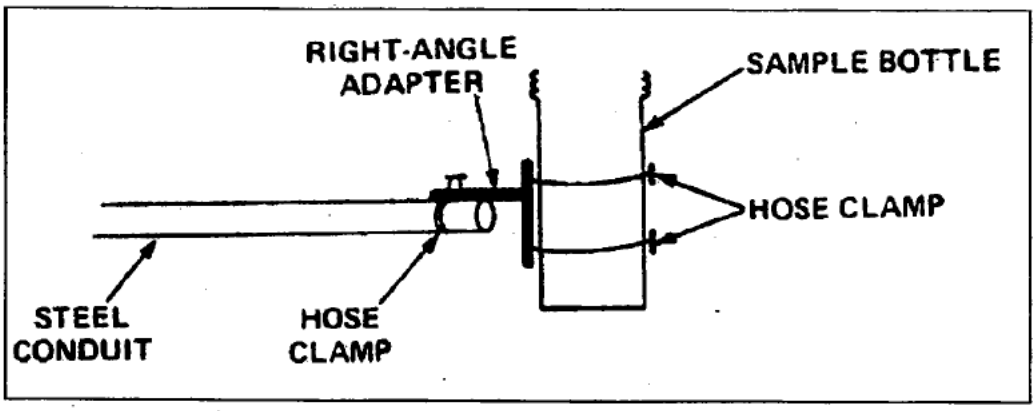
Depth (Ft.)	Lithology Change (Depth/Ft.)	MATERIAL DESCRIPTION Soil/Waste Characteristics (lithology, density, color, etc.)	USCS	Remarks	PID/FID READING Source (ppm)	BZ (ppm)

TEST PIT CROSS SECTION AND / OR PLAN VIEW

REMARKS: _____

PHOTO LOG: _____

ATTACHMENT D
REMOTE SAMPLE HOLDER FOR TEST PIT/TRENCH SAMPLING



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1.0 PURPOSE

The purpose of this procedure is to provide general reference information on Direct Push Technology (DPT). DPT is designed to collect soil, groundwater, and soil gas samples without using conventional drilling techniques. The advantage of using DPT over conventional drilling includes the generation of little or no drill cuttings, sampling in locations with difficult accessibility, reduced overhead clearance requirements, no fluid introduction during probing, and typical lower costs per sample than with conventional techniques. Disadvantages include a maximum penetration depth of approximately 15 to 40 feet in dense soils (although it may be as much as 60 to 80 feet in certain types of geological environments), reduced capability of obtaining accurate water-level measurements, and the inability to install permanent groundwater monitoring wells. The methods and equipment described herein are for collection of surface and subsurface soil samples and groundwater samples. Soil gas sampling is discussed in SOP SA-2.4.

2.0 SCOPE

This procedure provides information on proper sampling equipment and techniques for DPT. Review of the information contained herein will facilitate planning of the field sampling effort by describing standard sampling techniques. The techniques described shall be followed whenever applicable, noting that site-specific conditions or project-specific plans may require adjustments in methodology.

3.0 GLOSSARY

Direct Push Technology (DPT) - DPT refers to sampling tools and sensors that are driven directly into the ground without the use of conventional drilling equipment. DPT typically utilizes hydraulic pressure and/or percussion hammers to advance the sampling tools. A primary advantage of DPT over conventional drilling techniques is that DPT results in the generation of little or no investigation derived waste.

Geoprobe® - Geoprobe® is a manufacturer of a hydraulically-powered, percussion/probing machines utilizing DPT to collect subsurface environmental samples. Geoprobe® relies on a relatively small amount of static weight (vehicle) combined with percussion as the energy for advancement of a tool string. The Geoprobe® equipment can be mounted in a multitude of vehicles for access to all types of environmental sites.

HydroPunch™ - HydroPunch™ is a manufacturer of stainless steel and Teflon® sampling tools that are capable of collecting representative groundwater and/or soil samples without requiring the installation of a groundwater monitoring well or conventional soil boring. HydroPunch™ is an example of DPT sampling equipment.

Flame Ionization Detector (FID) - A portable instrument for the measurement of many combustible organic compounds and a few inorganic compounds in air at parts-per million levels. The basis for the detection is the ionization of gaseous species utilizing a flame as the energizing source.

Photo Ionization Detector (PID) - A portable instrument for the measurement of many combustible organic compounds and a few inorganic compounds in air at parts-per million levels. The basis for the detection is the ionization of gaseous species utilizing ultraviolet radiation as the energizing source.

4.0 RESPONSIBILITIES

Project Manager - The Project Manager is responsible for selecting and/or reviewing the appropriate DPT drilling procedure required to support the project objectives.

Field Operations Leader (FOL)- The FOL is primarily responsible for performing the DPT in accordance with the project-specific plan.

5.0 SOIL SAMPLING PROCEDURES

5.1 General

The common methodology for the investigation of the vadose zone is soil boring drilling and soil sampling. However, drilling soil borings can be very expensive. Generally the advantage of DPT for subsurface soil sampling is the reduced cost of disposal of drilling cuttings and shorter sampling times.

5.2 Sampling Equipment

Equipment needed for conducting DPT drilling for subsurface soil sampling includes, but is not limited to, the following:

- Geoprobe® Sampling Kit
- Cut-resistant gloves
- 4-foot x 1.5-inch diameter macrocore sampler
- Probe sampling adapters
- Roto-hammer with 1.5-inch bit
- Disposable acetate liners for soil macrocore sampler
- Cast aluminum or steel drive points
- Geoprobe® AT-660 Series Large Bore Soil Sampler, or equivalent
- Standard decontamination equipment and solutions

For health and safety equipment and procedures, follow the direction provided in the Safe Work Permit in Attachment 1, or the more detailed directions provided in the project's Health and Safety Plan.

5.3 DPT Sampling Methodology

There are several methods for the collection of soil samples using DPT drilling. The most common method is discussed in the following section. Variations of the following method may be conducted upon approval of the Project Manager in accordance with the project-specific plan.

- Macrocore samplers fitted with detachable aluminum or steel drive points are driven into the ground using hydraulic pressure. If there is concrete or pavement over a sampling location, a Roto-hammer is used to drill a minimum 1.5-inch diameter hole through the surface material. A Roto-hammer may also be used if very dense soils are encountered.

- The sampler is advanced continuously in 4-foot intervals or less if desired. No soil cuttings are generated because the soil which is not collected in the sampler is displaced within the formation.

- The sampler is retracted from the hole, and the 4-foot continuous sample is removed from the outer coring tube. The sample is contained within an inner acetate liner.

- Attach the metal trough from the Geoprobe® Sampling Kit firmly to the tail gate of a vehicle. If a vehicle with a tail gate is not available, secure the trough on another suitable surface.

- Place the acetate liner containing the soils in the trough.

- While wearing cut-resistant gloves (constructed of leather or other suitable material), cut the acetate liner through its entire length using the double-bladed knife that accompanies the Geoprobe® Sampling Kit. Then remove the strip of acetate from the trough to gain access to the collected soils. Do not attempt to cut the acetate liner while holding it in your hand.

- Field screen the sample with an FID or PID, and observe/examine the sample (according to SOP GH-1.3). If appropriate, transfer the sample to sample bottles for laboratory analysis. If additional volume is required, push an additional boring adjacent to the first and composite/mix the same interval. Field compositing is usually not acceptable for sample requiring volatile organics analysis.

- Once sampling has been completed, the hole is backfilled with bentonite chips or bentonite cement grout, depending upon project requirements. Asphalt or concrete patch is used to cap holes through paved or concrete areas. All holes should be finished smooth to existing grade.

- In the event the direct push van/truck cannot be driven to a remote location or a sampling location with difficult accessibility, sampling probes may be advanced and sampled manually or with air/electric operated equipment (e.g., jack hammer).

- Sampling equipment is decontaminated prior to collecting the next sample.

6.0 GROUNDWATER SAMPLING PROCEDURES

6.1 General

The most common methodology for the investigation of groundwater is the installation and sampling of permanent monitoring wells. If only groundwater screening is required, the installation and sampling of temporary well points may be performed. The advantage of temporary well point installation using DPT is reduced cost due to no or minimal disposal of drilling cuttings and well construction materials, and shorter installation/times sampling.

Two disadvantages of DPT drilling for well point installation are:

- In aquifers with low yields, well points may have to be sampled without purging or development.
- If volume requirements are high, this method can be time consuming for low yield aquifers.

6.2 Sampling Equipment

Equipment needed for temporary well installation and sampling using DPT includes, but is not limited, to the following:

- 2-foot x 1-inch diameter mill-slotted (0.005 to 0.02-inch) well point
- Connecting rods
- Roto-hammer with 1.5-inch bit
- Mechanical jack
- 1/4-inch OD polyethylene tubing
- 3/8-inch OD polyethylene tubing
- Peristaltic pump
- Standard decontamination equipment and solutions

6.3 DPT Temporary Well Point Installation and Sampling Methodology

There are several methods for the installation and sampling of temporary well points using DPT. The most common methodology is discussed below. Variations of the following method may be conducted upon approval of the Project Manager in accordance with the project specific plan.

- A 2-foot x 1-inch diameter mill-slotted (0.005 to 0.02-inch) well point attached to connecting rods is driven into the ground to the desired depth using a rotary electric hammer or other direct push drill rig. If there is concrete or pavement over a sampling location, a Roto-hammer or electric coring machine is used to drill a hole through the surface material.

- The well point will be allowed to equilibrate for at least 15 minutes, after which a measurement of the static water level will be taken. The initial measurement of the water level will be used to assess the amount of water which is present in the well point and to determine the amount of silt and sand infiltration that may have occurred.

- The well point will be developed using a peristaltic pump and polyethylene tubing to remove silt and sand which may have entered the well point. The well point is developed by inserting polyethylene tubing to the bottom of the well point and lifting and lowering the tubing slightly while the pump is operating. The pump will be operated at a maximum rate of approximately 2 liters per minute. After removal of sediment from the bottom of the well point, the well point will be vigorously pumped at maximum capacity until discharge water is visibly clear and no further sediments are being generated. Measurements of pH, specific conductance, temperature, and turbidity shall be recorded every 5 to 10 minutes during the purging process. After two consistent readings of pH, specific conductance, temperature and turbidity ($\pm$10 percent), the well may be sampled.

- A sample will be collected using the peristaltic pump set at the same or reduced speed as during well development. Samples (with the exception of the samples to be analyzed for volatile organic compounds, VOCs) will be collected directly from the pump discharge. Sample containers for VOCs will be filled by (first shutting off the pump) crimping the discharge end of the sample tubing when filled, removing the inlet end of the sample tubing from the well, suspending the inlet tubing above the vial, and allowing water to fill each vial by gravity flow.

- Once the groundwater sample has been collected, the connecting rods and well point will be removed from the hole with the direct push rig hydraulics. The hole will be backfilled with bentonite chips or bentonite cement grout, depending upon project requirements. Asphalt or concrete patch will be used to cap holes through paved or concrete areas. All holes will be finished smooth to existing grade.

- In the event the direct push van/truck cannot be driven to a remote location or sampling location with difficult accessibility, sampling probes may be advanced and sampled manually or with air/electric-operated equipment (e.g., jack hammer).

- Decontaminate the equipment before moving to the next location.

7.0 RECORDS

A record of all field procedures, tests, and observations must be recorded in the field logbook, boring logs, and sample log sheets, as needed. Entries should include all pertinent data regarding the investigation. The use of sketches and field landmarks will help to supplement the investigation and evaluation.

ATTACHMENT 1
SAFE WORK PERMIT FOR DPT OPERATIONS

Permit No. _____ Date: _____ Time: From _____ to _____

SECTION I: General Job Scope

I. Work limited to the following (description, area, equipment used): **Monitoring well drilling and installation through direct push technology**

II. Required Monitoring Instruments: _____

III. Field Crew: _____

IV. On-site Inspection conducted ☐ Yes ☐ No Initials of Inspector _____ _____
TtNUS

SECTION II: General Safety Requirements (To be filled in by permit issuer)

V. Protective equipment required
Level D ☒ Level B ☐
Level C ☐ Level A ☐
Detailed on Reverse

Respiratory equipment required
Full face APR ☐ Escape Pack ☐
Half face APR ☐ SCBA ☐
SKA-PAC SAR ☐ Bottle Trailer ☐
Skid Rig ☐ None ☒

Level D Minimum Requirements: Sleeved shirt and long pants, safety footwear, and work gloves. Safety glasses, hard hats, and hearing protection will be worn when working near or sampling in the vicinity of the DPT rig.

Modifications/Exceptions.

VI. Chemicals of Concern | Action Level(s) | Response Measures

VII. Additional Safety Equipment/Procedures

Hard-hat	☒ Yes	☐ No	Hearing Protection (Plugs/Muffs)	☒ Yes	☐ No
Safety Glasses	☒ Yes	☐ No	Safety belt/harness	☐ Yes	☒ No
Chemical/splash goggles	☐ Yes	☒ No	Radio	☐ Yes	☒ No
Splash Shield	☐ Yes	☒ No	Barricades	☒ Yes	☐ No
Splash suits/coveralls	☐ Yes	☐ No	Gloves (Type - _____)	☐ Yes	☐ No
Steel toe Work shoes or boots	☒ Yes	☐ No	Work/warming regimen	☐ Yes	☐ No

Modifications/Exceptions: Reflective vests for high traffic areas.

VIII. Procedure review with permit acceptors

	Yes	NA		Yes	NA
Safety shower/eyewash (Location & Use)	☐	☒	Emergency alarms	☐	☐
Daily tail gate meetings	☒	☐	Evacuation routes	☐	☐
Contractor tools/equipment/PPE inspected	☐	☐	Assembly points	☐	☐

IX. Site Preparation

Utility Clearances obtained for areas of subsurface investigation	☐ Yes	☐ No
Physical hazards removed or blockaded	☐ Yes	☐ No
Site control boundaries demarcated/signage	☐ Yes	☐ No

X. Equipment Preparation

	Yes	NA
Equipment drained/depressurized	☐	☒
Equipment purged/cleaned	☐	☒
Isolation checklist completed	☐	☒
Electrical lockout required/field switch tested	☐	☒
Blinds/misalignments/blocks & bleeds in place	☐	☒
Hazardous materials on walls/behind liners considered	☐	☒

XI. Additional Permits required (Hot work, confined space entry). ☐ Yes ☐ No
If yes, complete permit required or contact Health Sciences, Pittsburgh Office

XII. Special instructions, precautions:

Permit Issued by: _____ Permit Accepted by: _____

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1.0 PURPOSE

The purpose of this Standard Operating Procedure (SOP) is to provide information on sample preservation, packaging, and shipping procedures to be used in handling environmental samples submitted for chemical constituent, biological, or geotechnical analysis. Sample chain-of-custody procedures and other aspects of field documentation are addressed in SOP SA-6.3. Sample identification is addressed in SOP CT-04.

2.0 SCOPE

This procedure describes the appropriate containers to be used for samples depending on the analyses to be performed, and the steps necessary to preserve the samples when shipped off site for chemical analysis.

3.0 GLOSSARY

Hazardous Material - A substance or material which has been determined by the Secretary of Transportation to be capable of posing an unreasonable risk to health, safety, and property when transported in commerce, and which has been so designated. Under 49 CFR, the term includes hazardous substances, hazardous wastes, marine pollutants, and elevated temperature materials, as well as materials designated as hazardous under the provisions of §172.101 and §172.102 and materials that meet the defining criteria for hazard classes and divisions in Part 173. With slight modifications, IATA has adopted DOT "hazardous materials" as IATA "Dangerous Goods."

Hazardous Waste - Any substance listed in 40 CFR, Subpart D (~~y~~261.30 et seq.), or otherwise characterized as ignitable, corrosive, reactive, or toxic (as defined by Toxicity Characteristic Leaching Procedure, TCLP, analysis) as specified under 40 CFR, Subpart C (~~y~~261.20 et seq.), that would be subject to manifest requirements specified in 40 CFR 262. Such substances are defined and regulated by EPA.

Marking - A descriptive name, identification number, instructions, cautions, weight, specification or UN marks, or combination thereof required on outer packaging of hazardous materials.

n.o.i - Not otherwise indicated (may be used interchangeably with n.o.s.).

n.o.s. - Not otherwise specified.

Packaging - A receptacle and any other components or materials necessary for compliance with the minimum packaging requirements of 49 CFR 174, including containers (other than freight containers or overpacks), portable tanks, cargo tanks, tank cars, and multi-unit tank-car tanks to perform a containment function in conformance with the minimum packaging requirements of 49 CFR 173.24(a) & (b).

Placard - Color-coded, pictorial sign which depicts the hazard class symbol and name and which is placed on the side of a vehicle transporting certain hazardous materials.

Common Preservatives:

- Hydrochloric Acid - HCl
- Sulfuric Acid - H_2SO_4
- Nitric Acid - HNO_3
- Sodium Hydroxide - NaOH

Other Preservatives

- Zinc Acetate
- Sodium Thiosulfate - $Na_2S_2O_3$

Normality (N) - Concentration of a solution expressed as equivalent per liter, an equivalent being the amount of a substance containing 1 gram-atom of replaceable hydrogen or its equivalent.

Reportable Quantity (RQ) - For the purposes of this SOP, means the quantity specified in column 3 of the Appendix to DOT 49 CFR §172.101 for any material identified in column 1 of the appendix. A spill greater than the amount specified must be reported to the National Response Center.

Sample - A sample is physical evidence collected from a facility or the environment, which is representative of conditions at the location and time of collection.

4.0 RESPONSIBILITIES

Field Operations Leader - Directly responsible for the bottling, preservation, labeling, packaging, shipping, and custody of samples up to and including release to the shipper.

Field Samplers - Responsible for initiating the Chain-of-Custody Record (per SOP SA-6.3), implementing the packaging and shipping requirements, and maintaining custody of samples until they are relinquished to another custodian or to the shipper.

5.0 PROCEDURES

Sample identification, labeling, documentation, and chain-of-custody are addressed by SOP SA-6.3.

5.1 Sample Containers

Different types of chemicals react differently with sample containers made of various materials. For example, trace metals adsorb more strongly to glass than to plastic, whereas many organic chemicals may dissolve various types of plastic containers. Attachments A and B show proper containers (as well as other information) per 40 CFR 136. In general, the sample container shall allow approximately 5-10 percent air space ("ullage") to allow for expansion/vaporization if the sample warms during transport. However, for collection of volatile organic compounds, head space shall be omitted. The analytical laboratory will generally provide certified-clean containers for samples to be analyzed for chemical constituents. Shelby tubes or other sample containers are generally provided by the driller for samples requiring geotechnical analysis. Sufficient lead time shall be allowed for a delivery of sample container orders. Therefore, it is critical to use the correct container to maintain the integrity of the sample prior to analysis.

Once opened, the container must be used at once for storage of a particular sample. Unused but opened containers are to be considered contaminated and must be discarded. Because of the potential for introduction of contamination, they cannot be reclosed and saved for later use. Likewise, any unused containers which appear contaminated upon receipt, or which are found to have loose caps or a missing Teflon liner (if required for the container), shall be discarded.

5.2 Sample Preservation

Many water and soil samples are unstable and therefore require preservation to prevent changes in either the concentration or the physical condition of the constituent(s) requiring analysis. Although complete and irreversible preservation of samples is not possible, preservation does retard the chemical and biological

changes that inevitably take place after the sample is collected. Preservation techniques are usually limited to pH control, chemical addition(s), and refrigeration/ freezing (certain biological samples only).

5.2.1 Overview

The preservation techniques to be used for various analytes are listed in Attachments A and B. Reagents required for sample preservation will either be added to the sample containers by the laboratory prior to their shipment to the field or be added in the field (in a clean environment). Only high purity reagents shall be used for preservation. In general, aqueous samples of low-concentration organics (or soil samples of low- or medium-concentration organics) are cooled to 4°C. Medium-concentration aqueous samples, high-hazard organic samples, and some gas samples are typically not preserved. Low-concentration aqueous samples for metals are acidified with HNO_3, whereas medium-concentration and high-hazard aqueous metal samples are not preserved. Low- or medium-concentration soil samples for metals are cooled to 4°C, whereas high-hazard samples are not cooled.

The following subsections describe the procedures for preparing and adding chemical preservatives. Attachments A and B indicate the specific analytes which require these preservatives.

The FOL is responsible for ensuring that an accurate Chemical Inventory is created and maintained for all hazardous chemicals brought to the work site (see Section 5 of the TtNUS Health and Safety Guidance Manual). Furthermore, the FOL must ensure that a corresponding Material Safety Data Sheet (MSDS) is collected for every substance entered on the site Chemical Inventory, and that all persons using/handling/ disposing of these substances review the appropriate MSDS for substances they will work with. The Chemical Inventory and the MSDSs must be maintained at each work site in a location and manner where they are readily-accessible to all personnel.

5.2.2 Preparation and Addition of Reagents

Addition of the following acids or bases may be specified for sample preservation; these reagents shall be analytical reagent (AR) grade or purer and shall be diluted to the required concentration with deionized water before field sampling commences. To avoid uncontrolled reactions, be sure to Add Acid to water (not vice versa). A dilutions guide is provided below.

Acid/Base	Dilution	Concentration	Estimated Amount Required for Preservation
Hydrochloric Acid (HCl)	1 part concentrated HCl: 1 part double-distilled, deionized water	6N	5-10 mL
Sulfuric Acid (H_2SO_4)	1 part concentrated H_2SO_4: 1 part double-distilled, deionized water	18N	2 - 5 mL
Nitric Acid (HNO_3)	Undiluted concentrated HNO_3	16N	2 - 5 mL
Sodium Hydroxide (NaOH)	400 grams solid NaOH dissolved in 870 mL double-distilled, deionized water; yields 1 liter of solution	10N	2 mL

The amounts required for preservation shown in the above table assumes proper preparation of the preservative and addition of the preservative to one liter of aqueous sample. This assumes that the sample is initially at pH 7, is poorly buffered, and does not contain particulate matter; as these conditions vary, more preservative may be required. Consequently, the final sample pH must be checked using narrow-range pH paper, as described in the generalized procedure detailed below:

- Pour off 5-10 mL of sample into a dedicated, clean container. Use some of this sample to check the initial sample pH using wide range (0-14) pH paper. Never dip the pH paper into the sample; always apply a drop of sample to the pH paper using a clean stirring rod or pipette.

- Add about one-half of the estimated preservative required to the original sample bottle. Cap and invert gently several times to mix. Check pH (as described above) using medium range pH paper (pH 0-6 or pH 7.5-14, as applicable).

- Cap sample bottle and seal securely.

Additional considerations are discussed below:

- To test if ascorbic acid must be used to remove oxidizing agents present in the sample before it can be properly preserved, place a drop of sample on KI-starch paper. A blue color indicates the need for ascorbic acid addition.

  If required, add a few crystals of ascorbic acid to the sample and retest with the KI-starch paper. Repeat until a drop of sample produces no color on the KI-starch paper. Then add an additional 0.6 grams of ascorbic acid per each liter of sample volume.

  Continue with proper base preservation of the sample as described above.

- Samples for sulfide analysis must be treated by the addition of 4 drops (0.2 mL) of 2N zinc acetate solution per 100 ml of sample.

  The 2N zinc acetate solution is made by dissolving 220 grams of zinc acetate in 870 mL of double-distilled, deionized water to make 1 liter of solution.

  The sample pH is then raised to 9 using the NaOH preservative.

- Sodium thiosulfate must be added to remove residual chlorine from a sample. To test the sample for residual chlorine use a field test kit specially made for this purpose.

  If residual chlorine is present, add 0.08 grams of sodium thiosulfate per liter of sample to remove the residual chlorine.

  Continue with proper acidification of the sample as described above.

For biological samples, 10% buffered formalin or isopropanol may also be required for preservation. Questions regarding preservation requirements should be resolved through communication with the laboratory before sampling begins.

5.3 Field Filtration

At times, field-filtration may be required to provide for the analysis of dissolved chemical constituents. Field-filtration must be performed prior to the preservation of samples as described above. General procedures for field filtration are described below:

- The sample shall be filtered through a non-metallic, 0.45-micron membrane filter, immediately after collection. The filtration system shall consist of dedicated filter canister, dedicated tubing, and a peristaltic pump with pressure or vacuum pumping squeeze action (since the sample is filtered by mechanical peristalsis, the sample travels only through the tubing).

- To perform filtration, thread the tubing through the peristaltic pump head. Attach the filter canister to the discharge end of the silicon tubing (note flow direction arrow); attach the aqueous sample container to the intake end of the silicon tubing. Turn the peristaltic pump on and perform filtration. Run approximately 100 ml of sample through the filter and discard prior to sample collection.

- Continue by preserving the filtrate (contained in the filter canister), as applicable and generally described above.

5.4 Sample Packaging and Shipping

Only employees who have successfully completed the TtNUS "Shipping Hazardous Materials" training course are authorized to package and ship hazardous substances. These trained individuals are responsible for performing shipping duties in accordance with this training.

Samples collected for shipment from a site shall be classified as either environmental or hazardous material samples. Samples from drums containing materials other than Investigative Derived Waste (IDW) and samples obtained from waste piles or bulk storage tanks are generally shipped as hazardous materials. A distinction must be made between the two types of samples in order to:

- Determine appropriate procedures for transportation of samples (if there is any doubt, a sample shall be considered hazardous and shipped accordingly.)

- Protect the health and safety of transport and laboratory personnel receiving the samples (special precautions are used by the shipper and at laboratories when hazardous materials are received.)

Detailed procedures for packaging environmental samples are outlined in the remainder of this section.

5.4.1 Environmental Samples

Environmental samples are packaged as follows:

- Place properly identified sample container, with lid securely fastened, in a plastic bag (e.g. Ziploc baggie), and seal the bag.

- Place sample in a cooler constructed of sturdy material which has been lined with a large, plastic bag (e.g. "garbage" bag). Drain plugs on coolers must be taped shut.

- Pack with enough cushioning materials such as bubble wrap (shoulders of bottles must be iced if required) to minimize the possibility of the container breaking.

- If cooling is required (see Attachments A and B), place ice around sample container shoulders, and on top of packing material (minimum of 8 pounds of ice for a medium-size cooler).

- Seal (i.e., tape or tie top in knot) large liner bag.

- The original (top, signed copy) of the COC form shall be placed inside a large Ziploc-type bag and taped inside the lid of the shipping cooler. If multiple coolers are sent but are included on one COC form, the COC form should be sent with the cooler containing the vials for VOC analysis. The COC form should then state how many coolers are included with that shipment.

- Close and seal outside of cooler as described in SOP SA-6.3. Signed custody seals must be used.

Coolers must be marked as containing "Environmental Samples." The appropriate side of the container must be marked "This End Up" and arrows placed appropriately. No DOT marking or labeling is required; there are no DOT restrictions on mode of transportation.

6.0 REFERENCES

American Public Health Association, 1981. Standard Methods for the Examination of Water and Wastewater, 15th Edition. APHA, Washington, D.C.

International Air Transport Association (latest issue). Dangerous Goods Regulations, Montreal, Quebec, Canada.

U.S. Department of Transportation (latest issue). Hazardous Materials Regulations, 49 CFR 171-177.

U.S. EPA, 1984. "Guidelines Establishing Test Procedures for the Analysis of Pollutants under Clean Water Act." Federal Register, Volume 49 (209), October 26, 1984, p. 43234.

U.S. EPA, 1979. Methods for Chemical Analysis of Water and Wastes. EPA-600/4-79-020, U.S. EPA-EMSL, Cincinnati, Ohio.

ATTACHMENT A

GENERAL SAMPLE CONTAINER AND PRESERVATION REQUIREMENTS

Sample Type and Concentration			Container[1]	Sample Size	Preservation[2]	Holding Time[2]
WATER						
Organics (GC&GC/MS)	VOC	Low	Borosilicate glass	2 x 40 mL	Cool to 4°C HCl to ≤ 2	14 days[9]
	Extractables SVOCs and pesticide/PCBs)	(Low	Amber glass	2x2 L or 4x1 L	Cool to 4°C	7 days to extraction; 40 days after extraction
	Extractables SVOCs and pesticide/PCBs)	(Medium	Amber glass	2x2 L or 4x1 L	None	7 days to extraction; 40 days after extraction
Inorganics	Metals	Low	High-density polyethylene	1 L	HNO_3 to pH ≤2	6 months (Hg-28 days)
		Medium	Wide-mouth glass	16 oz.	None	6 months
	Cyanide	Low	High-density polyethylene	1 L	NaOH to pH>12	14 days
	Cyanide	Medium	Wide-mouth glass	16 oz.	None	14 days
Organic/ Inorganic	High Hazard		Wide-mouth glass	8 oz.	None	14 days
SOIL						
Organics (GC&GC/MS)	VOC		EnCore Sampler	(3) 5 g Samplers	Cool to 4°C	48 hours to lab preservation
	Extractables SVOCs and pesticides/PCBs)	(Low	Wide-mouth glass	8 oz.	Cool to 4°C	14 days to extraction; 40 days after extraction
	Extractables SVOCs and pesticides/PCBs)	(Medium	Wide-mouth glass	8 oz.	Cool to 4°C	14 days to extraction; 40 days after extraction
Inorganics	Low/Medium		Wide-mouth glass	8 oz.	Cool to 4°C	6 months (Hg - 28 days) Cyanide (14 days)
Organic/Inorganic	High Hazard		Wide-mouth glass	8 oz.	None	NA
Dioxin/Furan	All		Wide-mouth glass	4 oz.	None	35 days until extraction; 40 days after extraction
TCLP	All		Wide-mouth glass	8 oz.	None	7 days until preparation; analysis as per fraction
AIR						
Volatile Organics	Low/Medium		Charcoal tube -- 7 cm long, 6 mm OD, 4 mm ID	100 L air	Cool to 4°C	5 days recommended

1 All glass containers should have Teflon cap liners or septa.
2 See Attachment E. Preservation and maximum holding time allowances per 40 CFR 136.

ATTACHMENT B

ADDITIONAL REQUIRED CONTAINERS, PRESERVATION TECHNIQUES, AND HOLDING TIMES

Parameter Number/Name	Container[1]	Preservation[2][3]	Maximum Holding Time[4]
INORGANIC TESTS:			
Acidity	P, G	Cool, 4°C	14 days
Alkalinity	P, G	Cool, 4°C	14 days
Ammonia - Nitrogen	P, G	Cool, 4°C; H_2SO_4 to pH 2	28 days
Biochemical Oxygen Demand (BOD)	P, G	Cool, 4°C	48 hours
Bromide	P, G	None required	28 days
Chemical Oxygen Demand (COD)	P, G	Cool, 4°C; H_2SO_4 to pH 2	28 days
Chloride	P, G	None required	28 days
Chlorine, Total Residual	P, G	None required	Analyze immediately
Color	P, G	Cool, 4°C	48 hours
Cyanide, Total and Amenable to Chlorination	P, G	Cool, 4°C; NaOH to pH 12; 0.6 g ascorbic acid[5]	14 days[6]
Fluoride	P	None required	28 days
Hardness	P, G	HNO_3 to pH 2; H_2SO_4 to pH 2	6 months
Total Kjeldahl and Organic Nitrogen	P, G	Cool, 4°C; H_2SO_4 to pH 2	28 days
Nitrate - Nitrogen	P, G	None required	48 hours
Nitrate-Nitrite - Nitrogen	P, G	Cool, 4°C; H_2SO_4 to pH 2	28 days
Nitrite - Nitrogen	P, G	Cool, 4°C	48 hours
Oil & Grease	G	Cool, 4°C; H_2SO_4 to pH 2	28 days
Total Organic Carbon (TOC)	P, G	Cool, 4°C; HCl or H_2SO_4 to pH 2	28 days
Orthophosphate	P, G	Filter immediately; Cool, 4°C	48 hours
Oxygen, Dissolved-Probe	G Bottle & top	None required	Analyze immediately
Oxygen, Dissolved-Winkler	G Bottle & top	Fix on site and store in dark	8 hours
Phenols	G	Cool, 4°C; H_2SO_4 to pH 2	28 days
Phosphorus, Total	P, G	Cool, 4°C; H_2SO_4 to pH 2	28 days
Residue, Total	P, G	Cool, 4°C	7 days
Residue, Filterable (TDS)	P, G	Cool, 4°C	7 days
Residue, Nonfilterable (TSS)	P, G	Cool, 4°C	7 days
Residue, Settleable	P, G	Cool, 4°C	48 hours
Residue, Volatile (Ash Content)	P, G	Cool, 4°C	7 days
Silica	P	Cool, 4°C	28 days
Specific Conductance	P, G	Cool, 4°C	28 days
Sulfate	P, G	Cool, 4°C	28 days

ATTACHMENT B
ADDITIONAL REQUIRED CONTAINERS, PRESERVATION TECHNIQUES, AND HOLDING TIMES
PAGE TWO

Parameter Number/Name	Container[1]	Preservation[2][3]	Maximum Holding Time[4]
INORGANIC TESTS (Cont'd):			
Sulfide	P, G	Cool, 4°C; add zinc acetate plus sodium hydroxide to pH 9	7 days
Sulfite	P, G	None required	Analyze immediately
Turbidity	P, G	Cool, 4°C	48 hours
METALS:[7]			
Chromium VI (Hexachrome)	P, G	Cool, 4°C	24 hours
Mercury (Hg)	P, G	HNO_3 to pH 2	28 days
Metals, except Chromium VI and Mercury	P, G	HNO_3 to pH 2	6 months
ORGANIC TESTS:[8]			
Purgeable Halocarbons	G, Teflon-lined septum	Cool, 4°C; 0.008% $Na_2S_2O_3$[5]	14 days
Purgeable Aromatic Hydrocarbons	G, Teflon-lined septum	Cool, 4°C; 0.008% $Na_2S_2O_3$[5] HCl to pH 2 [9]	14 days
Acrolein and Acrylonitrile	G, Teflon-lined septum	Cool, 4°C; 0.008% $Na_2S_2O_3$[5] adjust pH to 4-5 [10]	14 days
Phenols[11]	G, Teflon-lined cap	Cool, 4°C; 0.008% $Na_2S_2O_3$[5]	7 days until extraction; 40 days after extraction
Benzidines[11], [12]	G, Teflon-lined cap	Cool, 4°C; 0.008% $Na_2S_2O_3$[5]	7 days until extraction[13]
Phthalate esters[11]	G, Teflon-lined cap	Cool, 4°C	7 days until extraction; 40 days after extraction
Nitrosamines[11], [14]	G, Teflon-lined cap	Cool, 4°C; store in dark; 0.008% $Na_2S_2O_3$[5]	7 days until extraction; 40 days after extraction
PCBs[11]	G, Teflon-lined cap	Cool, 4°C	7 days until extraction; 40 days after extraction
Nitroaromatics & Isophorone[11]	G, Teflon-lined cap	Cool, 4°C; 0.008% $Na_2S_2O_3$[5]; store in dark	7 days until extraction; 40 days after extraction
Polynuclear Aromatic Hydrocarbons (PAHs)[11],[14]	G, Teflon-lined cap	Cool, 4°C; 0.008% $Na_2S_2O_3$[5]; store in dark	7 days until extraction; 40 days after extraction
Haloethers[11]	G, Teflon-lined cap	Cool, 4°C; 0.008% $Na_2S_2O_3$[5]	7 days until extraction; 40 days after extraction
Dioxin/Furan (TCDD/TCDF)[11]	G, Teflon-lined cap	Cool, 4°C; 0.008% $Na_2S_2O_3$[5]	7 days until extraction; 40 days after extraction

ATTACHMENT B
ADDITIONAL REQUIRED CONTAINERS, PRESERVATION TECHNIQUES, AND HOLDING TIMES
PAGE THREE

(1) Polyethylene (P): generally 500 ml or Glass (G): generally 1L.
(2) Sample preservation should be performed immediately upon sample collection. For composite chemical samples each aliquot should be preserved at the time of collection. When use of an automated sampler makes it impossible to preserve each aliquot, then chemical samples may be preserved by maintaining at 4°C until compositing and sample splitting is completed.
(3) When any sample is to be shipped by common carrier or sent through the United States Mail, it must comply with the Department of Transportation Hazardous Materials Regulations (49 CFR Part 172).
(4) Samples should be analyzed as soon as possible after collection. The times listed are the maximum times that samples may be held before analysis and still be considered valid. Samples may be held for longer periods only if the permittee, or monitoring laboratory, has data on file to show that the specific types of samples under study are stable for the longer periods, and has received a variance from the Regional Administrator.
(5) Should only be used in the presence of residual chlorine.
(6) Maximum holding time is 24 hours when sulfide is present. Optionally, all samples may be tested with lead acetate paper before pH adjustments are made to determine if sulfide is present. If sulfide is present, it can be removed by the addition of cadmium nitrate powder until a negative spot test is obtained. The sample is filtered and then NaOH is added to pH 12.
(7) Samples should be filtered immediately on site before adding preservative for dissolved metals.
(8) Guidance applies to samples to be analyzed by GC, LC, or GC/MS for specific compounds.
(9) Sample receiving no pH adjustment must be analyzed within 7 days of sampling.
(10) The pH adjustment is not required if acrolein will not be measured. Samples for acrolein receiving no pH adjustment must be analyzed within 3 days of sampling.
(11) When the extractable analytes of concern fall within a single chemical category, the specified preservative and maximum holding times should be observed for optimum safeguard of sample integrity. When the analytes of concern fall within two or more chemical categories, the sample may be preserved by cooling to 4°C, reducing residual chlorine with 0.008% sodium thiosulfate, storing in the dark, and adjusting the pH to 6-9; samples preserved in this manner may be held for 7 days before extraction and for 40 days after extraction. Exceptions to this optional preservation and holding time procedure are noted in footnote 5 (re: the requirement for thiosulfate reduction of residual chlorine) and footnotes 12, 13 (re: the analysis of benzidine).
(12) If 1,2-diphenylthydrazine is likely to be present, adjust the pH of the sample to 4.0±0.2 to prevent rearrangement to benzidine.
(13) Extracts may be stored up to 7 days before analysis if storage is conducted under an inert (oxidant-free) atmosphere.
(14) For the analysis of diphenylnitrosamine, add 0.008% $Na_2S_2O_3$ and adjust pH to 7-10 with NaOH within 24 hours of sampling.
(15) The pH adjustment may be performed upon receipt at the laboratory and may be omitted if the samples are extracted within 72 hours of collection. For the analysis of aldrin, add 0.008% $Na_2S_2O_3$.

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1.0 PURPOSE

The purpose of this Standard Operating Procedure (SOP) is to identify and designate the field data record forms, logs, and reports generally initiated and maintained for documenting Tetra Tech NUS, Inc. (TtNUS) field activities.

2.0 SCOPE

Documents presented within this SOP (or equivalents) shall be used for all TtNUS field activities, as applicable. Other or additional documents may be required by specific client contracts or project planning documents.

3.0 GLOSSARY

None.

4.0 RESPONSIBILITIES AND PERSONNEL QUALIFICATIONS

Project Manager (PM) - The PM is responsible for obtaining hardbound controlled-distribution logbooks (from the appropriate source), as needed. In addition, the Project Manager is responsible for placing all field documentation used in site activities (i.e., records, field reports, sample data sheets, field notebooks, and the site logbook) in the project's central file upon the completion of field work.

Field Operations Leader (FOL) - The FOL is responsible for ensuring that the site logbook, notebooks, and all appropriate and current forms and field reports included in this SOP (and any additional forms required by the contract) are correctly used, accurately filled out, and completed in the required time frame.

General personnel qualifications for field documentation activities include the following:

- Occupational Safety and Health Administration (OSHA) 40-hour and applicable refresher training.
- Capability of performing field work under the expected physical and environmental (i.e., weather) conditions.
- Familiarity with appropriate procedures for documentation, handling, packaging, and shipping.

5.0 PROCEDURES

5.1 SITE LOGBOOK

5.1.1 General

The site logbook is a hard-bound, paginated, controlled-distribution record book in which all major on-site activities are documented. At a minimum, record or reference the following activities/events (daily) in the site logbook:

- All field personnel present
- Arrival/departure times and names of site visitors
- Times and dates of health and safety training
- Arrival/departure times of equipment
- Times and dates of equipment calibration

- Start and/or completion of borehole, trench, monitoring well installation activities, etc.
- Daily on-site activities
- Sample pickup information
- Health and safety issues (level of protection, personal protective equipment [PPE], etc.)
- Weather conditions

Maintain a site logbook for each project and initiate it at the start of the first on-site activity (e.g., site visit or initial reconnaissance survey). Make entries every day that on-site activities take place involving TtNUS or subcontractor personnel. Upon completion of the fieldwork, provide the site logbook to the PM or designee for inclusion in the project's central file.

Record the following information on the cover of each site logbook:

- Project name
- TtNUS project number
- Sequential book number
- Start date
- End date

Information recorded daily in the site logbook need not be duplicated in other field notebooks (see Section 5.2) but must summarize the contents of these other notebooks and refer to specific page locations in these notebooks for detailed information (where applicable). An example of a typical site logbook entry is shown in Attachment A.

If measurements are made at any location, either record the measurements and equipment used in the site logbook or reference the field notebook in which the measurements are recorded (see Attachment A).

Make all logbook, notebook, and log sheet entries in indelible ink (black pen is preferred). No erasures are permitted. If an incorrect entry is made, cross out the entry with a single strike mark, initial, and date it. At the completion of entries by any individual, the logbook pages used must be signed and dated by the person making the entries. The site logbook must also be signed by the FOL at the end of each day.

5.1.2 Photographs

Sequentially number movies, slides, or photographs taken of a site or any monitoring location to correspond to logbook/notebook entries. Enter the name of the photographer, date, time, site location, site description, and weather conditions in the logbook/notebook as the photographs are taken. A series entry may be used for rapid-sequence photographs. The photographer is not required to record the aperture settings and shutter speeds for photographs taken within the normal automatic exposure range. However, special lenses, films, filters, and other image-enhancement techniques must be noted in the logbook/notebook. If possible, such techniques shall be avoided because they can adversely affect the accuracy of photographs. Chain-of-custody procedures depend on the subject matter, type of camera (digital or film), and the processing it requires. Follow chain-of-custody procedures for film used for aerial photography, confidential information, or criminal investigation. After processed, consecutively number the slides of photographic prints and label them according to the logbook/notebook descriptions. Docket the site photographs and associated negatives and/or digitally saved images to compact disks into the project's central file.

5.2 FIELD NOTEBOOKS

Key field team personnel may maintain a separate dedicated field notebook to document the pertinent field activities conducted directly under their supervision. For example, on large projects with multiple investigative sites and varying operating conditions, the Health and Safety Officer may elect to maintain a

separate field notebook. Where several drill rigs are in operation simultaneously, each site geologist assigned to oversee a rig must maintain a field notebook.

5.3 FIELD FORMS

All TtNUS field forms (see list in Section 6.0 of this SOP) can be found on the company's intranet site (http://intranet.ttnus.com) under Field Log Sheets. Forms may be altered or revised for project-specific needs, subject to client approval. Care must be taken to ensure that all essential information can be documented. Guidelines for completing these forms can be found in the related sampling SOPs.

5.3.1 Sample Collection, Labeling, Shipment, Request for Analysis, and Field Test Results

5.3.1.1 Sample Log Sheet

Sample log sheets are used to record specified types of data while sampling. The data recorded on these sheets are useful in describing the sample as well as pointing out any problems, difficulties, or irregularities encountered during sampling. Complete a sample log sheet for each sample obtained, including field quality control (QC) samples.

5.3.1.2 Sample Label

A typical sample label is illustrated in Attachment B. Complete the required information on the adhesive labels and apply them to every sample container. Obtain sample labels from the appropriate program/project source, request that they be electronically generated in house, or request them the laboratory subcontractor.

5.3.1.3 Chain-of-Custody Record

The chain-of-custody record is a multi-part form that is initiated as samples are acquired and accompanies a sample (or group of samples) as they are transferred from person to person. This form must be used as follows for any samples collected for chemical or geotechnical analysis whether the analyses are performed on site or off site:

- Retain one carbonless copy of the completed chain-of custody form in the field.
- Send one copy is sent to the PM (or designee)
- Send the original to the laboratory with the associated samples. Place the original (top, signed copy) of the chain-of custody form inside a large Ziploc®-type bag taped inside the lid of the shipping cooler. If multiple coolers are sent but are included on one chain-of custody form, send the form with the cooler containing vials for volatile organic compound (VOC) analysis or the cooler with the air bill attached. Indicate on the air bill how many coolers are included with that shipment.

An example of a chain-of-custody form is provided as Attachment C. After the samples are received at the laboratory, the sample cooler and contents are checked and any problems are noted on the enclosed chain-of custody form (any discrepancies between the sample labels and chain-of custody form and any other problems that are noted are resolved through communication between the laboratory point-of-contact and the TtNUS PM). The chain-of custody form is signed and copied. The laboratory will retain the copy, and the original becomes part of the samples' corresponding analytical data package.

5.3.1.4 Chain-of-Custody Seal

Attachment D is an example of a custody seal. The custody seal is an adhesive-backed label that is part of a chain-of-custody process and is used to prevent tampering with samples after they have been collected in the field and sealed in coolers for transport to the laboratory. Sign and date custody seals

and affix them across the lid and body of each cooler (front and back) containing environmental samples (see SOP SA-6.1). Obtain custody seals from the laboratory (if available) or purchase them from a supplier.

5.3.1.5 Geochemical Parameters Log Sheets

Complete Field Analytical Log Sheets to record geochemical and/or natural attenuation field test results.

5.3.2 Hydrogeological and Geotechnical Forms

5.3.2.1 Groundwater Level Measurement Sheet

Complete a Groundwater Level Measurement Sheet for each round of water level measurements made at a site.

5.3.2.2 Data Sheet for Pumping Test

During the performance of a pumping test (or an in-situ hydraulic conductivity test), a large amount of data must be recorded, often within a short time period. Use a Pumping Test Data Sheet to facilitate this task by standardizing the data collection format for the pumping well and observation wells, and allowing the time interval for collection to be established in advance.

5.3.2.3 Packer Test Report Form

Complete a Packer Test Report Form for each well at which a packer test is conducted.

5.3.2.4 Boring Log

Complete a Summary Log of Boring, or Boring Log for each soil boring performed to document the materials encountered, operation and driving of casing, and locations/depths of samples collected. In addition, if volatile organics are monitored on cores, samples, cuttings from the borehole, or breathing zone, (using a photoionization detector [PID] or flame ionization detector [FID]), enter these readings on the boring log at the appropriate depth. When they become available, enter the laboratory sample number, concentrations of key contaminants, or other pertinent information in the "Remarks" column. This feature allows direct comparison of contaminant concentrations with soil characteristics.

5.3.2.5 Monitoring Well Construction Details Form

Complete a Monitoring Well Construction Details Form for every monitoring well, piezometer, or temporary well point installed. This form contains specific information on length and type of well riser pipe and screen, backfill, filter pack, annular seal and grout characteristics, and surface seal characteristics. This information is important in evaluating the performance of the monitoring well, particularly in areas where water levels show temporal variation or where there are multiple (immiscible) phases of contaminants. Depending on the type of monitoring well (in overburden or bedrock, stick-up or flush mount), different forms are used.

5.3.2.6 Test Pit Log

When a test pit or trench is constructed for investigative or sampling purposes, a Test Pit Log must be filled out by the responsible field geologist or sampling technician.

5.3.2.7 Miscellaneous Monitoring Well Forms

Miscellaneous monitoring well forms that may be required on a project-specific basis include the Monitoring Well Materials Certificate of Conformance and Monitoring Well Development Record. Use a Monitoring Well Materials Certificate of Conformance to document all materials utilized during each monitoring well installation. Use a Monitoring Well Development Record to document all well development activities.

5.3.2.8 Miscellaneous Field Forms – Quality Assurance and Checklists

Miscellaneous field forms/checklists forms that may be required on a project-specific basis include the following:

- Container Sample and Inspection Sheet – use this form when a container (drum, tank, etc.) is sampled and/or inspected.
- QA Sample Log Sheet – use this form when a QA sample such as an equipment rinsate blank, source blank, etc. is collected.
- Field Task Modification Request (FTMR) – use this form to document deviations from the project planning documents. The FOL is responsible for initiating the FTMRs. Maintain copies of all FTMRs with the on-site planning documents, and place originals in the final evidence file.
- Field Project Daily Activities Checklist and Field Project Pre-Mobilization Checklist – used these during both the planning and field effort to ensure that all necessary tasks are planned for and completed. These two forms are not requirements but are useful tools for most field work.

5.3.3 Equipment Calibration and Maintenance Form

The calibration or standardization of monitoring, measuring, or test equipment is necessary to ensure the proper operation and response of the equipment, to document the accuracy, precision, or sensitivity of the measurements, and determine if correction should be applied to the readings. Some items of equipment require frequent calibration, others infrequent. Some are calibrated by the manufacturer, others by the user.

Each instrument requiring calibration has its own Equipment Calibration Log, which documents that the manufacturer's instructions were followed for calibration of the equipment, including frequency and type of standard or calibration device. Maintain an Equipment Calibration Log for each electronic measuring device used in the field; make entries for each day the equipment is used or in accordance with manufacturer recommendations.

5.4 FIELD REPORTS

The primary means of recording on-site activities is the site logbook. Other field notebooks may also be maintained. These logbooks and notebooks (and supporting forms) contain detailed information required for data interpretation or documentation but are not easily used for tracking and reporting of progress. Furthermore, the field logbook/notebooks remain on site for extended periods of time and are thus not accessible for timely review by project management. Other reports useful for tracking and reporting the progress of field activities are described below.

5.4.1 Daily Activities Report

To provide timely oversight of on-site contractors, complete and submit Daily Activities Reports (DARs) as described below.

5.4.1.1 Description

The DAR documents the activities and progress for each day's field work. Complete this report on a daily basis whenever there are drilling, test pitting, well construction, or other related activities occurring that involve subcontractor personnel. These sheets summarize the work performed and form the basis of payment to subcontractors. The DAR form can be found on the TtNUS intranet site.

5.4.1.2 Responsibilities

It is the responsibility of the rig geologist to complete the DAR and obtain the driller's signature acknowledging that the times and quantities of material entered are correct.

5.4.1.3 Submittal and Approval

At the end of the shift, the rig geologist must submit the DAR to the FOL for review and filing. The Daily Activities Report is not a formal report and thus requires no further approval. The DARs are retained by the FOL for use in preparing the site logbook and in preparing weekly status reports for submission to the PM.

5.4.2 Weekly Status Reports

To facilitate timely review by project management, photocopies of logbook/notebook entries may be made for internal use.

In addition to those described herein, other summary reports may also be contractually required.

All TtNUS field forms can be found on the company's intranet site at http://intranet.ttnus.com under Field Log Sheets.

6.0 LISTING OF FIELD FORMS ON THE TtNUS INTRANET SITE

- Boring Log
- Container Sample and Inspection Sheet
- Daily Activities Checklist
- Daily Activities Record
- Equipment Calibration Log
- Field Task Modification Request
- Field Analytical Log sheet - Geochemical Parameters
- Groundwater Level Measurement Sheet
- Groundwater Sample Log Sheet
- Hydraulic Conductivity Test Data Sheet
- Low Flow Purge Data Sheet
- Bedrock Monitoring Well Construction (Stick Up)
- Bedrock Monitoring Well Construction Flush Mount
- Bedrock Monitoring Well Construction Open Hole
- Confining Layer Monitoring Well Construction
- Monitoring Well Development Record

- Monitoring Well Materials Certificate of Conformance
- Overburden Monitoring Well Construction Flush Mount
- Overburden Monitoring Well Construction Stick Up
- Packer Test Report Form
- Pumping Test Data Sheet
- QA Sample Log Sheet
- Soil/Sediment Sample Log Sheet
- Surface Water Sample Log Sheet
- Test Pit Log
- Field Project Pre-Mobilization Checklist

ATTACHMENT A
TYPICAL SITE LOGBOOK ENTRY

START TIME: _____ DATE: _____

SITE LEADER: _____
PERSONNEL:

TtNUS	DRILLER	SITE VISITORS
_____	_____	_____
_____	_____	_____
_____	_____	_____

WEATHER: Clear, 68°F, 2-5 mph wind from SE

ACTIVITIES:

1. Steam jenney and fire hoses were set up.
2. Drilling activities at well ____ resumes. Rig geologist was _____. See Geologist's Notebook, No. 1, page 29-30, for details of drilling activity. Sample No. 123-21-S4 collected; see sample logbook, page 42. Drilling activities completed at 11:50 and a 4-inch stainless steel well installed. See Geologist's Notebook, No. 1, page 31, and well construction details for well _____.
3. Drilling rig No. 2 steam-cleaned at decontamination pit. Then set up at location of well _____.
4. Well _____ drilled. Rig geologist was _____. See Geologist's Notebook, No. 2, page ____ for details of drilling activities. Sample numbers 123-22-S1, 123-22-S2, and 123-22-S3 collected; see sample logbook, pages 43, 44, and 45.
5. Well _____ was developed. Seven 55-gallon drums were filled in the flushing stage. The well was then pumped using the pitcher pump for 1 hour. At the end of the hour, water pumped from well was "sand free."
6. EPA remedial project manger arrives on site at 14:25 hours.
7. Large dump truck arrives at 14:45 and is steam-cleaned. Backhoe and dump truck set up over test pit _____.
8. Test pit _____ dug with cuttings placed in dump truck. Rig geologist was _____. See Geologist's Notebook, No. 1, page 32, for details of test pit activities. Test pit subsequently filled. No samples taken for chemical analysis. Due to shallow groundwater table, filling in of test pit ___ resulted in a very soft and wet area. A mound was developed and the area roped off.
9. Express carrier picked up samples (see Sample Logbook, pages 42 through 45) at 17:50 hours. Site activities terminated at 18:22 hours. All personnel off site, gate locked.

_____

Field Operations Leader

ATTACHMENT B
SAMPLE LABEL

Tetra Tech NUS, Inc. 661 Andersen Drive Pittsburgh, 15220 (412)921-7090	Project: Site: Location:		
Sample No:			Matrix:
Date:	Time:	Preserve:	
Analysis:			
Sampled by:	Laboratory:		

ATTACHMENT C
CHAIN-OF-CUSTODY RECORD FORM

TETRA TECH NUS, INC.

CHAIN OF CUSTODY | NUMBER 3413 | PAGE ___ OF ___

PROJECT NO: | FACILITY: | PROJECT MANAGER | PHONE NUMBER | LABORATORY NAME AND CONTACT:

SAMPLERS (SIGNATURE) | FIELD OPERATIONS LEADER | PHONE NUMBER | ADDRESS

CARRIER/WAYBILL NUMBER | CITY, STATE

STANDARD TAT ☐
RUSH TAT ☐
☐ 24 hr. ☐ 48 hr. ☐ 72 hr. ☐ 7 day ☐ 14 day

DATE YEAR	TIME	SAMPLE ID	LOCATION ID	TOP DEPTH (FT)	BOTTOM DEPTH (FT)	MATRIX (GW, SO, SW, SD, QC, ETC.)	COLLECTION METHOD GRAP (G) COMP (C)	No. OF CONTAINERS	CONTAINER TYPE PLASTIC (P) or GLASS (G) / PRESERVATIVE USED / TYPE OF ANALYSIS	COMMENTS

	DATE	TIME
1. RELINQUISHED BY	DATE	TIME
2. RELINQUISHED BY	DATE	TIME
3. RELINQUISHED BY	DATE	TIME

	DATE	TIME
1. RECEIVED BY	DATE	TIME
2. RECEIVED BY	DATE	TIME
3. RECEIVED BY	DATE	TIME

COMMENTS

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CUSTODY SEAL	**CUSTODY SEAL**
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Signature	**Signature**

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1.0 PURPOSE

Decontamination is the process of removing and/or neutralizing site contaminants that have contacted and/or accumulated on equipment. The purpose of this Standard Operating Procedure (SOP) is to protect site personnel, the general public, and the environment while preserving or maintaining sample integrity. It is further intended through this procedure to describe the steps necessary for proper decontamination of drilling equipment, earth-moving equipment , chemical sampling equipment and field operation and analytical equipment.

2.0 SCOPE AND APPLICABILITY

This procedure applies to all equipment used to provide access to/acquire environmental samples that may have become contaminated through direct contact with contaminated media including air, water, and soil. This equipment includes drilling and heavy equipment and chemical sampling and field analytical equipment. Where technologically and economically feasible, single-use sealed disposable equipment will be employed to minimize the potential for cross-contamination. This SOP also provides general reference information on the control of contaminated materials.

Decontamination methods and equipment requirements may differ from one project to another. General equipment items are specified in Section 6.0, but project-specific equipment must be obtained to address the project-specific decontamination procedures presented in Section 7.0 and applicable subsections.

3.0 GLOSSARY

Alconox/Liquinox - A brand of phosphate-free laboratory-grade detergent.

Decontamination Solution - A solution selected/identified in the Health and Safety Plan or Project-Specific Quality Assurance Plan. The solution is selected and employed as directed by the project chemist/health and safety professional.

Deionized Water (DI) - Tap water that has been treated by passing through a standard deionizing resin column. This water may also pass through additional filtering media to attain various levels of analyte-free status. The DI water should meet College of American Pathologists (CAP) and National Committee for Clinical Laboratory Standards (NCCLS) specifications for reagent-grade Type I water.

Potable Water - Tap water from any municipal water treatment system. Use of an untreated potable water supply is not an acceptable substitute for tap water.

Pressure Washing - Process employing a high-pressure pump and nozzle configuration to create a high-pressure spray of potable water. High-pressure spray is employed to remove solids from equipment.

Solvent – A liquid in which solid chemicals or other liquids are dissolved. The solvent of choice is pesticide-grade isopropanol. Use of other solvents (methanol, acetone, or hexane) may be required for particular projects or for a particular purpose (e.g., removal of concentrated waste) and must be justified in the project planning documents. For example, it may be necessary to use hexane when analyzing for trace levels of pesticides, PCBs, or fuels. In addition, because many of these solvents are not miscible in water, the equipment should be air dried prior to use. Solvents should not be used on PVC equipment or well construction materials.

Steam Pressure Washing - A cleaning method employing a high-pressure spray of heated potable water to remove various organic/inorganic chemicals from equipment.

4.0 RESPONSIBILITIES AND PERSONNEL QUALIFICATIONS

Project Manager - Responsible for ensuring that all field activities are conducted in accordance with approved project plan(s) requirements.

Decontamination Personnel - Individuals assigned the task of decontamination. It is the responsibility of these individuals to understand the use and application of the decontamination process and solutions as well as the monitoring of that process to ensure that it is working properly. This is accomplished through visual evaluation, monitoring instrument scanning of decontaminated items, and/or through the collection of rinsate blanks to verify contaminant removal.

Field Operations Leader (FOL) - Responsible for the implementation of project-specific planning documents. This includes on-site verification that all field activities are performed in compliance with approved SOPs or as otherwise dictated by the approved project plan(s). The FOL is also responsible for the completion and accuracy of all field documentation.

Site Safety Officer (SSO) - Exercises shared responsibility with the FOL concerning decontamination effectiveness. All equipment arriving on site (as part of the equipment inspection), leaving the site, and moving between locations is required to go through a decontamination evaluation. This is accomplished through visual examination and/or instrument screening to determine the effectiveness of the decontamination process. Improper or incomplete decontamination is sufficient to restrict equipment from entering the site, exiting the site, or moving to a new location on the site until the objectives are successfully completed.

General personnel qualifications for decontamination activities include the following:

- Occupational Safety and Health Administration (OSHA) 40-hour and applicable refresher training.
- Capability of performing field work under the expected physical and environmental (i.e., weather) conditions.
- Familiarity with appropriate decontamination procedures.

5.0 HEALTH AND SAFETY

In addition to the health and safety issues and reminders specified in subsections of this SOP, the following considerations and requirements must be observed as SOPs for field equipment decontamination activities:

- If any solvents or hazardous chemicals (e.g., isopropyl alcohol) are to be used in equipment decontamination activities, the FOL must first obtain the manufacturer's/supplier's Material Safety Data Sheet (MSDS) and assure that it is reviewed by all users (prior to its use), added to the site Hazardous Chemical Inventory, and maintained on site as part of the project Hazard Communication Program.
- Review and observe specific health and safety requirements (e.g., personal protective equipment [PPE]) specified in the project-specific health and safety plan for this activity.

6.0 EQUIPMENT LIST

- Wood for decontamination pad construction, when applicable (see Section 7.1).

- Tools for constructing decontamination pad frame, when applicable (see Section 7.1).
- Visqueen sheeting or comparable material to cover decontamination pad frame, when applicable (see Section 7.1).
- Wash/drying racks for auger flights and drill/drive rods, when applicable (see Section 7.2).
- PPE as specified in the project health and safety plan.
- Soap and water for washing and rinsing.
- Deionized water for final rinsing.
- Solvents (e.g., pesticide-grade isopropanol) for rinsing (see applicable portions of Section 7.2).
- Tubs, buckets, etc. for containerizing rinse water (see applicable portions of Section 7.2).
- Sample bottles for collecting rinsate blanks (see Section 7.2).
- Calibrated photoionization detector (PID) or flame ionization detector (FID) to monitor decontaminated equipment for organic vapors generated through the existence of residual contamination or the presence of decontamination solvent remaining after the piece was rinsed.
- Aluminum foil or clear clean plastic bag for covering cleaned equipment (see applicable portions of Section 7.2).
- Paper towels or cloths for wiping.
- Brushes, scrapers, or other hand tools useful for removing solid materials from equipment.
- Clear plastic wrap for covering or wrapping large decontaminated equipment items (see Section 7.2.2).
- Drum-moving equipment for moving filled waste drums (optional) (see Section 7.3).
- Drum labels for waste drums (see Attachment A).

7.0 PROCEDURES

The process of decontamination is accomplished through the removal of contaminants, neutralization of contaminants, or isolation of contaminants. To accomplish this activity, preparation is required including site preparation, equipment selection, and evaluation of the decontamination requirements and processes. Site contaminant types, concentrations, and media types are primary drivers in the selection of the types of decontamination and where it will be conducted. For purposes of this SOP, discussion is limited to decontamination procedures for general environmental investigations.

Decontamination processes will be performed at the location(s) specified in project-specific planning documents. Typical decontamination locations include the following:

- Temporary decontamination pads/facilities
- Sample locations
- Centralized decontamination pad/facilities

- Combination of some or all of the above

The following discussion includes general considerations for the decontamination process. Specific construction and implementation procedures will be as specified in the project-specific planning documents and/or may be as dictated by site-specific conditions as long as the intent of the requirements in the planning documents is met. This intent is to contain any residual fluids and solids generated through the decontamination process.

7.1 Decontamination Pad Design/Construction Considerations

7.1.1 Temporary Decontamination Pads

Temporary decontamination pads may be constructed at satellite locations within the site area in support of temporary work areas. These structures are generally constructed to support the decontamination of heavy equipment such as drill rigs and earth-moving equipment but can be employed for smaller articles.

The purpose of the decontamination pad is to contain wash waters and potentially contaminated soil generated during decontamination procedures. Therefore, construction of these pads should take into account the following considerations:

- Site location – The decontamination site selected should be far enough from the work site to maximize decontamination effectiveness while minimizing travel distance. The location of the decontamination site shall be selected to provide, in the judgment of the FOL or FOL designee, compliance with as many of the following characteristics as practicable:

  - Well removed from pedestrian/vehicle thoroughfares.

  - Avoidance of areas where control/custody cannot be maintained.

  - Avoidance of areas where potential releases of contaminated media or decontamination fluids may be compounded through access to storm water transport systems, streams, or other potentially sensitive areas.

  - Avoidance of potentially contaminated areas.

  - Avoidance of areas too close to the ongoing operation, where cross-contamination may occur.

  The selected decontamination site should include the following, where possible:

  - Areas where potable water and electricity are provided.

> ***Safety Reminder***
>
> When utilizing electrical power sources, either hard-wired or portable-generated sources, ensure that:
>
> - All power is routed through a Ground Fault Circuit Interrupter (GFCI).
>
> - All power cords are in good condition (no physical damage), rated for the intended energy load, and designated for outdoor use.
>
> In situations where accomplishing these elements is not possible, it will be necessary to implement a site electrical grounding program.

- Areas where support activities such as removing decontamination waters soil and sediment are possible without entering an active exclusion zone.

- Areas that offer sufficient size to carry out the specific decontamination sequence.

- Decontamination pad (decon pad) – The decon pad shall be constructed to meet the following characteristics:

  - Size – The size of the pad should be sufficient to accept the equipment to be decontaminated as well as permitting free movement around the equipment by the personnel conducting the decontamination. The size should permit these movements utilizing pressure/steam washer wands and hoses and minimizing splash due to work in close quarters.

  - Slope – An adequate slope will be constructed to permit the collection of water and potentially contaminated soil within a trough or sump constructed at one end. The collection point for wash waters should be of adequate distance that the decontamination workers do not have to walk through the wash waters while completing their tasks. Because the pad will be sloped, place a light coating of sand over the plastic to minimize potential slips and falls. See the text about liners below.

  - Sidewalls – The sidewalls shall be at least 6 inches in height (or as high as possible if 6 inches is not achievable) to provide adequate containment for wash waters and soil. If splash represents a potential problem, splash guards should be constructed to control overspray. Sidewalls may be constructed of wood, inflatables, sand bags, etc. to permit containment. Splash guards are typically wood frames with Visqueen coverings to control overspray.

  - Liner – Depending on the types of equipment and decontamination method to be used, the liner should be of sufficient thickness to provide a puncture-resistant barrier between the decontamination operation and the unprotected environment. Care should be taken to examine the surface area prior to placing the liner to remove sharp articles (sticks, stones, debris) that could puncture the liner. Liners are intended to form an impermeable barrier. The thickness may vary from a minimum recommended thickness of 10 mil to 30 mil. The desired thickness may be achieved through layering materials of lighter construction. It should be noted that various materials (rubber, polyethylene sheeting) become slippery when wet. To minimize this potential hazard associated with a sloped liner, a light coating of sand shall be applied to provide traction as necessary.

  - Wash/drying racks – Auger flights, drill/drive rods, and similar equipment require racks positioned off of the ground to permit these articles to be washed, drained, and dried while secured from falling during this process.

For decontamination of direct-push technology (DPT) equipment, the pad may be as simple as a mortar tub containing buckets of soapy water for washing and an empty bucket to capture rinse waters. Decontamination may be conducted at the rear of the rig to permit rapid tool exchange.

- Maintenance – Maintain the decontamination area by:

  - Periodically clearing the work area of standing water, soil, and debris, and coiling hoses to aid in eliminating slip, trip, and fall hazards. In addition, these articles will reduce potential backsplash and cross-contamination.

- Regularly changing the decontamination fluids to ensure proper cleaning and prevent cross-contamination.

- PPE – Periodically evaluate the condition of, and maintain the decontamination equipment, including regular cleaning of face shields and safety glasses. This is critical to ensuring the safety of decontamination personnel and the integrity of the decontamination process, and it will ensure that equipment is functioning properly.

7.1.2 Decontamination Activities at Drill Rigs/DPT Units

During subsurface sampling activities including drilling and DPT activities, decontamination of drive rods, Macro Core Samplers, split spoons, etc. is typically conducted at an area adjacent to the operation. Decontamination is generally accomplished using a soap/water wash and rinse utilizing buckets and brushes. This area requires sufficient preparation to accomplish the decontamination objectives.

Buckets shall be placed within mortar tubs or similar secondary containment tubs to prevent splash and spills from reaching unprotected environmental media. Drying racks shall be employed as directed for temporary pads to permit parts to dry and be evaluated prior to use/reuse. Methodology regarding this activity is provided in Section 7.2.

7.1.3 Decontamination Activities at Remote Sample Locations

When sampling at remote locations, sampling equipment such as trowels and pumps/tubing should be evacuated of potentially contaminated media to the extent possible. This equipment should be wrapped in plastic for transport to the temporary/centralized decontamination location for final cleaning and disposition. Flushing and cleaning of single-use equipment such as disposable trowels, tubing, and surgeon's gloves may allow disposal of this equipment after visible soil and water remnants have been removed.

7.2 Equipment Decontamination Procedures

The following represents procedures to be employed for the decontamination of equipment that may have contacted and/or accumulated contamination through site investigation activities.

7.2.1 Monitoring Well Sampling Equipment

7.2.1.1 Groundwater sampling equipment – This includes pumps inserted into monitoring wells such as bladder pumps, Whale pumps, and Redi-Flo pumps and reusable bailers, etc.

1. Evacuate to the extent possible, any purge water within the pump/bailer.

2. Scrub using soap and water and/or steam clean the outside of the pump/bailer and, if applicable, the pump tubing.

3. Insert the pump and tubing/bailer into a clean container of soapy water. Pump/run a sufficient amount of soapy water through the pump/bailer to flush out any residual well water. After the pump is flushed, circulate soapy water through the pump to ensure that the internal components are thoroughly flushed.

4. Remove the pump and tubing/bailer from the container

5. Rinse external pump components using tap water.

6. Insert the pump and tubing/bailer into a clean container of tap water. Pump/run a sufficient amount of tap water through the pump/bailer to evacuate all of the soapy water (until clear).

> ***CAUTION***
> Do not rinse PE, PVC, and associated tubing with solvents –
> Use the procedures defined in the project-specific planning documents. If they are not defined, contact the FOL for guidance. The solvent rinse described in Step 7 may be omitted if groundwater does not contain oil, grease, PAHs, PCBs, or other hard to remove organic materials.

7. If groundwater contains or is suspected to contain oil, grease, PAHs, PCBs, or other hard to remove organic materials, rinse the equipment to be cleaned with pesticide-grade isopropanol.

8. Pass deionized water through the hose to flush out the tap water and solvent residue as applicable.

9. Drain residual deionized water to the extent possible.

10. Allow components of the equipment to air dry.

11. For bladder pumps, disassemble the pump and wash the internal components with soap and water, then rinse with tap water, isopropanol, and deionized water and allow to dry. After the parts are dry, conduct a visual inspection and a monitoring instrument scan to ensure that potential contaminants and all decontamination solvent have been removed. Collect a rinsate blank in accordance with the project-specific planning documents to ensure that the decontamination process is functioning as intended. The typical frequency of collection for rinsate blanks is 1 per 20 field samples. In addition, wipe samples or field tests such as UV light may be used.

12. Wrap pump/bailer in aluminum foil or a clear clean plastic bag for storage.

> ***SAFETY REMINDER***
> Remember when handling powered equipment to disconnect the power source and render the equipment to a zero energy state (both potential and kinetic) before opening valves, disconnecting lines, etc.

7.2.1.2 Electronic Water Level Indicators/Sounders/Tapes

During water level measurements, rinsing the extracted tape and probe with deionized water and wiping the surface of the extracted tape between locations is acceptable. However, periodic full decontamination should be conducted as follows:

1. Wash with soap and water
2. Rinse with tap water
3. Rinse with deionized water

> ***NOTE***
> In situations where oil, grease, free product, other hard to remove materials are encountered, probes and exposed tapes should be washed in hot soapy water. If probes or tapes cannot be satisfactorily decontaminated (they are still stained, discolored, etc.), they should be removed from service.

7.2.1.3 Miscellaneous Equipment

Miscellaneous equipment including analytical equipment (water quality testing equipment) shall be cleaned per manufacturers' instructions. This generally includes wiping the sensor housing and rinsing with tap and deionized water.

Coolers/shipping containers employed to ship samples are received from the laboratory in a variety of conditions including marginal to extremely poor. Coolers shall be evaluated prior to use for the following:

- Structural integrity – Coolers missing handles or having breaks in the outer housing should be removed and not used. Notify the laboratory that the risk of shipping samples in the cooler(s) provided is too great and request a replacement unit.

- Cleanliness – As per protocol, only volatile organic samples are accompanied by a trip blank. If a cooler's cleanliness is in question (visibly dirty/stained) or if there are noticeable odors, the cooler should be decontaminated prior to use as follows:

  1. Wash with soap and water
  2. Rinse with tap water
  3. Dry

If these measures fail to clean the cooler to an acceptable level, remove the unit from use as a shipping container and ask the cooler provider (e.g., the analytical laboratory) to provide a replacement unit.

7.2.2 Downhole Drilling Equipment

This includes any portion of the drill rig that is over the borehole, including auger flights, drill stems, rods, and associated tooling that would extend over the borehole. The following procedure is to be employed prior to initiating the drilling/sampling activity, then between locations:

> ***CAUTION***
> Exercise care when using scrapers to remove soil and debris from downhole drilling equipment. Inadvertent slips of scrapers have resulted in cuts, scrapes, and injured knuckles, so use scrapers carefully when removing soil from these items.

1. Remove loose soil using shovels, scrapers, etc.

2. Through a combination of scrubbing using soap and water and/or steam cleaning or pressure washing, remove visible dirt/soil from the equipment being decontaminated.

> ***CAUTION***
> In Step 3, do not rinse PE, PVC, and associated tubing with solvents. The appropriate procedures should be defined within the project-specific planning documents. If they are not defined, contact the FOL for guidance. The solvent rinse described in Step 4 may be omitted if groundwater does not contain oil, grease, PAHs, PCBs, or other hard to remove organic materials.

3. Rinse the equipment with tap water, where applicable (steam cleaning and pressure washing incorporate rinsing as part of the process).

4. If the equipment has directly or indirectly contacted contaminated sample media and is known or suspected of being contaminated with oil, grease, PAHs, PCBs, or other hard to remove organic materials, rinse equipment with pesticide-grade isopropanol

5. To the extent possible, allow components to air dry.

6. If the decontaminated equipment is to be used immediately after decontamination, screen it with a calibrated photoionization detector (PID)/flame ionization detector (FID) to ensure that all contaminants and possible decontamination solvents (if they were used) have been adequately removed.

7. Wrap or cover equipment in clear plastic until it is time to be used.

SAFETY REMINDER

Even when equipment is disconnected from power sources, dangers such as the following may persist:

Falls - An auger flight standing on its end may fall and injure someone. Secure all loose articles to prevent heavy articles from falling onto people or equipment.

Burns - Steam cleaner water is heated to more than 212 ˚F and exhibits thermal energy that can cause burns. Prevent contact of skin with hot water or surfaces.

High water pressure - Pressure washer discharge can have 2,000 to 4,000 psi of water pressure. Water under this amount of pressure can rupture skin and other human tissues. Water at 4,000 psi exiting a 0˚ tip can be dangerous because of its relatively high cutting power. The exit velocity and cutting power of the water are reduced when exiting a 40˚ fan tip, but damage to soft tissues is still possible.

In general, follow the rules below to avoid injury, equipment damage, or incomplete decontamination:

1. Read the operating manual and follow the manufacturers' recommended safety practices before operating pressure washers and steam cleaners.

2. Never point the pressure washer or steam cleaner at another person or use to clean your boots or other parts of your body. Water lacerations and burns may appear to be minor at first but can be life threatening. Do not attempt to hold small parts in your hand while washing them with high-temperature or high-pressure water.

3. Always wear PPE as specified in the HASP such as:

   - Hard hat, safety glasses, splash shield, impermeable apron or splash suit, and hearing protection. Remember that excessive noise is a hazard when operating gas-powered engines and electrically driven pressure washers. PPE will be identified in your project specific planning documents.

4. Inspect each device before use. An inspection checklist will be provided in the project-specific planning documents. If it is a rented device, safety measures are typically provided by the vendor. In all cases, if you are not familiar with the operation of a pressure washer/steam cleaner, do not operate it until you obtain and thoroughly review operating instructions and recommended safety practices.

5. Do not modify equipment unless the manufacturer has approved the modifications.

7.2.3 Soil/Sediment Sampling Equipment

This section applies to soil sampling equipment including but not limited to hand augers, stainless steel trowels/spoons, bowls, dredges, scoops, split spoons, Macro Core samplers, etc.

1. Remove all loose soil from the equipment through manual means.

2. Through a combination of scrubbing using soap and water and/or steam cleaning or pressure washing, remove visible dirt/soil from the equipment.

3. Rinse the equipment with tap water.

> ***CAUTION***
> Do not rinse PE, PVC, and associated tubing with solvents. The appropriate procedures should be defined within the project-specific planning documents. If they are not defined, contact the FOL for guidance. The solvent rinse described in Step 4 may be omitted if groundwater does not contain oil, grease, PAHs, PCBs, or other hard to remove organic materials.

4. If the equipment is contaminated or suspected to be contaminated with oil, grease, PAHs, PCBs, or other hard to remove organic materials, rinse the equipment with pesticide-grade isopropanol.

5. Rinse the equipment with deionized water.

6. To the extent possible, allow components to air dry.

7. If the equipment is to be used immediately after decontamination, screen it with a calibrated PID/FID to ensure that all solvents (if they were used) and trace contaminants have been adequately removed.

8. After the equipment has dried, wrap it in aluminum foil for storage until use.

Dredges employed in sediment sampling are typically decontaminated as follows:

- Remove the sediment sample from the sampling device

- If sufficient associated surface water is available at the sampling site, place the dredge in the water and flush to remove visible sediment.

- Extract the dredge and wash it in soap and water per the project-specific planning documents.

> ***CAUTION***
> When handling dredges, the primary safety concern is trapping fingers or extremities in the larger dredge samplers within the jaws or pinch points of the mechanical jaws. Keep hands, fingers, and extremities away from these pinch and compression points. Either handle the device by the rope or preferably lock the jaws in place to control the potential for closing during maintenance and/or cleaning.

7.3 Contact Waste/Materials

During the course of field investigations, disposable/single-use equipment becomes contaminated. These items include tubing, trowels, PPE (gloves, overboots, splash suits, etc.), and broken sample containers.

With the exception of the broken glass, single-use articles should be cleaned (washed and rinsed) of visible materials and disposed as normal refuse. The exception to this rule is that extremely soiled materials that cannot be cleaned shall be containerized for disposal in accordance with applicable federal, state, and local regulations.

7.3.1 Investigation-Derived Wastes - Decontamination Wash Waters and Sediments

NOTE
Requirements for waste storage may differ from one facility to the next. Facility-specific directions for waste storage areas will be provided in project-specific documents, or separate direction will be provided by the Project Manager.

1. Assume that all investigation-derived waste (IDW) generated from decontamination activities contains the hazardous chemicals associated with the site unless there are analytical or other data to the contrary. Waste solution volumes could vary from a few gallons to several hundred gallons in cases where large equipment required cleaning.

2. Where possible, use filtering systems to extend the use of water within a closed system wash unit to recycle water and to reduce possible waste amounts.

NOTE
Containerized waste rinse solutions are best stored in 55-gallon drums (or equivalent containers) that can be sealed until ultimate disposal at an approved facility.

3. Label waste storage containers appropriately labeled (see Attachment A).

4. Ensure that the IDW storage area is configured to meet the following specifications to permit access to the containers and to conduct spill/leak monitoring, sampling, and extraction when the disposal route is determined:

   - Enclose areas accessible by the general public using construction fencing and signs.

   - Stored materials in 55-gallon drums on pallets with four (or fewer) drums per pallet.

   - Maintain the retaining bolt and label on the outside of storage containers where readily visible.

   - Provide at least 4 feet of room between each row of pallets to allow access to containers for sampling, drum removal, and spill response.

   - As directed in project-specific planning documents, maintain an IDW Inventory List and provide the list to the site Point of Contact at the termination of each shift.

   - Maintain spill response equipment at the IDW storage area in case it is required for immediate access.

- Where possible, use equipment for moving containers. Where not possible, obtain help to manipulate containers.

CAUTION

Each container of water can weigh up to 490 pounds. Each 55-gallon drum of wet soil can weigh more than 750 pounds. Fill drums and temporary containers to 80 percent capacity to minimize spill and handling difficulties. Use drum carts to move filled drums.

See safe lifting techniques provided in Section 4.4 of the Tetra Tech NUS, Inc. Health and Safety Guidance Manual.

When placing drums, keep your fingers out of pinch and smash points such as between the drums. In some cases such as well development and/or purge water, you can place the drums to be filled on the pallet and transport materials in smaller easier to handle containers.

7.4 Decontamination Evaluation

Upon decontamination of equipment, determine the effectiveness of the decontamination process in the following manner:

- Visual evaluation – A visual evaluation will be conducted to ensure the removal of particulate matter. This shall be done to ensure that the washing/rinsing process is working as intended.

- Instrument Screening – A properly calibrated PID/FID should be used to evaluate the presence of site contaminants and solvents used in the cleaning process. The air intake of the instrument shall be passed over the article to be evaluated. Avoid placing the instrument probe into residual waters. A PID/FID reading greater than the daily established background level requires a repeat of the decontamination process, followed by rescreening with the PID/FID. This sequence must be repeated until no instrument readings greater than the daily established background level are observed. It should be noted that the instrument scan is only viable if the contaminants are detectable within the instrument's capabilities.

NOTE

When required by project-specific planning documents, collection of rinsate blanks (see next step) shall be completed without exception unless approval to not collect these samples is obtained from the Project Manager.

- Collection of Rinsate Blanks – It is recommended that rinsate samples be collected to:

  - Evaluate the decontamination procedure representing different equipment applications (pumps versus drilling equipment) and different decontamination applications.

  - Single-use disposable equipment – The number of samples should represent different types of equipment as well as different lot numbers of single-use articles.

  - The collection and the frequency of collection of rinsate samples are as follows unless specified differently in the project-specific planning documents:

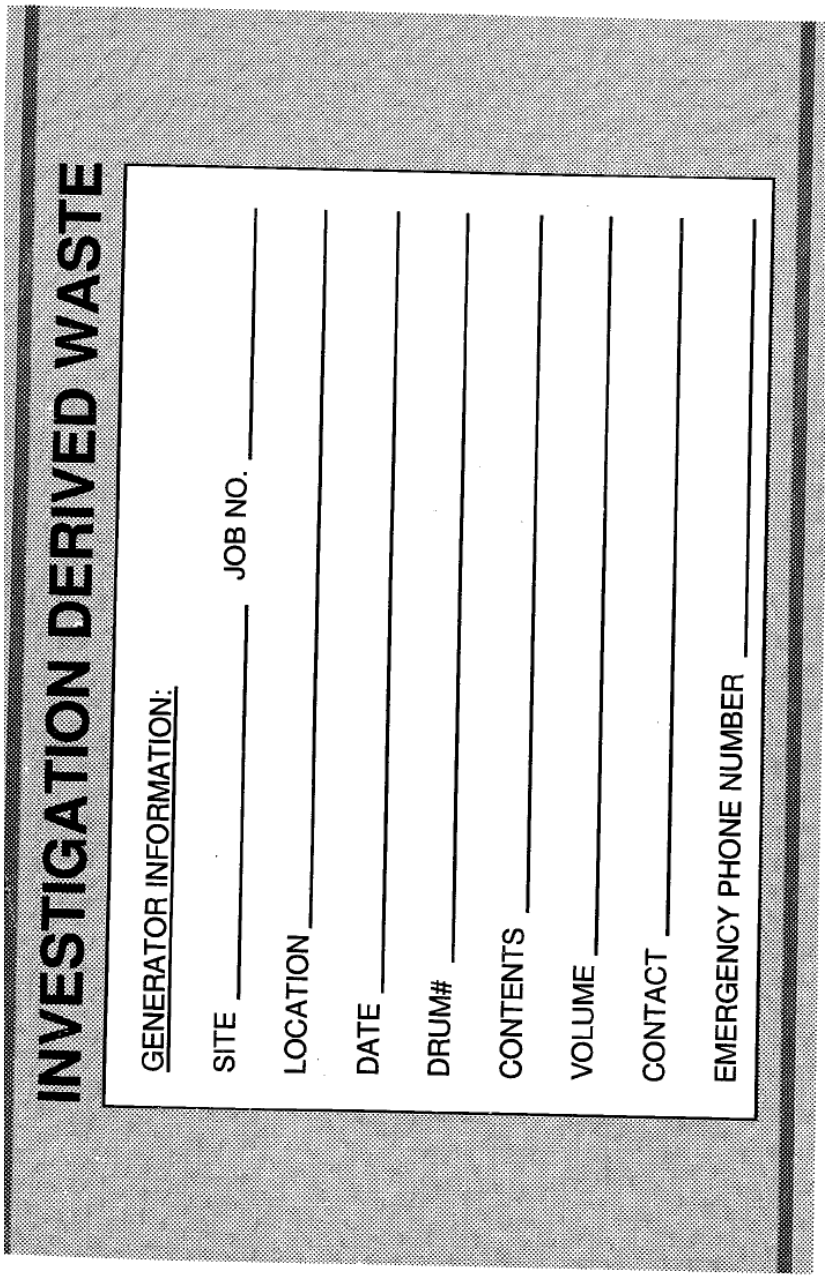
    - Per decontamination method
    - Per disposable article/batch number of disposable articles

NOTE

It is recommended that an initial rinsate sample be collected early in the project to ensure that the decontamination process is functioning properly and to avoid using a contaminated batch of single-use articles. It is recommended that a follow-up sample be collected later during the execution of the project to ensure that those conditions do not change.

Rinsate samples collection may be driven by types of and/or levels of contaminant. Difficult to remove contaminants, oils/greases, some PAHs/PCBs, etc. may also support the collection of additional rinsates due to the obvious challenges to the decontamination process. This is a field consideration to be determined by the FOL.

Attachment A
iDW Label



APPENDIX B

FIELD DOCUMENTATION FORMS

TETRA TECH NUS, INC.

ANALYTICAL SERVICE
Packing List/Chain-of-Custody

Case No. _____ Page _____ of _____

Subcontract No. _____

Project No.	Laboratory Name:	Container Type	Container Type	Container Type	Container Type	Container Type
Sampler Signatures	Date Shipped Carrier Airbill No. No. of Coolers	Analysis	Analysis	Analysis	Analysis	Analysis

Sample Number	Matrix	Date/Time	Sample Location	Tag Number(s)	QC	Preservative	Preservative	Preservative	Preservative	Preservative

Relinquished By: (Signature)	Date/Time	Received By: (Signature)	Shipment for Case Complete? YES NO	Remarks
Relinquished By: (Signature)	Date/Time	Received for Laboratory By:	Date/Time	

TtNUS Form 0022

Tetra Tech NUS, Inc.

BORING LOG

PROJECT NAME: _____ BORING No.: _____
PROJECT NUMBER: _____ DATE: _____
DRILLING COMPANY: _____ GEOLOGIST: _____
DRILLING RIG: _____ DRILLER: _____

Sample No. and Type or RQD	Depth (Ft.) or Run No.	Blows / 6" or RQD (%)	Sample Recovery / Sample Length	Lithology Change (Depth/Ft.) or Screened Interval	MATERIAL DESCRIPTION			USCS *	Remarks	PID/FID Reading (ppm)			
					Soil Density/ Consistency or Rock Hardness	Color	Material Classification			Sample	Sampler BZ	Borehole**	Driller BZ**

* When rock coring, enter rock brokeness.

** Include monitor reading in 6 foot intervals @ borehole. Increase reading frequency if elevated reponse read.

Drilling Area Background (ppm): _____

Remarks: _____

Converted to Well: Yes _____ No _____ Well I.D. #: _____

TETRA TECH NUS, INC.

FIELD MODIFICATION RECORD

Site Name: _____ Location: _____

Project Number: _____ Task Assignment: _____

To: _____ Location: _____ Date: _____

Description:_____

_____

_____

_____

Reason for Change: _____

_____

_____

Recommended Action: _____

_____

_____

Field Operations Leader (Signature): _____ Date: _____

Disposition/Action:_____

_____

_____

Project Manager (Signature): _____ Date: _____

Distribution:

		Others as Required:
Program Manager:	_____	
Project Manager:	_____	_____
Quality Assurance Officer:	_____	_____
Field Operations Leader:	_____	_____
Project File:	_____	_____

TtNUS Form 0003

TETRA TECH NUS, INC.

PHOTOIONIZATION DETECTOR FIELD CALIBRATION LOG

Serial No.: _____ Model No.: _____ Decal No.: _____

Site Name/Location: _____ Tetra Tech NUS Charge No.: _____

CALIBRATION DATE	STANDARD GAS-ISOBUTYLENE	(AM) CALIBRATION READING Isobutylene Equiv. (ppm)	(PM) CALIBRATION CHECK Isobutylene Equiv. (ppm)	SIGNATURE	COMMENTS
	Lot # _____ Conc. = _____ ppm	/		AM: PM:	
	Lot # _____ Conc. = _____ ppm	/		AM: PM:	
	Lot # _____ Conc. = _____ ppm	/		AM: PM:	
	Lot # _____ Conc. = _____ ppm	/		AM: PM:	
	Lot # _____ Conc. = _____ ppm	/		AM: PM:	
	Lot # _____ Conc. = _____ ppm	/		AM: PM:	
	Lot # _____ Conc. = _____ ppm	/		AM: PM:	
	Lot # _____ Conc. = _____ ppm	/		AM: PM:	
	Lot # _____ Conc. = _____ ppm	/		AM: PM:	

TtNUS Form 0006

Tetra Tech NUS, Inc.

QA SAMPLE LOG SHEET

Project Site Name: _____ Sample ID Number: _____
Project Number: _____ Sampled By: _____
Sample Location: _____ C.O.C. Number: _____
QA Sample Type:

[] Trip Blank [] Rinsate Blank
[] Source Water Blank [] Other Blank _____

SAMPLING DATA:

Date: _____
Time: _____
Method: _____

WATER SOURCE:

[] Laboratory Prepared [] Tap
[] Purchased [] Fire Hydrant
[] Other _____

PURCHASED WATER INFORMATION (If Applicable as Source or Rinsate Water):

Product Name: _____
Supplier: _____
Manufacturer: _____
Order Number: _____
Lot Number: _____
Expiration Date: _____

RINSATE INFORMATION (If Applicable):

Media Type: _____
Equipment Used: _____
Equipment Type:

[] Dedicated
[] Reusable

SAMPLE COLLECTION INFORMATION:

Analysis	Preservative	Container Requirements	Collected
Volatiles	Cool 4°C & HCl		YES / NO
Semivolatiles	Cool 4°C		YES / NO
Pesticide / PCB	Cool 4°C		YES / NO
Metals	Cool 4°C & HNO_3		YES / NO
Cyanide	Cool 4°C & NaOH		YES / NO

OBSERVATIONS / NOTES:

Signature(s):

TETRA TECH NUS, INC.

SAMPLE COLLECTION SUMMARY RECORD

PROJECT NAME: _____ TETRA TECH NUS CHARGE NUMBER: _____

SAMPLING EVENT: _____ CASE NO.: _____ DAS NO.: _____

DATE	TIME	SAMPLE LOCATION	FIELD QC							COMMENTS

TtNUS Form 0012

TETRA TECH NUS, INC.

SITE ENTRY LOG

Site Name: _____ Date: _____

Location: _____ Project Number: _____

NAME	REPRESENTING	TIME IN (HOURS)	TIME OUT (HOURS)	INITIALS

TtNUS Form 0002

Tetra Tech NUS, Inc.

SOIL & SEDIMENT SAMPLE LOG SHEET

Project Site Name: _____
Project No.: _____

[] Surface Soil
[] Subsurface Soil
[] Sediment
[] Other: _____
[] QA Sample Type: _____

Sample ID No.: _____
Sample Location: _____
Sampled By: _____
C.O.C. No.: _____

Type of Sample:
[] Low Concentration
[] High Concentration

GRAB SAMPLE DATA:

Date:	Depth Interval	Color	Description (Sand, Silt, Clay, Moisture, etc.)
Time:			
Method:			
Monitor Reading (ppm):			

COMPOSITE SAMPLE DATA:

Date:	Time	Depth Interval	Color	Description (Sand, Silt, Clay, Moisture, etc.)
Method:				
Monitor Readings (Range in ppm):				

SAMPLE COLLECTION INFORMATION:

Analysis	Container Requirements	Collected	Other

OBSERVATIONS / NOTES:

MAP:

Circle if Applicable:

MS/MSD	Duplicate ID No.:

Signature(s):

APPENDIX C

LABORATORY STANDARD OPERATING PROCEDURES

KATAHDIN ANALYTICAL SERVICES, INC.
STANDARD OPERATING PROCEDURE

SOP Number: CA-101
Revision History
Cover Page
Page 1

TITLE: **EQUIPMENT MAINTENANCE AND TROUBLESHOOTING**

Prepared By: Julie Ricardi Date: 8-96

Approved By:

Group Supervisor: _____ Date: _____

Operations Manager: Joel C. Burton Date: 12/15/00

QA Officer: Deborah J. Nadeau Date: 12-13-00

General Manager: JC Burton for D. McGrath Date: 12/15/00

Revision History:

SOP Revision	Changes	Approval Initials	Approval Date	Effective Date
01	Added requirements for recording maintenance in appropriate log. Added Archon maintenance. Modified Lachat maintenance. Attached equipment list.	DN	12-13-00	12-13-00
02	Removed references to General Manager. Removed furnace (GFAA) maintenance from Figure 1 and added ICP-MS. Updated equipment list.	DN	10-22-02	10-22-02
03	Changed Supervisor to department manager. Added maintenance for the ASE and general lab maintenance. Updated equipment list.	HRC	06.03.04	06.03.04
04	Added new equipment list.	LAD	01-28-05	01-28-05
05	Added Horizon SPE extractor & HPLC maintenance to Table 1. Added TOC analyzer, IC & miscellaneous instrument maintenance to Table 2. Updated equipment list.	DN	03-06	03-06

TITLE: **EQUIPMENT MAINTENANCE AND TROUBLESHOOTING**

SOP Revision	Changes	Approval Initials	Approval Date	Effective Date
06	Updated ICP maintenance to include maintenance for new ICP (7500). Updated equipment list.	DR	04·07	04·07
07	Updated equipment list.	DR	0708	07·08
08	Added more detail to section 7.3.3 describing corrective action documentation. Added maintenance for GPC. Updated equipment list. Added sections on unscheduled maintenance and troubleshooting and on service contracts and outside maintenance	DR	08/09	08/09
09	Added Section 7.3 - Unscheduled Maintenance and Troubleshooting. Updated Equipment List. Updated Title to include Troubleshooting	LAD	09/10	09/10

TITLE: **EQUIPMENT MAINTENANCE AND TROUBLESHOOTING**

Please acknowledge receipt of this standard operating procedure by signing and dating both of the spaces provided. Return the bottom half of this sheet to the QA Department.

I acknowledge receipt of copy ___ of document **CA-101-09**, titled **EQUIPMENT MAINTENANCE AND TROUBLESHOOTING**.

Recipient: _____Date:_____

KATAHDIN ANALYTICAL SERVICES, INC.
STANDARD OPERATING PROCEDURE

I acknowledge receipt of copy ___ of document **CA-101-09**, titled **EQUIPMENT MAINTENANCE AND TROUBLESHOOTING**.

Recipient: _____Date:_____

TITLE: **EQUIPMENT MAINTENANCE AND TROUBLESHOOTING**

1.0 SCOPE AND APPLICATION

The consistent generation of high quality analytical results requires properly operating analytical equipment. Accordingly, Katahdin Analytical Services, Inc. has an equipment maintenance program, which prescribes the necessary maintenance measures required and also schedules the frequency of conduct and documentation of those measures.

The purpose of this SOP is to describe the routine scheduled maintenance procedures employed for analytical and support equipment and to discuss non-scheduled maintenance of analytical and support equipment utilized by Katahdin Analytical personnel. It is applicable to all equipment utilized by laboratory personnel for analytical and support work. The procedures outlined in this SOP provide general guidance for equipment maintenance and documentation. The appropriate equipment manufacturer's manual(s) and specific analytical SOPs must be available and may provide specific maintenance and cleaning procedures.

1.1 Definitions

1.2 Responsibilities

It is the responsibility of each technical employee to carry out and document the required routine equipment maintenance at the required frequency for the instrumentation that they use.

It is the responsibility of each Department Manager to ensure that maintenance performed in-house is conducted properly by experienced personnel familiar with the equipment. On a routine basis, the department manager or qualified designee reviews equipment maintenance activities and recordkeeping requirements. Deficiencies are brought to the attention of the analyst who is responsible for an unacceptable procedure or entry, and any corrections are made by the appropriate analyst.

The Quality Assurance Officer is responsible for conducting periodic audits of the equipment maintenance program and documentation in each analytical area. Maintenance logs and contracted vendor maintenance records are reviewed for completeness and frequency of maintenance. Deficiencies are immediately brought to the attention of the Supervisor who is responsible for informing his/her staff and initiating the necessary corrective or improved actions in his/her analytical area.

2.0 SUMMARY OF METHOD

Not applicable.

3.0 INTERFERENCES

Refer to specific instrument manufacturer’s operating manuals.

TITLE: **EQUIPMENT MAINTENANCE AND TROUBLESHOOTING**

4.0 APPARATUS AND MATERIALS

Not applicable.

5.0 REAGENTS

Not applicable.

6.0 SAMPLE COLLECTION, PRESERVATION AND HANDLING

Not applicable.

7.0 PROCEDURES

The laboratory is equipped with all equipment needed for analysis and support activities. All equipment is maintained in working condition through a schedule of preventive maintenance and/or outside service contracts or appointments as needed. All maintenance, including internal maintenance and outside service calls, is documented. Any out-of-service equipment is marked as such until it can be repaired and shown by calibration or testing to perform correctly. In cases where outside equipment is rented or borrowed, any records necessary to demonstrate equipment calibration or maintenance will be requested from the provider.

All equipment must be maintained so that its performance is acceptable for its intended use. For example, an instrument that does not have sufficient sensitivity should not be used for low-level analysis or a balance not verified above 100 grams should not be used to weigh items over 100 grams.

7.1 ROUTINE PREVENTIVE MAINTENANCE

Preventive maintenance (PM) may be conducted by qualified Katahdin personnel or may be performed under contract by authorized service technicians. Between service visits, instruments having PM service contracts are cleaned and maintained according to manufacturer’s specifications by experienced Katahdin personnel. Instruments not under service contracts are cleaned and maintained by experienced laboratory personnel according to manufacturer's specifications and based on professional experience. The frequency of maintenance performed depends on the equipment. Preventive maintenance in each analytical section at Katahdin Analytical is scheduled, conducted and documented on a regular basis by the analytical section staff. Many maintenance needs (e.g., accidental breakage, part failure) are not satisfied by scheduled maintenance and are performed as needed. This would apply to routine daily instrument maintenance as well as non-scheduled instrument maintenance (e.g.

replacement of GC injection port liners, replacement of volatiles Tekmar traps, etc.). Maintenance procedures indicated in Tables 1 and 2 are documented in appropriate logbooks maintained in each analytical area. Included in the documentation are general remarks describing the maintenance operations performed, the date maintenance was performed, and the signature or initials of the individuals who completed the maintenance. If a specific instrument problem prompted the need for maintenance, the problem and its resolution are documented along with the description of maintenance performed. Specific requirements for maintenance logs are described in Section 7.3.

7.2 PREVENTIVE MAINTENANCE SCHEDULES

Tables 1 and 2 summarize the routine preventive maintenance procedures and schedules followed within Katahdin Analytical for major laboratory instrumentation. These items are required to be documented in the applicable instrument or maintenance log. Refer to Section 7.3 for specific requirements for maintenance log documentation.

7.3 UNSCHEDULED MAINTENANCE & TROUBLESHOOTING

In addition to preventive maintenance, analysts are often required to perform unscheduled maintenance due to sporadic instrument problems. The instrument problems could be obvious, such as those caused by “nasty” samples, or not so obvious. The problem could be more mechanical, such as an autosampler jamming or a needle clogging, or the problems could be more technical such as failing QC for no apparent reason.

In all cases, analysts shall proceed through a series of troubleshooting steps to investigate the problem. The following general steps should be used as guidelines:

7.3.1. Determine what the problem is, i.e., is it a mechanical or technical QC problem?

7.3.2. If the problem is mechanical, determine whether a part needs to be fixed or replaced.

7.3.3. If the instrument is still under warranty, contact the instrument manufacturer to schedule a service call.

7.3.4. If there is no warranty, order parts from an approved vendor or replace parts with spares, if available. Consult another trained analyst or your department manager for information regarding the problem. Also refer to #9 below.

7.3.5. If the analyst is unable to fix the parts or replace the parts, contact the manufacturer or authorized repair company to set up a service call.

7.3.6. If the problem is technical in nature, i.e. failing QC, be sure that all affected QC samples have been prepared correctly. Reanalyze failing QC after repreparation to see if the problem corrects itself.

7.3.7. Be sure that all instrument conditions are correctly set and that there are no obvious instrument issues, i.e. disconnected lines, broken parts, etc.

7.3.8. Consult another trained analyst or your department manager for information regarding the problem.

7.3.9. Consult the instrument manuals, other approved technical manuals, on-line instrument manufacturer's websites, or contact the instrument manufacturer or other approved service provider for troubleshooting techniques.

7.3.10. When troubleshooting, changing only one parameter and/or part at a time is critical to ascertain which change may improve or correct a problem.

All troubleshooting steps and outcomes must be recorded in the applicable instrument maintenance logbook for future reference and guidance. The steps taken, which correct the problem should be noted as such. If it is determined that a problem with the equipment exists, and that the problem has had an impact on the quality of past completed data, an immediate Corrective Action Report (CAR) must be initiated. A thorough investigation of all impacted data must be completed and corrective action must be implemented. Refer to the current revision of Katahdin SOP, QA-803, Laboratory Quality Assurance Self Inspection System, for further details.

7.4 MAINTENANCE LOG (or equivalent) REQUIREMENTS

Maintenance must be recorded in either the instrument run log or in a separate maintenance log. For equipment that does not have a run log or does not necessitate a separate maintenance log (i.e. little maintenance required), any maintenance may be recorded in the appropriate logbook (i.e. balance maintenance recorded in the balance calibration log). Attachment A provides a list of analytical equipment for which maintenance activities are recorded. Balances are not listed, although maintenance activities are recorded for these.

7.4.1 Maintenance logs (or equivalent) shall include the type of equipment and the analytical group/analysis for which it is designated, the manufacturer's model number and serial number, as well as any laboratory-assigned identifier (e.g., GC08, MS2, etc.). Each lab-assigned identifier must be unique and each instrument must have only one lab-assigned identifier. As new instrumentation is received, the date acquired, condition when received (new, used, reconditioned), and date put into use should be recorded in the new instrument's maintenance log.

7.4.2 Each page of the maintenance logbook (or equivalent) must clearly indicate the type of equipment and laboratory-assigned identifier in the header information. Maintenance entries shall include the date and signature or initials of the individual performing the maintenance as well as a brief explanation of the maintenance performed.

7.4.3 If maintenance is conducted as the result of a suspected or known instrument problem, the maintenance record must clearly describe the following:

- Statement of the Problem: brief description of the problem (i.e. calibrations are failing)
- Cause Analysis: what might be causing the problem? This could be something that occurred just prior to the problem (i.e. electrical outage, analysis of nasty samples) or something that is unknown.
- Corrective Action Plan: What might fix the problem (i.e. replacing liners, tubing or column that could be "damaged" from a nasty sample)
- CAP Implementation: an indication of when the maintenance is performed
- Demonstration of CAP Implementation: an indication of whether the problem was resolved and the date when return to control was noted. Document any changes resulting from the CAP.

7.4.4 On a routine basis the Department Manager or qualified designee shall review equipment maintenance activities and adherence to recordkeeping requirements. Deficiencies are brought to the attention of the analyst who was responsible for the unacceptable procedure or entry, and any corrections are made by the appropriate analyst. Documentation of the maintenance log review can be made by initialing and dating each page of the log or by indicating "reviewed by", initials and date on the front cover of the maintenance log (or equivalent).

7.4.5 On a periodic basis the laboratory QA Officer shall conduct audits of the equipment maintenance program and documentation in the analytical areas. Maintenance logs and contracted vendor maintenance records are reviewed for completeness and adherence to this SOP. Deficiencies are immediately brought to the attention of the Department Manager who is responsible for informing his/her staff and initiating the necessary corrective actions in his/her analytical area.

7.5 SERVICE CONTRACTS

Katahdin will maintain service contracts for major instrumentation as needed. The need for a service contract will depend on factors such as the cost, the estimated down time, the availability of back-up instrumentation, and the availability of skilled analysts to perform non-routine maintenance. The decision to purchase a service contract is made by the management team of the Vice President, the President, the Operations Manager and the Department Managers.

In cases where a service contract is not in place, and a problem with an instrument or piece of support equipment cannot be corrected in-house, Katahdin will use reputable service companies to perform the repair and/or troubleshooting work. Relationships are maintained with several companies to perform these services.

TITLE: **EQUIPMENT MAINTENANCE AND TROUBLESHOOTING**

Occasionally, equipment may need to be sent out to the service company for repair. All equipment must be packaged in large enough boxes to leave room for at least four inches of bubble wrap on every side, including the top and bottom. Any small movable parts must be removed and wrapped separately. When available, a manufacturer's box with appropriate Styrofoam inserts should be used. All equipment returning to the laboratory must be checked and recalibrated to be sure all instrument capabilities and conditions have been maintained.

A preventive maintenance contract is in place for all support equipment and thermometers for cleaning, calibrating to manufacturer's specifications and verifying against NIST traceable sources. The support equipment includes all pH meters, conductivity meters, turbidity meters, balances, spectrophotometers, autoclaves, ovens, and incubators. Field equipment meters are included in this annual verification. All equipment supported under this contract are labeled by the outside calibration company with the last calibration date, and when the next calibration is due. All additional comments of the outside calibration are maintained in files with the QA Officer.

Records of all service contract visits, third party services and preventive maintenance services are maintained to document support equipment performance. All equipment not meeting manufacturer's specifications or those required by the test are removed from service until appropriate corrective actions can be taken.

8.0 QUALITY CONTROL AND ACCEPTANCE CRITERIA

Not applicable.

9.0 METHOD PERFORMANCE

Not applicable.

10.0 APPLICABLE DOCUMENTS/REFERENCES

Applicable equipment manufacturer's operating manuals.

List of Tables & Attachments

Table 1 – Routine Maintenance Schedule for Organics Instrumentation
Table 2 - Routine Maintenance Schedule for Inorganics Instrumentation
Table 3 - Routine Maintenance Schedule for General Laboratory Equipment
Attachment A – Analytical Equipment

TITLE: **EQUIPMENT MAINTENANCE AND TROUBLESHOOTING**

TABLE 1

ROUTINE MAINTENANCE SCHEDULE FOR ORGANICS INSTRUMENTATION

GC/MS

Regularly performed maintenance includes, but is not limited to, the following for GC/MS instrumentation:

- Check to ensure the pressure on the primary regulator never runs below 100 psi
- Check to ensure the gas supply is sufficient for the day's activity, and delivery pressures are set as described in the SOP.
- Change septa weekly or as needed.
- Replace/cut GC column as needed.
- Replace GC injector glass liner weekly or as needed.
- Replace glass jet splitter as needed.
- Replace pump oil as needed.
- Change gas line dryers as needed.
- Replace electron multiplier as needed.

GC

Regularly performed maintenance includes, but is not limited to, the following for GC instrumentation:

- Check to ensure the pressure on the primary regulator never runs below 100 psi.
- Check to ensure the gas supply is sufficient for the day's activity, and delivery pressures are set as described in the SOP.
- Change septa weekly or as needed.
- Replace/cut GC column as needed.
- Replace GC injector glass liner as needed.
- Change O_2/moisture traps as needed
- Clean/replace GC detector as needed.

TABLE 1, cont'd

ROUTINE MAINTENANCE SCHEDULE FOR ORGANICS INSTRUMENTATION

Purge and Trap Sample Concentrator

Regularly performed maintenance includes, but is not limited to, the following:

- Check to ensure the gas supply is sufficient for the day's activity and delivery pressures are set as described in the SOP.
- Replace trap as needed.
- Decontaminate the system after running high concentration samples or as required by blank analysis.
- Check system for leaks when problem suspected.

Archons

Regularly performed maintenance includes, but is not limited to, the following:

- Visually inspect sampler for corrosion or significant water seepage past plunger.
- Check system pressure (denotes leaks).
- Check for sufficient standard materials in standard vials.
- Recalibrate x, y, z components, i.e. robotic arm, as needed.

Accelerated Solvent Extractor (ASE)

Regularly performed maintenance includes, but is not limited to, the following:

- Check for leaks at the pump solvent reservoir, valves and other components.
- Inspect needle alignment of source needle.
- Check alignment of autoseal arms.
- Change peek seals and o-rings on cell caps after about 50 extractions per cell.
- Inspect cell edges for nicks and gouges on cell body.
- Inspect stainless steel frits and sonicate in solvent if needed.

TABLE 1, cont'd

ROUTINE MAINTENANCE SCHEDULE FOR ORGANICS INSTRUMENTATION

Horizon SPE Automated Extractor System

Regularly performed maintenance includes, but is not limited to, the following:

- Check and clean sensors with a KIMWipe.
- Change sensors as needed.
- Purge system with solvent before use and after use.
- Clean system with hot water by running method 15 after samples are analyzed and before purging system.

HPLC

Regularly performed maintenance includes, but is not limited to, the following for HPLC instrumentation:

- Check and sonicate pump valves as needed.
- Backflush column as needed.
- Replace analytical column or guard column as needed.
- Filter and replace solvent with every use.
- Replace the UV lamp as needed.
- Perform a column wash at the end of each run
- Change needle and/or needle seat as needed

GPC

Regularly performed maintenance includes, but is not limited to, the following for GPC instrumentation:

- Fill solvent reservoir as needed.
- Empty waste container as needed.

TITLE: **EQUIPMENT MAINTENANCE AND TROUBLESHOOTING**

TABLE 2

ROUTINE MAINTENANCE SCHEDULE FOR INORGANICS INSTRUMENTATION

ICP/MS

Regularly performed maintenance includes, but is not limited to, the following for ICP instrumentation:

- Clean torch assembly and spray chamber when discolored.
- Clean nebulizer as needed.
- Check to ensure that the argon supply is sufficient for the day's activity, and that delivery pressures are set as described in the SOP. Change argon tanks as necessary.
- Replace peristaltic pump tubing when it becomes stretched or develops flat spots.
- Check coolant water level weekly; replenish as necessary.
- Check rinse solution level daily; replenish as necessary.
- Check waste container level daily; empty as necessary.
- Check cleanliness of instrument air filters weekly; clean or replace as necessary.
- Check instrument computer date and time at the start of each day; correct as necessary.
- Check condition of vacuum pump oil weekly, replace as necessary.
- Clean sampling and skimmer cones every 2-4 weeks.
- Clean extraction lenses monthly, or as needed.
- Clean Einzel lenses every 3-6 months.

ICP

Regularly performed maintenance includes, but is not limited to, the following for ICP instrumentation:

- Clean torch assembly and spray chamber when discolored.
- Clean nebulizer as needed.

TABLE 2, cont'd

ROUTINE MAINTENANCE SCHEDULE FOR INORGANICS INSTRUMENTATION

ICP, cont'd

- Check to ensure that the argon supply is sufficient for the day's activity, and that delivery pressures are set as described in the SOP. Change argon tanks as necessary.
- Replace peristaltic pump tubing when it becomes stretched or develops flat spots.
- Check coolant water level weekly; replenish as necessary.
- Check rinse solution level daily; replenish as necessary.
- Check waste container level daily; empty as necessary.
- Check instrument computer date and time at the start of each day; correct as necessary.

Mercury Analyzer

Regularly performed maintenance includes, but is not limited to, the following:

- Replace drying tube as necessary
- Replace peristaltic pump tubing when it becomes stretched or develops flat spots.
- Replace mercury lamp as necessary.
- Clean optical cell quarterly or as needed.
- Clean liquid/gas separator when it becomes cloudy. Replace as needed.
- Check waste container level before each use; empty as necessary.
- Check exhaust system integrity before each use; correct as necessary.
- Check instrument computer date and time at the start of each day; correct as necessary.

TABLE 2, cont'd

ROUTINE MAINTENANCE SCHEDULE FOR INORGANICS INSTRUMENTATION

Lachat Autoanalyzer

Regularly performed maintenance includes, but is not limited to, the following:

- Check pump tubing; replace as needed.
- Clean interference filter with Kimwipe.
- Check reagent levels and expiration dates; refill or replace as needed.
- Rinse manifolds with water after analysis.
- Check manifold board surfaces; clean as needed by running under tap water.
- Check supplies and reagents; order as needed
- Check for leaks
- Check autosampler and autosampler trays; clean and/or lubricate as needed.
- Check fittings and o-rings on boards; replace as needed.
- Check peristaltic pump rollers; clean and lubricate as needed.
- Inspect manifold tubing for kinks and/or stains; replace as needed.
- Inspect valve flares; clean or replace as needed.
- Inspect reagent and waste lines; replace as needed.
- Check flow cell; clean as needed with Kimwipe.

Konelab AutoAnalyzer

Regularly performed maintenance includes, but is not limited to, the following:

- Rinse and refill distilled water container weekly.

TABLE 2, cont'd

ROUTINE MAINTENANCE SCHEDULE FOR INORGANICS INSTRUMENTATION

Konelab AutoAnalyzer, cont'd

- Check cleanness of segments weekly.
- Wash reagent tubes monthly.
- Change lamp as needed.
- Change diluent and wash tubes as needed.
- Change mixing paddles as needed.
- Change syringes as needed.
- Change dispensing needles as needed.
- Change drain and waste tubes as needed.
- Check used cuvettes and waste daily.

TOC Combustion Analyzer

Regularly performed maintenance includes, but is not limited to, the following:

- Check level of dilution water, drain vessel water, humidifier water, autosampler rinse water, and phosphoric acid vessel and fill as needed.
- Replace oxygen cylinder as needed.

IC

Regularly performed maintenance includes, but is not limited to, the following for IC instrumentation:

- Check regenerate pump tubing and replace as needed.
- Clean or regenerate column as needed.

TABLE 2, cont'd

ROUTINE MAINTENANCE SCHEDULE FOR INORGANICS INSTRUMENTATION

IC, cont'd

- Replace analytical column or guard column as needed.
- Change suppressor as needed.

Miscellaneous Support Instrumentation (including field testing equipment)

Regularly performed maintenance includes, but is not limited to, the following:

- Replace spectrophotometer lamps as needed.
- Inspect DO probe membrane for tears and check for air bubbles under the membrane.
- Replace the DO probe membrane cap and electrolyte solution as needed.
- Clean pH electrode as needed.
- Change the autotitrator filling solution as needed.
- Clean, check, calibrate to manufacturers' specifications all pH, DO, conductivity, and turbidity meters annually (minimum); clean, check, calibrate to manufacturers' specifications all spectrophotometers and balances annually. All calibrations must be NIST traceable.

TITLE: **EQUIPMENT MAINTENANCE AND TROUBLESHOOTING**

TABLE 3

ROUTINE MAINTENANCE SCHEDULE FOR GENERAL LABORATORY EQUIPMENT

General Laboratory Areas

- Clean and calibrate balances annually (minimum).
- Check balance calibration each day of use.
- Clean balance pan prior to each use.
- Calibrate automatic pipettes with each use.
- Calibrate spirit thermometers yearly against an NIST traceable thermometer; calibrate digital thermometers quarterly.
- Record refrigerator, freezer, incubator and oven temperatures each day, when appropriate.
- General housekeeping: keep counter tops, hoods, and floors clean.
- Check airflow in hoods once a week.

TITLE: **EQUIPMENT MAINTENANCE AND TROUBLESHOOTING**

ATTACHMENT A

ANALYTICAL EQUIPMENT LIST

Katahdin ANALYTICAL SERVICES

ACCREDITED IN ACCORDANCE WITH nelac

ANALYTICAL INSTRUMENTATION

KEY INSTRUMENTATION	DATE IN SERVICE	USED FOR ANALYSIS	Instrument Identification
Hewlett Packard 5973 GC/MS with EPC, Centurion Autosampler with foam sensor option and EST ENCON Evolution Purge and Trap Concentrator with heated purge capability	2008	5030/8260, 5035/8260, 624, Current versions of CLP SOWs (OLM, OLC, & SOM) (VOA), & 524.2	C
Hewlett Packard 6890 GC/MS with EPC, Archon Autosampler with foam sensor option and EST ENCON Evolution Purge and Trap Concentrator with heated purge capability	2008	5030/8260, 5035/8260, 624, Current versions of CLP SOWs (OLM, OLC, & SOM) (VOA), & 524.2	D
Hewlett Packard 5972 GC/MS with EPC; Tekmar LSC-3000 Purge and Trap concentrator; Archon autosampler capable of low soils per Method 5035.	1993	5030/8260, 5035/8260, 624, Current versions of CLP SOWs (OLM, OLC, & SOM) (VOA), & 524.2	F
Hewlett Packard 5972 GC/MS with EPC, Centurion Autosampler with foam sensor option and EST ENCON Purge and Trap Concentrator	2006	5030/8260, 624, Current versions of CLP SOWs (OLM & SOM) (VOA)	T
Hewlett Packard 5972 GC/MS with EPC; Tekmar LSC-3000 Purge and Trap concentrator; Archon autosampler capable of low soils per Method 5035.	1998	5030/8260, 5035/8260, 624, Current versions of CLP SOWs (OLM, OLC, & SOM) (VOA), & 524.2	S
Hewlett Packard 5972 GC/MS with EPC; Encon Purge and Trap concentrator; Archon autosampler capable of low soils per method 5035.	1995	5030/8260, 5035/8260, 624, Current versions of CLP SOWs (OLM, OLC, & SOM) (VOA), & 524.2	M
Hewlett Packard 5973 GC/MS with EPC, Centurion Autosampler with foam sensor option and EST ENCON Evolution Purge and Trap Concentrator with heated purge capability	2010	5030/8260, 5035/8260, 624, Current versions of CLP SOWs (OLM, OLC, & SOM) (VOA), & 524.2	z

TITLE: **EQUIPMENT MAINTENANCE AND TROUBLESHOOTING**

ATTACHMENT A

ANALYTICAL EQUIPMENT LIST, cont'd

Katahdin ANALYTICAL SERVICES

ACCREDITED IN ACCORDANCE WITH nelac

ANALYTICAL INSTRUMENTATION

KEY INSTRUMENTATION	DATE IN SERVICE	USED FOR ANALYSIS	Instrument Identification
Hewlett Packard 6890N GC/MS with EPC and Model 6890 GC and Agilent 7683 autosampler.	**2008**	8270, 625 & Current versions of CLP SOWS (OLM, OLC, & SOM) (SVOA)	G
Hewlett Packard 5973 GC/MS with EPC and Model 6890 GC and Agilent 7683 autosampler.	**2006**	8270, 625 & Current versions of CLP SOWS (OLM, OLC, & SOM) (SVOA)	R
Hewlett Packard 5973 GC/MS with EPC and Model 6890 GC and Agilent 7683 autosampler.	**1999/ 2001**	8270, 625 & Current versions of CLP SOWS (OLM, OLC, & SOM) (SVOA)	U
Agilent Model 6890 gas chromatograph with one EPC injection ports and micro electron capture detectors; Agilent Model 7683 autosampler	**2008**	608, 8081, 8082 (including congeners), current versions of CLP SOWs (OLM, OLC, & SOM) (P/P)	GC01
Hewlett Packard Model 6890 gas chromatograph with flame ionization detector and photo ionization detector; Tekmar LSC 3000 purge and trap, Archon autosampler.	**2010**	8015 MOD., MAVPH, GRO	GC02
Hewlett Packard Model 5890 gas chromatograph with flame ionization detector; Tekmar ALS 2016 autosampler; Tekmar LSC 2000 purge and trap.	**1991**	8015 MOD., GRO	GC04
Hewlett Packard Model 5890 gas chromatograph with a flameionization detector; Agilent Technologies G1888 Network Headspace Analyzer.	**1991/ 2005**	Methane, Ethane and Ethene	GC05
Hewlett Packard Model 5890 gas chromatograph with EPC and dual electron capture detectors(ECD); Hewlett Packard Model 7673 autosampler.	**1993**	8081, 8082, 608	GC06

TITLE: **EQUIPMENT MAINTENANCE AND TROUBLESHOOTING**

ATTACHMENT A

ANALYTICAL EQUIPMENT LIST, cont'd

Katahdin ANALYTICAL SERVICES

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ANALYTICAL INSTRUMENTATION

KEY INSTRUMENTATION	DATE IN SERVICE	USED FOR ANALYSIS	Instrument Identification
Agilent Model 6890 gas chromatograph with dual EPC injection ports and micro electron capture detectors; Agilent Model 7683 autosampler	**2000**	504, 608, 8011, 8081, 8082 (including congeners), 8151, current versions of CLP SOWs (OLM, OLC, & SOM) (P/P)	GC07
Agilent Model 6890 gas chromatograph with one EPC injection ports and micro electron capture detectors; Agilent Model 7683 autosampler	**2009**	608, 8081, 8082 (including congeners), current versions of CLP SOWs (OLM, OLC, & SOM) (P/P)	GC08
Hewlett Packard Model 5890 gas chromatograph with flame ionization detector and photo ionization detector; Tekmar ALS 2016 autosampler; Tekmar LSC 3000 purge and trap.	**1988**	8015 MOD., MAVPH, GRO	GC09
Hewlett Packard Model 5890 gas chromatograph with EPC and dual flame ionization detectors; Hewlett Packard Model 7673 autosampler.	**1993/ 1996**	8015 MOD., MAEPH, DRO	GC10
Hewlett Packard Model 5890 gas chromatograph with flame ionization and nitrogen-phosphorous detectors; Hewlett Packard Model 7673 autosampler.	**1992/ 1996**	ALCOHOLS, DMF, GLYCOLS	GC11
Hewlett Packard Model 5890 gas chromatograph with EPC and dual flame ionization detectors; Hewlett Packard Model 7673 autosampler.	**1987**	8015 MOD., MAEPH, DRO	GC12
Hewlett Packard series 1100 HPLC with Quaternary pump, Multiwavelength detector and autosampler	**2008**	8330, 8332	HPLC02

TITLE: **EQUIPMENT MAINTENANCE AND TROUBLESHOOTING**

ATTACHMENT A

ANALYTICAL EQUIPMENT LIST, cont'd

Katahdin ANALYTICAL SERVICES

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ANALYTICAL INSTRUMENTATION

KEY INSTRUMENTATION	DATE IN SERVICE	USED FOR ANALYSIS	Instrument Identification
J2 Scientific AccuPrep MPS™ GPC with internal UV detection	2009	GPC-3640 Current versions of CLP SOWS (OLM, OLC, & SOM)	GPC01
Horizon SPE-DEX 4790 Automated Extractor System equipped with 4 extractors.	2001/ 2005	3535 method development	Horizon #1
Horizon SPE-DEX 3000 Automated Extractor System equipped with 3 extractors.	2006	1664, 9070, 9071	Horizon #2
Thermo ICAP 6500 ICP Emission Spectrometer with autosampler.	2006	6010, 200.7, ILM05.4	I
Agilent 7500a ICP-MS with autosampler.	2007	6020, 200.8, ILM05.4	J
CETAC M-6100 Automated Mercury Analyzer with Autosampler	2004	7470/7471, 245.1, 245.5, ILM05.4	H
Tekran Series 2600 automated mercury analyzer with gold amalgam preconcentration and atomic fluorescence detector; Model 2620 autosampler.	2000	Ultra-trace level mercury (1631)	G
CPI ModBlock™ Metals Digestion Unit – Two 48 Place Units.	2000	Metals Aqueous Digestions	Digestion Unit #1 Digestion Unit #2
LACHAT Quickchem 8000 Continuum Series – Automated Ion Analyzer and autosampler.	2000	Various	WC1
Shimadzu TOC-V Combustion Analyzer, PC Controlled, High Sensitivity, Auto-Aqueous TOC Autosampler w/ 40 mL vials; Model SSM-5000A Solid Sample Module.	2002	TOC	WC2

TITLE: **EQUIPMENT MAINTENANCE AND TROUBLESHOOTING**

ATTACHMENT A

ANALYTICAL EQUIPMENT LIST, cont'd

Katahdin ANALYTICAL SERVICES

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ANALYTICAL INSTRUMENTATION

KEY INSTRUMENTATION		DATE IN SERVICE	USED FOR ANALYSIS	Instrument Identification
Waters 717 Plus Autosampler, Waters 431 conductivity detector, Spectra System P4000 pump.	Dionex IonPak AS4A column; Dionex AMMS III chemical suppression system	1991/ 2004	Ion chromatography – Various Anions	See "Key Instrumentation " column for identification
	Dionex AS16 column; Dionex ultra ASRS electronic suppression system.		Ion Chromatography - Perchlorate	See "Key Instrumentation " column for identification
Scanning Fluorescence Detector		1997	Out of Service	NA
10 position Lab Crest Cyanide Midi-Distillation system.		1998	Cyanide	WC3
Spectronic 401 spectrophotometer.		2000	Various	WC4
HACH Turbidimeter, Model 2100A.		1993	Turbidity	WC6
Accumet pH/Conductivity Meter, Model 20.		1998	Various	WC8
Mettler DL25 Autotitrator & Mettler ST20A sample changer.		1993	Alkalinity	WC9
YSI Dissolved Oxygen Meter.		1990	Dissolved Oxygen & Biochemical Oxygen Demand	WC10
Konelab 20 Multi-Wavelength Photometric Analyzer.		2003	Various	Konelab #1
Dionex Accelerated Solvent Extractor ASE 200.		2003	3545	ASE #1
Waters HPLC system with 600E multisolvent delivery system, 717 plus autosampler, Spectra System UV200 detector		2003/2004	Food Testing	HPLC01

TITLE: **EQUIPMENT MAINTENANCE AND TROUBLESHOOTING**

ATTACHMENT A

ANALYTICAL EQUIPMENT LIST, cont'd

Katahdin ANALYTICAL SERVICES

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ANALYTICAL INSTRUMENTATION

KEY INSTRUMENTATION	DATE IN SERVICE	USED FOR ANALYSIS	Instrument Identification
Thermo Spectronic Genesys 10uv spectrophotometer	**2005**	Food Testing	Food #1
DryVap Concentrator System 5000	**2005**	GC and GC/MS Extractables	DryVap #1

KATAHDIN ANALYTICAL SERVICES, INC.
STANDARD OPERATING PROCEDURE

SOP Number: CA-202
Revision History
Cover Page
Page 1

TITLE: ANALYSIS OF VOAs BY PURGE AND TRAP GC/MS: SW-846 METHOD 8260

Prepared By: GC/MS Group Date: 2/97

Approved By:

Group Supervisor: J. Haley Date: 011201

Operations Manager: Joel C. Burton Date: 1/15/01

QA Officer: Deborah J. Nadeau Date: 1·23·01

General Manager: Dennis P. Lufkin Date: 1/16/01

Revision History:

SOP Revision	Changes	Approval Initials	Approval Date	Effective Date
03 8260B	Format changes, added pollution prevention, changes to calibration section, new limits, added instrument. Other minor changes throughout.	DN	1·23·01	1·23·01
04 8260B	Revised sections 7.5.3.1, 7.5.5, 7.7.1, 7.8.2 + Table 2 to comply with South Carolina. Added NH oxygenates to calibration.	DN	5·23·01	5·23·01
05 8260B	Updated VOA calibration standard mixes. Added statistical limits for LCS/MS/MSD recoveries and the updated corrective actions	DN	5·21·02	5·21·02
06 8260B	Reorganization of sections 4, 5, 6 and 7, and Tables and Figures. Added definitions and information for the new data processing system.	MRC	05.03.04	05.03.04
07 8260B	minor changes rewording of sect. 7.6.3 preservation of calcareous soils	LAD	020305	020305

TITLE: ANALYSIS OF VOAs BY PURGE AND TRAP GC/MS: SW-846 METHOD 8260

SOP Revision	Changes	Approval Initials	Approval Date	Effective Date
08 8260 B	Added references, setup and operation for the Encon / Centurion autosampler / Purge and trap. Added ref. to instrument "T" and removed instrument "Q". Edited std. conc. to reflect new instrumentation. Minor changes throughout to reflect current practise and correct typos.	LAD	04/06	04/06
09 8260B	Sect. 4H - added list of waste streams generated and location of satellites. Clarified RT window studies. Added reference to MI Sop. Removed Grand Mean Calibration model. Added wording for project specific acceptance criteria. Added LCS marginal outlier criteria. Added wording clarifying calibration verification std. criteria and corrective action. Reworded correlation	LAD	LAD 7-25-07 ~~03/07~~ 07/07	~~03/07~~ 07/07
10	coefficient criteria updated sections 7.4.5, 7.4.6, 7.4.7, 7.5.2, 8.1, 10.0 and Table 1 with DoD QSM version 4.1 criteria	LAD	08/09	08/09
11	Added Table 2 with DoD QSM V. 4.1 QC Requirements. Added if the MSD Batch requirement cannot be fulfilled, a LCSD must be analyzed. Removed "2" instrument and added the "C" and "D" instruments.	LAD	04/10	04/10

TITLE: **ANALYSIS OF VOAs BY PURGE AND TRAP GC/MS: SW-846 METHOD 8260**

Please acknowledge receipt of this standard operating procedure by signing and dating both of the spaces provided. Return the bottom half of this sheet to the QA Department.

I acknowledge receipt of copy ___ of document **SOP CA-202-11**, titled **ANALYSIS OF VOAs BY PURGE AND TRAP GC/MS: SW-846 METHOD 8260**.

Recipient: _____ Date: _____

KATAHDIN ANALYTICAL SERVICES, INC.
STANDARD OPERATING PROCEDURE

I acknowledge receipt of copy ___ of document **SOP CA-202-11**, titled **ANALYSIS OF VOAs BY PURGE AND TRAP GC/MS: SW-846 METHOD 8260**.

Recipient: _____ Date: _____

TITLE: **ANALYSIS OF VOAs BY PURGE AND TRAP GC/MS: SW-846 METHOD 8260**

1.0 SCOPE AND APPLICATION

The purpose of this SOP is to describe the procedures utilized by Katahdin Analytical Services, Inc. laboratory personnel to prepare and analyze aqueous and solid matrix samples for purgeable organics by GC/MS in accordance with SW-846 Method 8260, current revision.

This SOP will consolidate all aspects of the analyses in one working document, to be revised as necessary, for the purposes of consistency in data quality.

1.1 Definitions

VOC: Volatile Organic Compounds

VOA: Volatile Organic Analysis

ANALYTICAL BATCH: 20 or fewer samples that are analyzed together with the same method sequence and the same lots of reagents and with the handling practices common to each sample within the same time period or in continuous sequential time periods.

METHOD BLANK (laboratory reagent blank): A quality control sample designed to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus. Laboratory reagent grade water is used as a blank matrix. The blank is taken through the appropriate steps of the process.

CALIBRATION CHECK: Verification of the ratio of instrument response to analyte amount, a calibration check is done by analyzing a mid point standard. The calibration check verifies that instrument conditions are sufficiently similar to those at initial calibration.

CALIBRATION STANDARD (WORKING STANDARD): A solution prepared from the stock standard solution that is used to calibrate the instrument response with respect to analyte concentration.

INDEPENDANT CALIBRATION STANDARD: A solution prepared from a stock standard solution independent of the standard that is used to calibrate the instrument. This is prepared as an LCS and analyzed after the calibration before any sample analysis.

LABORATORY CONTROL SAMPLE (LCS): A blank that has been spiked with the analyte(s) from an independent source and is analyzed exactly like a sample. Its purpose is to determine whether the methodology is in control and to measure the degree of accuracy of the determination.

MATRIX SPIKE/MATRIX SPIKE DUPLICATE (MS/MSD): Predetermined quantities of stock solutions containing target analytes are added to a sample matrix prior to sample extraction, in the case of soils, and/or analysis. Samples are split into duplicates, spiked and analyzed. Percent recoveries are calculated for each of the spiked analytes. The relative percent difference between the samples is calculated and used to assess analytical precision.

STANDARD CURVE (CALIBRATION CURVE): A curve that plots concentration of known analyte standard versus the instrument response to the analyte.

STOCK STANDARD SOLUTION: A concentrated solution containing a single analyte or mix of certified standards, or a concentrated solution of a single analyte prepared in the laboratory with an assay reference compound. Stock standard solutions are used to prepare calibration standards.

SURROGATES: Organic compounds which are similar to analytes of interest in chemical composition as well as extraction and chromatography characteristics, but which are not normally found in environmental samples. These compounds are spiked into all blanks, standards, samples and spiked samples prior to analysis. Percent recoveries are calculated for each surrogate. Surrogates provide an indication of the accuracy for the analytical determination in a discrete sample matrix.

TARGET: A software system that combines full processing, reporting and comprehensive review capabilities, regardless of chromatographic vendor and data type.

TARGET DB: An oracle database used to store and organize all Target data files.

QUICKFORMS: A laboratory reporting software for Target and Target DB. The QuickForms report module for Target is preconfigured with generalized forms and US EPA CLP report forms and disk deliverables, which can be customized.

1.2 Responsibilities

This method is restricted to use by, or under the supervision of analysts experienced in the analysis of volatile organics by the current revision of EPA Method 8260. Each analyst must demonstrate and document their ability to generate acceptable results with this method. Refer to Katahdin SOP QA-805, current revision, "Personnel Training and Demonstration of Capability".

It is the responsibility of all Katahdin technical personnel involved in analysis of volatile organics by Method 8260 to read and understand this SOP, to adhere to the procedures outlined, and to properly document their data in the appropriate logbook. Any deviations from the test or irregularities with the samples should also be recorded

in the lab logbook and reported to the Department Manager or designated qualified data reviewer responsible for this data.

It is the responsibility of the Department Manager to oversee that members of their group follow this SOP, to ensure that their work is properly documented and to initiate periodic review of the associated logbooks.

1.3 Safety

Users of this procedure must be cognizant of inherent laboratory hazards, proper disposal procedures for contaminated materials and appropriate segregation of hazardous wastes. The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical should be treated as a potential health hazard. A reference file of material safety data sheets is available to all personnel involved in the chemical analysis. Everyone involved with the procedure must be familiar with the MSDSs (material safety data sheets) for all the materials used in this procedure.

Each qualified analyst or technician must be familiar with Katahdin Analytical Health and Safety Manual including the Katahdin Hazardous Waste Management Plan and must follow appropriate procedures. These include the use of appropriate personal protective equipment (PPE) such as safety glasses, gloves and lab coats when working with chemicals or near an instrument and not taking food or drink into the laboratory. Each analyst should know the location of all safety equipment. Each analyst shall receive a safety orientation from their Department Manager, or designee, appropriate for the job functions they will perform.

1.4 Pollution Prevention/Waste Disposal

Whenever possible, laboratory personnel should use pollution prevention techniques to address their waste generation. Refer to the current revision of the Katahdin Hazardous Waste Management Program for further details on pollution prevention techniques.

After analysis, partially-filled VOA vials and sample jars are returned to the appropriate refrigerators to be disposed of in adherence with the Katahdin Hazardous Waste Management Plan and Safety Manual and SOP SD-903, Sample Disposal, current revision. Expired standards are lab packed, placed in the Katahdin hazardous waste storage area, and disposed of in accordance with this SOP SD-903.

Sample aliquots used for analysis are disposed of in accordance with SOP SD-903 and the Katahdin Hazardous Waste Management Plan and Safety Manual. The soil samples must be decanted and the soil fraction disposed of separately in compliance with Katahdin's disposal policies.

There are three general types of waste generated while performing the 8260 method. The "K" waste is a combination of water, sample aliquot (post analysis), as well as internal and surrogate standards. "K" waste is generated when preparing QC, during sample analysis, and procedural cleanup. There are "K" satellites attached to each GC/MS instrument as well as an additional satellite located adjacent to the VOA sample preparation bench. "O" waste consists of methanol (as well as trace amounts of volatile analytes) and is generated when standard preparation syringes are rinsed three times with methanol. The "O" waste stream satellite is located inside the fume hood. Organic soil waste stream "I" consists of any solid left over from sample preparation and/or analysis and is located inside the fume hood. All satellites listed above are stored in a secondary container and are located in the Volatile Organics Laboratory room 111.

2.0 SUMMARY OF METHOD

The general methodology involves purging aqueous and soil samples with helium, an inert gas, for a set period of time to efficiently transfer purgeable organics to the gaseous phase. Soil samples with higher contaminant levels are extracted with methanol prior to the helium purge. These volatile organics are then retained on a cooled trap (commercially available trap suitable for the methodology) before heating causes desorption into a gas chromatograph for compound separation. Detection occurs with an electron impact ionization mass spectrometer.

3.0 INTERFERENCES

Interfering contamination may occur when a sample containing low concentrations of VOCs is analyzed immediately after a sample containing high concentrations of VOCs. During initial data review, all analyses are evaluated for potential carryover. Any samples that have suspected carryover are reanalyzed. GC/MS policy is to reanalyze a sample with positive detects greater than the Practical Quantitation Limit (PQL) that has been run immediately after a sample with the same positive detects over the upper limit of the calibration. Typically 2 or 3 rinsing blanks are analyzed at the end of a sequence. Samples are not analyzed on the instrument until a blank with no detects above PQL can be obtained. If the lines are determined to be contaminated, then the entire Tekmar or Archon must be backflushed with warm methanol and water.

4.0 APPARATUS AND MATERIALS

4.1 GC: Hewlett Packard 6890 & 5890

4.2 Mass Spectrometers (MS): HP5973, HP5972 and HP5970

4.3 Helium: Carrier gas for routine applications. All carrier gas lines must be constructed from stainless steel or copper tubing; non-polytetrafluoroethylene (non-PTFE) thread sealant or flow controllers with rubber component are not to be used.

4.4 Columns: RTX-VMS, 40 meter, 0.18 mm ID or equivalent.

4.5 Purge and Traps: Archon 5100, Tekmar 2016 and Centurion auto samplers, and Tekmar 2000, 3000 and Encon concentrators.

4.6 Purge tubes: 5 mL fritted and 25 mL fritted purge vessels and 40 mL VOA vials for soil analysis.

4.7 Hamilton Gastight syringes: 2.00 uL to 25.00 mL.

4.8 Acquisition System: The acquisition system must be interfaced to the MS and allow continuous acquisition of data throughout the duration of the chromatographic program. It must permit, at a minimum, the output of time vs. intensity (peak height or peak area). Hewlett Packard Chemstation or equivalent.

4.9 Data System: The Target software is used for processing data and generating forms.

5.0 REAGENTS

5.1 Purge and trap grade methanol

5.2 Organic-free Laboratory reagent grade water: Siemens, Poland Spring, or equivalent. This water may need to be purged with nitrogen to eliminate organic contaminants such as Methylene chloride and Chloroform, which are commonly found at ambient levels in the laboratory.

5.3 Standards: Stock standards and working standards are received and recorded in accordance with SOP CA-106 “Standard Preparation and Documentation”.

5.3.1 The expiration date for all standards is six months from date of opening the ampule with the following exceptions:

Volatile gases expire within 2 weeks of opening ampule (gases are dichlorodifluoromethane, chloromethane, bromomethane, vinyl chloride, chloroethane, and trichlorofluoromethane).

New standards must be opened if degradation is observed.

5.3.2 Secondary dilution standards

5.3.2.1 Calibration Mix – Prepare a standard in purge and trap methanol containing the compounds listed below. The final concentration of each compound is 200 ug/mL (some individual analyte concentrations may vary, i.e. Ketones). The standard should be prepared in a 1.0 mL conical vial with a mini-inert valve cap. The standard must be prepared every 7 days and stored in the VOA standards freezer between uses.

Acetone
Benzene
Bromobenzene
Bromochloromethane
Bromodichloromethane
Bromoform
Bromomethane
2-Butanone
n-Butylbenzene
sec-Butylbenzene
tert-Butylbenzene
Carbon Disulfide
Carbon Tetrachloride
Chlorobenzene
Chloroethane
2-Chloroethylvinyl Ether
Chloroform
Chloromethane
2-Chlorotoluene
4-Chlorotoluene
Cyclohexane
1,2-Dibromo-3-Chloropropane
Isopropylbenzene
Dibromochloromethane
1,2-Dibromoethane
Dibromomethane
1,2-Dichlorobenzene
1,3-Dichlorobenzene
1,4-Dichlorobenzene
Dichlorodifluoromethane
1,1-Dichloroethane
1,2-Dichloroethane
1,1-Dichloroethene
cis-1,2-Dichloroethene
Trans-1,2-Dichloroethene
1,2-Dichloropropane
1,3-Dichloropropane
2,2-Dichloropropane
1,1-Dichloropropene
Cis-1,3-Dichloropropene
Trans-1,3-Dichloropropene
Ethylbezene
Hexachlorobutadiene
2-Hexanone
Idomethane
Methyl Tert-Butyl Ether
P-Isopropyltoluene
Methylene Chloride
4-Methyl-2-Pentanone
Naphthalene
N-Propylbenzene
Styrene
1,1,1,2-Tetrachloroethane
1,1,2,2-Tetrachloroethane
Tetrachloroethene
Tetrahydrofuran
Toluene
1,2,3-Trichlorobenzene
1,2,4-Trichlorobenzene
1,1,1-Trichloroethane
1,1,2-Trichloroethane
Trichloroethene
Trichlorofluoromethane
1,2,3-Trichloropropane
1,2,4-Trimethylbenzene
Vinyl Acetate
Vinyl Chloride
1,3,5-Trimethylbenzene
1-Chlorohexane

5.3.2.2 Extras mix – Prepare a standard as above containing the compounds listed below. The final concentration of each compound is 200 ug/mL. The standard should be prepared in a 1.0 mL conical vial with a mini-inert valve cap. The standard must be prepared every 30 days and stored in the VOA standards freezer between uses.

Acetonitrile
Acrolein
Acrylonitrile
Allyl Chloride
Chloroprene
Diethyl Ether
Cis-1,4-Dichloro-2-Butene
Trans-1,4-Dichloro-2-Butene
1,4-Dioxane
Di-Isopropyl Ether
Ethyl Methacrylate
Ethyl Tertiary-Butyl Ether
Freon-113
Isobutyl Alcohol
Methacrylonitrile
Methylcyclohexane
Methyl Acetate
Methyl Methacrylate
Methyl Tert-Butyl Ether
Pentachloroethane
Propionitrile
Tertiary-Amyl Methyl Ether
Tertiary-Butyl Alcohol
1,3,5-Trichlorobenzene
1,2,3-Trimethylbenzene

5.3.2.3 Independent Calibration Verification Standard, Laboratory Control Spike and MS/MSD Mixture - Prepare a standard as above containing the compounds listed in Table 3. The final concentration of each compound is 200 ug/mL (some individual analyte concentrations may vary, i.e. Ketones). The standard should be prepared in a 1.0 mL conical vial with a mini-inert valve cap. The standard must be prepared every 7 days and stored in the VOA standards freezer between uses.

5.3.2.4 Surrogate Spiking Solution - Prepare a standard as above containing the compounds listed below. The final concentration of each compound is 250 ug/mL or 50 ug/mL depending on which autosampler you will be using. The standard must be prepared every 14 days and stored on the Archon and/or the Centurion autosampler in a pressurized vial or in the VOA standards freezer between uses.

4-Bromofluorobenzene
1,2-Dichloroethane-D_4
Toluene-D_8
Dibromofluoromethane

5.3.2.5 Internal Standard Solution - Prepare a standard as above containing the compounds listed below. The final concentration of each compound is 250 ug/mL or 50 ug/mL depending on which autosampler you will be using. The standard must be prepared every 14 days and stored on the Archon and/or the Centurion autosampler in a pressurized vial or in the VOA standards freezer between uses.

Pentafluorobenzene
1,4-Difluorobenzene
Chlorobenzene-D_5
1,4-Dichlorobenzene-D_4

5.3.2.6 BFB Solution - Prepare a standard as above containing 4-BFB. The final concentration is 25 ug/mL. The standard must be prepared every 30 days and stored in the VOA standards freezer between uses.

5.3.2.7 See Table 4 for a complete list of standards, concentration, and vendors.

NOTE: The concentrations of standards may vary depending on the type of autosampler being used.

6.0 SAMPLE COLLECTION, PRESERVATION AND HANDLING

All aqueous samples must be analyzed within 14 days from sample collection if preserved (by addition of HCl to pH <2) or within 7 days from sample collection if unpreserved. All soil/sediments must be analyzed within 14 days from sample collection. For specific projects, soil may be received in pre-weighed vials containing methanol, with an aliquot of the methanol used for analysis. For these projects, the methanol aliquot must be analyzed within 14 days from sample collection. Samples must be stored at 4°C ± 2°C from the time of receipt at the lab until analysis.

7.0 PROCEDURES

7.1 NAMING AND CODING CONVENTIONS FOR ANALYTICAL STANDARDS – Used in accordance with SOP CA-106 "Standard Preparation and Documentation".

7.2 COMPUTER (DATA SYSTEM) CONVENTIONS -

Conventions for all instruments are as follows:

Sub-Directory for data acquisition: C:\HPCHEM\1\DATA

Tune file: BFB.U

Method files: I826AXX.M (all samples and standards)
Where:
XX = the calibration number in chronological order
I = instrument ID (C, D, F, M, S or T).
A = matrix (A for water, S for soil and SB for sodium bisulfate soils)

BFB288AQ.M (waters) or BFB288SL.M (soils) (BFB tuning acquisition)

Data files for BFB: IB_ _ _.D where _ _ _ is a number in chronological order from 000 to 999, and I is the instrument ID (C, D, F, M, S or T).

All other data files: I_ _ _ _.D where _ _ _ _ is a number in chronological order from 0000 to 9999, and I is the instrument ID (C, D, F, M, S or T). This file also contains the Quantitation output file.

7.3 INSTRUMENT TUNING - Prior to the analysis of any calibration standards, blanks, or samples, the GC/MS system must be shown to meet the mass spectral ion abundance criteria for a 50 ng injection of p-Bromofluorobenzene (p-BFB), tabulated below:

Mass	Criteria
50	15.0-40.0% of mass 95
75	30.0-60% of mass 95
95	base peak, 100% relative abundance
96	5.0-9.0% of mass 95
173	less than 2.0% of mass 174
174	greater than 50.0% of mass 95
175	5.0-9.0% of mass 174
176	greater than 95.0%, but less than 101.0% of mass 174
177	5.0-9.0% of mass 176

7.3.1 The following are the GC/MS operating conditions for injection of BFB.

GC/MS type: 5970

Column:	RTX-VMS, 40 meter, 0.18 mm ID
Temperatures: Injection port:	170°
Transfer line:	150°
Source:	170°
Analyzer:	170°
Isothermal temperature:	150°
Run time:	10 minutes
Scan start time:	4 minutes
Scan parameters:	not to exceed 2 sec per scan
Mass range:	35-300
Number of A/D samples:	8
GC peak threshold:	1000 counts
Threshold:	10 counts

GC/MS type: 5972 and 5973

Column:	RTX-624, 40 meter, 0.18 mm I.D or RTX-VMS, 40 meter, 0.18 mm ID.
Temperatures: Injection port:	200°
Transfer line:	150°
Detector:	240°
Isothermal temperature:	150°
Run time:	8 minutes
Scan start time:	3 minutes
Scan parameters:	not to exceed 2 sec per scan
Mass range:	35-300
Number of A/D samples:	8
GC peak threshold:	1000 counts
Threshold:	10 counts

The BFB solution must be analyzed once at the beginning of each 12-hour period, the time stamp of the injection of the BFB is the beginning of the 12-hour clock. All calibrations and samples must be run within the 12-hour clock as the method specifies.

When the BFB run has concluded, the run must be evaluated to determine if sample analysis can proceed. The chromatography and the ion ratios must be examined. The BFB run is processed using the current algorithms in the Target software.

If the results indicate the system does not meet acceptance criteria, the GC/MS must be manually tuned. Once the manual tune procedure is completed, BFB must be re-injected and reevaluated. If the instrument still does not meet criteria, notify your Department Manager. Under no circumstances should calibration proceed if the instrument BFB tune is not in criteria.

7.4 INSTRUMENT CONFIGURATION / CALIBRATION

7.4.1 Tekmar LSC 3000/Archon 5100/ Tekmar 2016, Setup/Operation: Please refer to the Tekmar or Archon Manuals for more detailed operations for these instruments.

To begin, set the Tekmar LSC 2000/3000 to the specification listed in section 2-12 of the Archon manual. Edit method 14 as follows:

Method 14 should include:

Standby:	35°
Prepurge:	0 min
Preheat Temp:	0°
Sample Temp:	0°
Purge:	11 min
Dry purge:	2-4 min
Desorb preheat:	245°
Desorb Temp:	250°
Desorb time:	2-5 min
Dry purge:	2-4 min
Bake Time:	10 min
Bake Temp:	260°
Auto drain:	On
Bake gas by pass:	Off
Valve Temp:	120°
Line Temp:	120°
Runs per sample:	1

The above temperature settings are for a Vocarb 3000 trap, these temperatures may vary with the use of alternative traps. Temperature settings may also vary to optimize system performance.

The Archon autosampler should be set up according to the specifications in the manual. The setting of particular concern, with regards to keeping the Tekmar and Archon in coordination with each other, is the desorb time. There are several other programmable features on the Archon; the settings for this feature will depend on the sample matrix and method of analysis. Please refer to the Archon manual for more specifics on its programming features.

7.4.2 Encon/Centurion, Setup/Operation

Please refer to the Encon or Centurion manuals for more detailed operations for the instruments.

To begin, the Encon operation method should contain:

Purge Conditions:	Purge Gas: Helium Purge Time: 11.0 ±0.1 minute Purge Flow Rate: approx. 24-40 mL/min Purge Temperature: Ambient (water)
Desorb Conditions:	DesorbTemp: 250°C Desorb Flow rate: 15 mL/min Desorb Time: 2.0 ± 0.1 min Bake Time: 10 min Bake Temperature: 260°C

The above temperature settings are for a Vocarb 3000 trap, these temperatures may vary with the use of alternative traps. Temperature settings may also vary to optimize system performance.

The Centurion autosampler should be set up according to the specifications in the manual.

7.4.3 Initial Calibration for Method 8260

Once the instrument has achieved BFB tuning criteria, calibration of the instrument can begin.

To determine the linearity of response, the GC/MS must be initially calibrated at six different levels.

For aqueous calibration, target analytes and surrogate are prepared at the following concentrations; 1.0, 5.0, 20, 50, 100 and 200 ug/L. The curve is analyzed at ambient temperature.

For a soil calibration target analytes and surrogates are prepped at the following concentrations: 5.0, 10, 20, 50, 100 and 200 ug/L. The calibration standards are stirred and heated to 40ºC.

The following amounts standards should be added to 100 mL of organic-free laboratory reagent grade water in order to generate a 6-point initial calibration curve:

	STD. ID	CAL. Mix 200 ug/mL	Extras Mix 200 ug/mL	Surr. Mix 250 ug/mL Archon	Surr. Mix 50 ug/mL Centurion
AQ curve only	VSTD001	0.5 uL	0.5 uL	0.4 uL	2.0 uL
	VSTD005	2.5 uL	2.5 uL	2.0 uL	10 uL
SL curve only	VSTD010	5.0 uL	5.0 uL	4.0 uL	20 uL
	VSTD020	10 uL	10 uL	8.0 uL	40 uL
CC	VSTD050	25 uL	25 uL	20 uL	100 uL
	VSTD100	50 uL	50 uL	40 uL	200 uL
	VSTD200	100 uL	100 uL	80 uL	400 uL

The internal standard is spiked by the autosampler. Due to different spike amounts separate standards are used depending on which autosampler is being used.

After analysis of the six points, the standard analyses must be quantitated and evaluated for adherence to QC criteria, as follows. Minimum requirements for method files are use of specific quantitation ions and quantitating a specific set of target compound and surrogates with a specified internal standard. These requirements are found in Tables 3 and 5.

7.4.4 Initial Calibration Criteria

The percent (%) RSD for six calibration check compounds (CCC) must be less than or equal to 30%. CCCs are 1,1-Dichloroethene, Chloroform, 1,2-Dichloropropane, Toluene, Ethylbenzene, and Vinyl Chloride.

A system performance check must be performed as part of initial calibration. The five system performance check compounds (SPCC) and the minimum acceptable average relative response factors (RRF) for these compounds are as follows (taken from 8260B):

SPCC	RRF
Chloromethane	0.10
1,1-Dichloroethane	0.10
Bromoform	0.10
Chlorobenzene	0.30
1,1,2,2-Tetrachloroethane	0.30

The SPCCs are used to check both the standard and instrument stability.

7.4.4.1 Linearity of Target Analytes

If the RSD of any target analyte is 15% or less using the average response factor, then the response factor is presumed to be constant over the calibration range, and the average response factor may be used for quantitation.

If the RSD of any target analyte exceeds 15% using the average response factor, then a calibration option outlined in section 7.0 of method 8000 will need to be employed. Please note that some options may not be allowable for certain states, federal programs, or clients.

Option 1 (Section 7.5.2 of method 8000 - Rev. 2, 12/96), is a linear regression of instrument response versus the standard concentration. The correlation coefficient (r) for each target analyte and surrogate must be greater than or equal to 0.995. For linear models, Target calculates the correlation coefficient and then squares it (r^2). This is what is reported on all Target forms. The value for r^2 must be greater than or equal to 0.990.

Option 2 (Section 7.5.3 of method 8000 - Rev. 2, 12/96), is a non-linear calibration model not to exceed a third order (seven calibration points required) polynomial. The lab would use a quadratic model or second order polynomial. The use of a quadratic model requires six calibration points. In order for the quadratic model to be acceptable, the coefficient of determination must be greater than or equal to 0.99.

7.4.5 Independent Calibration Verification

Immediately following an initial calibration, an independent calibration standard must be analyzed. This standard contains all target compounds, internal standards and surrogates at a concentration of 50 ug/L and is obtained from a source independent of the initial calibration source. Please refer to section 8.1 and Table 1 for acceptance criteria and corrective action for this standard.

For projects or clients requiring DoD QSM 4.1 all project analytes must fall between 80-120% of the true value. No samples may be run until the ICV criteria are met.

7.4.6 Calibration Verification

Once a valid initial calibration curve has been achieved, a continuing calibration standard containing all the target compounds, internal standards and surrogates at a concentration of 50 ppb must be analyzed every 12-hour clock for Method 8260, timed from the injection of BFB. The relative response factor from the 50 ppb continuing calibration check standard must be compared to the average response factor data from the initial calibration.

The EICP (extracted ion current profile) area for any of the internal standards in the calibration verification must not change by more than a factor of two (-50% to +100%) from the same level standard in the last initial calibration. The retention time for any internal standard cannot shift by more than 30 seconds from the same level standard in the last initial calibration.

For Method 8260, if the percent difference for each CCC is less than or equal to 20%, and all of the SPCCs have a relative response factor greater than or equal to those listed in Section 7.4.3, the continuing calibration is considered valid.

For projects or clients requiring DoD QSM 4.1 all project analytes must have ± 20%D.

Continuing calibration check criteria must be met before sample analysis can proceed.

7.4.7 Retention Time Windows

Retention time windows are set at the midpoint standard of the calibration curve, following every ICAL. When a CV is analyzed (and not an ICAL), the retention time windows of the daily CV must be within 30 seconds of the midpoint calibration standard of the most recent ICAL. The samples analyzed following the daily CV must have retention times within 30 seconds of those for the daily CV. Each successive daily CV must be compared to the most recent ICAL midpoint standard.

For projects or clients requiring DoD QSM 4.1, IS responses and retention time windows for QC and samples are compared to the midpoint of the most recent ICAL.

7.5 QUALITY CONTROL SAMPLE ANALYSIS

When preparing standards in water or spiking samples with internal standards/surrogates or matrix spike solution, be sure to rinse all syringes a minimum of three times with purge and trap grade methanol between uses. Failure to do this will result in cross-contamination of samples and standards.

7.5.1 Laboratory Control Sample (LCS)

The LCS mix is prepared from a secondary source vendor (i.e. different vendor from the calibration standards). The LCS is analyzed immediately after the initial calibration curve or calibration check and prior to the method blank to minimize any analyte carryover possibilities in samples. Acceptance criteria for the LCS are outlined in Section 8.0.

To prepare the water and medium-level soil LCS, 25 uL of the LCS standard mix at 200 ug/mL are spiked into 100 mL of analyte-free laboratory reagent grade water for a final concentration of 50 ug/L. The Archon autosampler adds 1 uL of internal and 1 uL of surrogate standard to a 5 mL aliquot of this preparation for analysis. The Centurion autosampler adds 5 uL of both surrogates and internal standards to a 5 mL aliquot. To prepare the low-level soil LCS, a stir bar is added to 5 mL of the above solution in a VOA vial. The Archon unit adds an additional 10 mL of water to which the internal and surrogate standards have been added; this preparation is then heated, stirred and purged.

To prepare the water and medium-level soil LCS for analysis on the LSC 2000 / 2016 autosampler, 1.25 uL of the LCS standard mix at 200 ug/mL are spiked into 5 mL of analyte-free laboratory reagent grade water for a final concentration of 50 ug/L.

In the event that the batch MS/MSD requirement cannot be fulfilled, a laboratory Control Spike Duplicate must be analyzed.

7.5.2 Method Blank Analysis

After calibration criteria have been met, a method blank must be analyzed before sample analysis can proceed. A method blank analysis must be performed once for each 12-hour calibration immediately after analysis of the calibration standard(s) and prior to sample analysis.

The aqueous method blank is a volume of analyte free laboratory reagent grade water spiked with internal and surrogate standards.

The low-level soil method blank is a volume of analyte free laboratory reagent grade water spiked with internal and surrogate standards. This method blank is analyzed using the low soil specification.

The method blank must contain less than the Practical Quantitation Level (PQL) for all analytes of interest for the samples associated with the blank.

For projects requiring DoD QSM 4.1 no analytes may be detected >1/2 the PQL and > than the 1/10th the measured amount in any sample or 1/10th the regulatory limit, whichever is larger. Except for common laboratory contaminants which may not be detected > than the PQL.

7.5.3 Surrogate Recovery Limits

Laboratory established limits are derived for each of the surrogates. Please refer to the current revision of Katahdin Analytical Services SOP # QA-808 for further information on statistical limits. All samples including blanks, laboratory control samples, matrix spikes and client samples, must meet the statistical limits for the analysis to be considered valid. If surrogate recoveries do not meet these limits, reanalysis must occur to confirm matrix interference.

7.5.4 Internal Standard Area Recoveries / Retention Times.

The internal standard responses and retention times in the method blank must be evaluated immediately after or during data acquisition. If the EICP (extracted ion current profile) area for any of the internal standard changes by a factor of two (-50% to +100%), from the last daily calibration standard, the GC/MS must by inspected, and corrective action taken. If the retention time for any internal standard has shifted by more than 30 seconds from the mid-point standard level of the most recent calibration sequence, the GC/MS must be inspected, and corrective action taken. All samples and QC must also meet the EICP area and retention time criteria or must be reanalyzed.

7.5.5 Matrix Spike/Matrix Spike Duplicate (MS/MSD) Analysis

An MS/MSD must be analyzed every twenty samples of a similar matrix. The MS/MSD is prepared in a manner similar to the LCS, except that 40 mL aliquots (aqueous) or 5 g aliquots (soil), of environmental samples are used in place of the analyte-free laboratory reagent grade water. Note that trip blanks and field/equipment blanks should not be used for MS/MSD analyses. The spike solution (section 7.5.1) is added to the sample at a concentration of 50 ppb. Acceptance criteria for the MS/MSD are outlined in Section 8.0.

In the event that sufficient volume of sample is not supplied to the laboratory so that an MS/MSD set cannot be analyzed within a batch of 20 samples, a laboratory control spike duplicate must be analyzed.

7.6 SAMPLE ANALYSIS

When new samples are received, they should be checked for past sample history. If sample history cannot be located or the sites are different than past sites, the project manager should be consulted. He/she may be able to provide more information about the sample. Sample history is used to determine what order in which to run the samples and at what dilution. Refer to Katahdin Analytical Services SOPCA-106, "Basic Laboratory Technique", current revision for information on subsampling.

Samples are removed from the VOA refrigerator and appropriate chain of custody form is completed. Remove only the vials that have not been opened yet (opened vials will be upside down). Note in sample run log any bubbles, and significant discoloration or sediment in the sample vials.

7.6.1 SAMPLE ANALYSIS FOR 8260B WATER

7.6.1.1 Tekmar LSC 2000 / 2016 units

Rinse a 5.0 mL gas-tight syringe a minimum of three times with analyte-free laboratory reagent grade water (e.g., Poland Spring or equivalent). Pour sample at ambient temperature into the syringe until nearly overflowing. Carefully insert and adjust plunger to sample volume of 5.0 mL. While adjusting plunger to final volume, expel extra volume of sample onto pH paper for sample pH verification. Add 1.0 uL of the internal and surrogate mixtures (250 ug/mL). Immediately inject contents of the syringe into the ALS sparger.

Record the sample pH in the injection logbook. Continue as above for each sample, ensuring that the 5.0 mL gas-tight syringe is rinsed a minimum of three times with laboratory reagent grade water between each sample.

7.6.1.2 Tekmar LSC 3000 / Archon 5100 units

Place the sample vials into the Archon sample tray and program the Archon for the appropriate sample volume and or dilution for the sample. The Archon unit will automatically transfer the sample to the sparge vessel while adding the internal and surrogate standard. The Archon can be programmed to run as many samples as will fit in the twelve-hour window. The auto sampler hot water rinses the sparge

vessel, transfer lines, purge needle, and syringe between samples to minimize possible carryover.

Record the sample pH in the injection logbook after sample analysis is complete (usually the day after the analysis is done) and return the sample vial to the sample refrigerator.

7.6.1.3 Centurion/Encon unit

Place the sample vials into the Centurion sample tray and program the Centurion for the proper sequence. The Centurion will automatically transfer the sample to the sparge vessel while adding the internal and surrogate standards. Using the Centurion software, the analyst can program the Centurion to run as many samples that will fit into a 12 hour clock. The autosampler uses hot water to rinse the sparge vessel, transfer lines, purge needle and sample needle to minimize carryover.

Record the sample pH in the injection logbook after sample analysis is complete (usually the day after the analysis is done) and return the sample vial to the sample refrigerator.

Make sure that all entries in the injection log have been made in a complete, neat, and legible manner. Corrections in any logbook must be crossed through with a single line, dated, initialed and have a written explanation or the applicable error code.

If for any reason a sample needs to be rerun, diluted or duplicated, a note in the comments field of the injection logbook must be entered, addressing the reason why in the logbook to facilitate answering any questions that may arise during the review process.

To minimize carryover from samples that contain a target compound at a level exceeding the upper limit of the calibration curve, the following <u>must</u> be done: monitor both the samples immediately after the contaminated sample as well as the next run of the contaminated sample in the same purge inlet for the target(s) in question; both must have levels <PQL.

7.6.2 ANALYSIS OF LOW-LEVEL SOIL SAMPLES

Method 5035 Closed System Purge & Trap procedure for low level soils (5 ug/Kg -200 ug/Kg)

Selecting the appropriate technique may depend on cleanup goals, confidence levels, and anticipated levels of contamination. Field sampling activities typically result in Encore or Encore-like devices being submitted to the lab. These devices must be extruded within 48 hours. It is the laboratory's standard policy to extrude soil samples into 5 mL of Laboratory reagent free laboratory reagent grade water that contains a magnetic stir bar. The sample is subsequently frozen until analysis within 14 days. Note that the sample must be extruded and frozen within 48 hours of sampling, until analysis can begin. This approach is preferred over extrusion into sodium bisulfate because it is believed that the sodium bisulfate reacts with calcium carbonate in highly calcareous soils causing effervescence and driving the volatile analytes out of solution. There is also anecdotal information to suggest that acetone may be generated when bisulfate preservation occurs. The Katahdin sample ID, extrusion date, and time are recorded in the GC/MS extrusion logbook. Please refer to the Katahdin method 5035 SOP, CA-214 for more detail.

In lieu of the use of Encore samplers, the lab may pre-weigh 40 mL VOA vials containing 5 mL of laboratory reagent grade water or a 20% sodium bisulfate solution and a magnetic stir bar and ship these to the field. The vial is assigned a vial specific number prior to shipment to the field. The vial and weight will be recorded with its vial specific number in the methanol soil logbook. If possible the field sampler should weigh the sealed vial to ensure that 5 +/- 0.5 grams of sample were added in the field. When the lab receives the vials back from the field, the vials will be weighed and the weight recorded. The samples must be frozen within 48 hours of sampling, until analysis can begin.

The subsequent analysis is performed on a specially developed autosampler that heats, stirs, and purges the sample simultaneously without exposing the contents of the vial to the atmosphere. This procedure will help to minimize the loss of VOC's due to transport, handling, and analysis and may help minimize ambient lab contribution. The expected detection limits are consistent with the traditional low soil technique from method 5030. The Archon is programmed to heat each vial to 40°C during the purge time. Initiate purging for 11.0 minutes; the sample must be heated to 40°C ± 1°C before purging can begin. If you have questions concerning setting up the Tekmar or initiating a GC/MS batch run, consult the Organic Department Manager, or senior chemist within the group.

If the client does not require method 5035, method 5030 for analysis of low-level soils may be followed. This means that the Tekmar ALS 2016 unit may be used for the preparative step, as well as the Archon units.

7.6.3 ANALYSIS OF MEDIUM-LEVEL SOIL SAMPLES

Method 5030 Procedure for higher concentration soils (> 200 ug/Kg)

Higher concentration soils may be sampled as either a bulk sample or field preserved with a water miscible solvent such as methanol. If sampled in an Encore unit, the soil is extruded into methanol upon receipt at the lab.

Bulk Sample- A sample is placed in a glass jar or vial and returned to the lab for extraction and analysis. In this approach the lab takes an aliquot of soil and extracts with purge & trap grade methanol, a portion of the methanol is then analyzed for volatile analytes.

Extraction

Calibrate the balance properly (See SOP CA-102) and note it in the appropriate logbook. Place 5.0 grams of thoroughly mixed, undecanted soil sample in a 40.0 mL vial. Add 5.0 mL reagent grade methanol. Shake for 2 minutes. Let stand for 3 minutes. Record extraction in soil prep logbook.

Methanol Field Preservation - A 5 gram sample is added to a VOA vial that has been previously charged with purge and trap grade methanol (the volume of methanol is dependent upon client request). The vial with methanol has been previously weighed in the lab and assigned a vial specific number prior to shipment to the field. The vial and methanol weight will be recorded with its vial specific number in the VOA vial prep logbook. If possible the field sampler should weigh the sealed vial to ensure that 5 +/- 0.5 grams of sample were added in the field. When the lab receives the vials back from the field, the vials will be weighed and the weight recorded. A portion of the methanol is then analyzed for volatile analytes.

For analysis on Archon or Centurion autosamplers, add 400 uL of the extract into 20 mL of organic-free laboratory reagent grade water (e.g., Poland Spring or equivalent). IS and SS is added by the Archon and/or Centurion autosampler for analysis. This will give an estimated calibration range between 500-10000 ug/Kg.

7.7 FINAL DATA PACKAGE

7.7.1 Initial Data Review (IDR)

The initial data review is performed by the analyst who ran the samples. This review is of sufficient quality and detail to provide a list of samples that need to be reanalyzed or diluted and reanalyzed. The initial data review is performed on the detailed quantitation reports of the analyzed sample. This

data review examines criteria that directly impact whether or not the sample needs to be reanalyzed.

- Surrogate recoveries
- stability of internal standard responses
- LCS spike recoveries
- method blank acceptance
- chromatography
- target compound detection/quantitation / review for false positives

The analyst must evaluate all data using the QA Acceptance Criteria table found within this SOP (Table 1). This table gives acceptance criteria and corrective actions for criteria that are not met. In addition to evaluating QC elements, the chromatography and quantitation of target analytes must be reviewed.

7.7.1.1 Chromatography

The chromatography should be examined for the presence or absence of any "ghost" peaks and can also be used as an indication of whether or not matrix interferences might be influencing surrogate recoveries and/or ISTD area recoveries. Whether or not the chromatography is acceptable is a judgment call on the part of the analyst and should be used in conjunction with other monitored QC (e.g., Surrogate recoveries) to determine the necessity of reanalyses.

Manual integrations are to be performed when chromatographic conditions preclude the computer algorithm from correctly integrating the peak of concern. In no instance shall a manual integration be performed solely to bring a peak within criteria.

Each peak of concern is examined by the primary analyst to ensure that the peak was integrated properly by the computer algorithm. An "M" qualifier will automatically be printed on the quantitation report summary.
This manual integration package must then be submitted to the Organic Department Manager or his/her designee, who will review each manual integration.

For specific procedures on how to manually integrate, refer to Katahdin SOP QA-812, "Manual Integration", current revision.

7.7.1.2 Target Compound Detection/Quantitation

The method files have been set up to error on the side of false positives, that is to identify and quantitate peaks as target compounds that may not necessarily be valid hits.

The requirements for qualitative verification by comparison of mass spectra are as follows:

- all ions present in the standard mass spectra at a relative intensity > 25% must be present in the sample spectrum.
- the relative intensities of primary and secondary ions must agree within ±20% between the standard and sample spectra.
- ions greater than 25% in the sample spectrum but not present in the standard spectrum must be considered and accounted for by the analyst.

If a compound cannot be verified by all three criteria above, but, in the technical judgment of the mass spectral interpretation specialist, the identification is correct, then the laboratory shall report that compound on the Form 1 as a valid hit.

If any target concentration exceeds the upper limit, a dilution must be made and analyzed. The dilution chosen should keep the response of the largest target compound hit in the upper half of the initial calibration range.

The GC/MS laboratory initial data review must be completed within twelve hours of batch completion; in the majority of instances, the initial data review should be accomplished at the beginning of a work shift for the previous set of analyses. After the analyst has completed his or her initial data review, the data should immediately be forwarded to the Organic Department Manager, or his/her designee.

7.7.1.3 Tentatively Identified Compounds (TIC)

TIC's may be requested by certain clients for samples. Refer to SOP CA-207 "GC/MS Library Search and Quantitation".

7.7.2 Reporting

After the chromatograms have been reviewed and any target analytes have been quantitated using Target, the necessary files are brought into QuickForms. Depending on the QC level requested by the client, a Report of Analysis (ROA) and additional reports, such as LCS forms and chronology forms, are generated. The package is assembled to include the necessary forms and raw data. The data package is reviewed by the

primary analyst and then forwarded to the secondary reviewer. The secondary reviewer validates the data and checks the package for any errors. When completed, the package is sent to the department manager for final review. A completed review checklist is provided with each package. The final data package from the Organics department is then processed by the Data Management department.

8.0 QUALITY CONTROL AND ACCEPTANCE CRITERIA

Refer to Table 1 and to details in this section for a summary of QC requirements, acceptance criteria, and corrective actions. These criteria are intended to be guidelines for analysts. The criteria does not cover all possible situations. If any of the QC requirements are outside the recovery ranges listed in this section or in Table 1, all associated samples must be evaluated against all the QC. In some cases data may be reported, but may be reanalyzed in other cases. Making new reagents and standards may be necessary if the standardization is suspect. The corrective actions listed in this section and in Table 1 may rely on analyst experience to make sound scientific judgments. These decisions are based on holding time considerations, client and project specific Data Quality Objectives and on review of chromatograms. The Department Manager, Operations Manager, and/or Quality Assurance Officer may be consulted to evaluate data. Some samples may not be able to be reanalyzed within hold time. In these cases "qualified" data with narration may be advisable after consultation with the client.

In some cases the standard QC requirements listed in this section and in Table 1 may not be sufficient to meet the Data Quality Objectives of the specific project. Much of the work performed at the lab is analyzed in accordance with specific QC requirements spelled out in a project specific Quality Assurance Project Plan (QAPP) or in a program specific Quality Systems Manual (QSM). The reporting limits, acceptance criteria and/or corrective actions may be different than those specified in this SOP. In these cases the appropriate information will be communicated to the Department Manager and/or senior chemists before initiation of the analyses so that specific product codes can be produced for the project. In addition, the work order notes for each project will describe the specific QAPP or QSM to be followed.

8.1 Independent Calibration Verification, LCS and MS/MSD Criteria

Statistical limits are compiled annually for LCS recoveries (archived in QA office). Statistical limits are only calculated when at least 30 usable data points are obtained for any given compound. If insufficient data points are available, nominal limits are set by the Organic Department Manager, Laboratory Operations Manager and Quality Assurance Officer. Refer to Katahdin SOP QA-808, "Generation and Implementation of Statistical QC Limits and/or Control Charts," current revision.

The use of statistical limits versus nominal limits is dependent on the client and project. This information is communicated to the Organic Department Manager

through the Katahdin project manager. It is standard practice to use statistical limits for reporting purposes and to evaluate any QC criteria exceedances. However, nominal limits of 60-140% or 70-130% may be used for some projects or states.

The LCS recoveries for all analytes are evaluated. All of the compounds of interest must fall within the established statistical limits with the following sporadic exceedance allowances.

Number of Analytes	Number of Allowable Exceedances
> 90	5
71 – 90	4
51 – 70	3
31 – 50	2
11 – 30	1
<11	0

If less than the number of allowable exceedances fail the statistical limits, no corrective action is needed. If greater than the number of allowable exceedances fail the statistical limits, corrective action may be taken. Corrective actions may vary with each situation. However, in the case where the failures are high and the samples are non-detect for those compounds, then no corrective action is required. Otherwise, corrective action may involve reanalysis or recalibration. The specific corrective actions taken will rely on analyst experience to make sound scientific judgments while considering client objectives, other quality control indicators and/or the ability to reanalyze a sample within holding time.

The MS/MSD recoveries for all analytes are evaluated. If the LCS results are acceptable but the MS/MSD is not, narrate. If both the LCS and MS/MSD are unacceptable reprep the samples and QC.

Please note that for compounds with only nominal limits (i.e. insufficient data points were available to generate statistical limits), no corrective action is required for out-of-criteria recoveries until enough data points are established to generate statistical limits.

For projects or clients requiring DoD QSM 4.1 all project analytes in the ICV must fall between 80-120% of the true value. No samples may be run until the ICV criteria is met. Laboratory established recovery limits for LCS and MS/MSDs must be within 3 standard deviations of the mean LCS recovery. MS/MSD pairs must be run once per analytical/preparatory batch. RPDs must be less than or equal to 30% between MS and MSDs.

For analytes with no available DoD acceptance criteria, laboratory established limits shall be used.

8.2 Surrogate Recovery Criteria

Statistical limits are compiled annually for surrogate recoveries (archived in QA office). Statistical limits are only calculated when at least 30 usable data points are obtained for any given compound. If insufficient data points are available, nominal limits are set by the Organic Department Manager, Laboratory Operations Manager and Quality Assurance Officer. The use of statistical limits versus nominal limits is dependent on the client and project. This information is communicated to the Organic Department Manager through the Katahdin project manager. It is standard practice to use statistical limits for reporting purposes and to evaluate any QC criteria exceedances. However, nominal limits of 60-140% or 70-130% may be used for some projects or states.

8.3 QC Requirements

Refer to Table 1 for a summary of QC requirements, acceptance criteria, and corrective actions. Table 1 criteria are intended to be guidelines for analysts. The table does not cover all possible situations. If any of the QC requirements are outside the recovery ranges listed in Table 1, all associated samples must be evaluated against all the QC. In some cases data may be reported, but may be reanalyzed in other cases. Making new reagents and standards may be necessary if the standardization is suspect. The corrective actions listed in Table 1 may rely on analyst experience to make sound scientific judgments. These decisions are based on holding time considerations, client and project specific Data Quality Objectives and on review of chromatograms. The Department Manager, Operations Manager, and/or Quality Assurance Officer may be consulted to evaluate data. Due to the 14-day hold time associated with this method, samples may not be able to be reanalyzed within hold time. In these cases "qualified" data with narration may be advisable after consultation with the client.

9.0 METHOD PERFORMANCE

The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. The MDLs are determined annually per type of instrument and filed with the Organic Department Manager and with the QAO. Refer to the current revision of Katahdin SOP QA-806, Method Detection Limit, Instrument Detection Limit and Reporting Limit Studies and Verifications, for procedures on determining the MDL.

Refer to the current revision of Method 8260 for other method performance parameters and requirements.

TITLE: **ANALYSIS OF VOAs BY PURGE AND TRAP GC/MS: SW-846 METHOD 8260**

10.0 APPLICABLE DOCUMENTS/REFERENCES

Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, USEPA SW846, 3rd Edition, Final Updates I, II, IIA, IIB, III, IIIA, IIIB and IV, February 2007, Method 8260B.

"Department of Defense Quality Systems Manual for Environmental Laboratories" (DoD QSM), Version 4.1, 04/22/09.

"The National Environmental Laboratory Accreditation Conference (NELAC) Standards," June 2003.

Katahdin SOP CA-101, Equipment Maintenance and Troubleshooting, current revision.

Katahdin SOP QA-806, Method Detection Limit, Instrument Detection Limit and Reporting Limit Studies and Verifications, current revision.

LIST OF TABLES AND FIGURES

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TABLE 1

QC REQUIREMENTS - VOLATILE ORGANICS, METHOD 8260

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action
Check of mass spectral ion intensities using BFB	Prior to initial calibration and calibration verification	Refer to the criteria listed in Section 7.3 of this SOP	Retune instrument, and verify
Six-point calibration for all analytes	Initial calibration prior to sample analysis	SPCCs average RF ≥0.30, except chloromethane, 1,1-DCA and bromoform ≥0.10; RSD for RFs ≤ 30% for CCCs. Refer to section 7.4.3 also.	Repeat initial calibration
Independent Calibration Verification	Once, immediately following calibration	Statistically derived from lab data or nominal limits depending on the project. Refer to QA records for statistical limits. Nominal limits are used as default limits. See also section 8.1 of this SOP for more information on allowable exceedances	Evaluate the samples and associated QC: i.e. If an MS/MSD was performed and acceptable, narrate. If an LCS/LCSD was performed and only one of the set was unacceptable, narrate. If the surrogate recoveries in the LCS are also low but are acceptable in the blank and samples, narrate. If the LCS recovery is high but the sample results are <PQL, narrate. Otherwise, reprep a blank and the remaining samples.
Calibration verification	Once per each 12 hours, prior to sample analysis in absence of initial cal	SPCCs minimum RF ≥ 0.30, except chloromethane, 1,1-DCA and bromoform ≥ 0.10; RF for CCC analytes ≤ 20% (%D) of average initial multipoint RF	Repeat initial calibration and reanalyze all samples analyzed since the last successful calibration verification
IS	During data acquisition of calibration check standard	Retention time ± 30 seconds; EICP area within -50% to +100% of last calibration verification (12 hours) for each IS	Inspect mass spectrometer or GC for malfunctions; mandatory reanalysis of samples analyzed while system was malfunctioning
Method Blank	One per batch of 20 or fewer samples.	No analytes of interest detected > PQL with the exception of Methylene Chloride	(1) Investigate source of contamination (2) Evaluate the samples and associated QC: i.e. If the blank results are above the PQL, report sample results which are <PQL or > 10X the blank concentration. Otherwise, reprep a blank and the remaining samples.

TABLE 1 (cont.)

QC REQUIREMENTS - VOLATILE ORGANICS, METHOD 8260

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action
LCS	One per batch of 20 or fewer samples.	Statistically derived from lab data or nominal limits depending on the project. Refer to QA records for statistical limits. Nominal limits are used as default limits. See also section 8.4 of this SOP for more information on allowable exceedances.	Evaluate the samples and associated QC: i.e. If an MS/MSD was performed and acceptable, narrate. If an LCS/LCSD was performed and only one of the set was unacceptable, narrate. If the surrogate recoveries in the LCS are also low but are acceptable in the blank and samples, narrate. If the LCS recovery is high but the sample results are <PQL, narrate. Otherwise, reprep a blank and the remaining samples.
Surrogate spike	Every sample, control, standard and method blank	Statistically derived limits.	Reprep and reanalyze for confirmation of matrix interference when appropriate.
MS/MSD	One MS/MSD per every 20 samples.	Statistically derived from lab data or nominal limits depending on the project. Statistical limits are used as default limits.	(1) Evaluate the samples and associated QC: i.e. If the LCS results are acceptable, narrate. (2) If both the LCS and MS/MSD are unacceptable reprep the samples and QC.
MDL Study	Refer to KAS SOP QA-806, "Method Detection Limit, Instrument Detection Limit and Reporting Limit Studies and Verifications", current revision.		
Demonstrate ability to generate acceptable P & A using 4 replicate analyses of a QC check standard	Once per year for each analyst; 4 reps	All recoveries within method QC acceptance limits	Recalculate results; locate and fix problem; rerun P & A study for those analytes that did not meet criteria prior to sample analysis

TABLE 2

DOD QSM Version 4.1 QC Requirements

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 significant change in instrument type, personnel, test method, or sample matrix.	QC acceptance criteria published by DoD, if available; otherwise, method-specific 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.
LOD determination and verification	Refer to current revision of SOP QA-806				
LOQ establishment and verification	Refer to current revision of SOP QA-806				
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. 2. RSD for RFs for CCCs ≤ 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).	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.

TABLE 2 (cont)

DOD QSM Version 4.1 QC Requirements

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
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 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 ≥ 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 ≤ 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 failed standards.	Sample results are not acceptable without a valid IS verification.

TITLE: **ANALYSIS OF VOAs BY PURGE AND TRAP GC/MS: SW-846 METHOD 8260**

TABLE 2 (cont)

DOD QSM Version 4.1 QC Requirements

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Method blank	One per preparatory batch.	No analytes detected > ½ RL (> RL for common lab contaminants) 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 the problem. Report sample results that are <LOD or >10x the blank concentration. Reprepare and reanalyze the method blank and all associated samples with results > LOD and < 10x the contaminated blank result. Contact Client if samples cannot be reprepped within hold time.	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.	The laboratory shall use laboratory control limits (CLs) or use DoD-generated LCS-CLs, if available depending on project requirements. In-house CLs may not be greater than ± 3 times the standard deviation of the mean LCS recovery. A number of analytes may fall outside the CL but within marginal exceedance limit depending on the total number of analytes in the LCS.	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. Refer to Table G-1 for number of marginal exceedences allowed. Contact Client if samples cannot be reprepped within hold time.	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 if sufficient sample is available.	For matrix evaluation, use LCS acceptance criteria.	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 there is a matrix effect or analytical error.
Matrix spike duplicate (MSD) or sample duplicate	One per preparatory batch per matrix if sufficient sample is available.	MSD: For matrix evaluation, use LCS acceptance criteria. MS/MSD: RPD ≤ 30% .	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 2 (cont)

DOD QSM Version 4.1 QC Requirements

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Surrogate spike	All field and QC samples.	The laboratory shall use laboratory surrogate CLs or use DoD-generated surrogate CLs, if available depending on project requirements. .	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. Contact Client if samples cannot be reprepped within hold time.	Apply Q-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 J-flag to all results between DL and LOQ.	

TITLE: **ANALYSIS OF VOAs BY PURGE AND TRAP GC/MS: SW-846 METHOD 8260**

TABLE 3

SUMMARY OF METHOD MODIFICATIONS

TOPIC	KATAHDIN SOP CA-202-11	METHOD 8260, current revision
Apparatus/Materials	None	
Reagents	None	
Sample preservation/ handling	Preserved samples analyzed within 14 days. Unpreserved samples analyzed within 7 days.	Preserved samples analyzed within 14 days. No criteria for unpreserved samples.
Procedures	(1) Use laboratory reagent grade water for low level soil calibration, method blanks, and laboratory control samples to minimize clogging of archon soil needles with sand. (2) Internal Standards- pentafluoro-benzene, 1,4-difluorobenzene, chlorobenzene-d5, 1,4-dichloro-benzene-d4	(1) Use an aliquot of a clean (control) matrix similar to the sample matrix. (2) Recommended internal standards – fluorobenzene, chlorobenzene-d5, 1,4-dichloro-benzene-d4
QC - Spikes	None	
QC - LCS	None	
QC - Accuracy/Precision	PQL – Practical Quantitation Level – three to ten times the MDL.	EQL – Estimated Quantitation Level – five to ten times the MDL
QC - MDL	None	

TABLE 4

VOA COMPOUNDS AND CHARACTERISTIC IONS

COMPOUND	1° ION	2° ION
Acetone	43	58
Acetonitrile	41	40, 39
Acrolein	56	55, 58
Acrylonitrile	53	52, 51
Allyl Chloride	76	41, 39
Benzene	78	-
Bromobenzene	156	77, 158
Bromochloromethane	128	49, 130
Bromodichloromethane	83	85, 127
Bromoform	173	175, 254
Bromomethane	94	96
2-Butanone	43	72
n-Butylbenzene	91	92, 134
Sec-Butylbenzene	105	134
Tert-Butylbenzene	119	91, 134
Carbon Disulfide	76	78
Carbon Tetrachloride	117	119
Chlorobenzene	112	77, 114
Chloroethane	64	66
2-Chloroethylvinyl Ether	63	65, 106
Chloroform	83	85
Chloromethane	50	52
Chloroprene	53	88, 90
2-Chlorotoluene	91	126
4-Chlorotoluene	91	126
Cyclohexane	56	84, 60
1,2-Dibromo-3-Chloropropane	75	155, 157
Dibromochloromethane	129	127
1,2-Dibromoethane	107	109, 188
Dibromomethane	93	95, 174
Diethyl Ether	74	45, 59
1,2-Dichlorobenzene	146	111, 148
1,3-Dichlorobenzene	146	111, 148
1,4-Dichlorobenzene	146	111, 148
Dichlorodifluoromethane	85	87
1,1-Dichloroethane	63	65, 83
1,2-Dichloroethane	62	98
1,1-Dichloroethene	96	61, 63
Cis-1,2-Dichloroethene	96	61, 98
Trans-1,2-Dichloroethene	96	61, 98
1,2-Dichloropropane	63	112

TABLE 4 (cont.)

VOA COMPOUNDS AND CHARACTERISTIC IONS

COMPOUND	1° ION	2° ION
1,3-Dichloropropane	76	78
2,2-Dichloropropane	77	97
1,1-Dichloropropene	75	110, 77
Cis-1,3-Dichloropropene	75	77, 39
Trans-1,3-Dichloropropene	75	77, 39
Cis-1,4-Dichloro-2-butene	75	53, 77
Trans-1,4-Dichloro-2-butene	53	88, 75
1,4-Dioxane	88	58, 43
Di-Isopropyl Ether	45	43, 87
Ethylbezene	91	106
Ethyl Methacrylate	69	41, 99
Ethyl Tertiary-Butyl Ether	59	87, 57
Freon-113	151	101
Hexachlorobutadiene	225	223, 227
2-Hexanone	43	58, 57, 100
Idomethane	142	127, 141
Isobutyl Alcohol	43	41, 42
Isopropylbezene	105	120
P-ISOPROPYLTOLUENE	119	134, 91
Methacrylonitrile	41	67, 39
Methylcyclohexane	83	55, 98
Methylene Chloride	84	86, 49
Methyl Acetate	43	74
Methyl Methacrylate	69	41, 100
4-Methyl-2-Pentanone	43	58, 85, 100
Methyl Tert-Butyl Ether	73	57, 41
Naphthalene	128	-
Pentachloroethane	167	130, 132
Propionitrile	54	52, 55
N-PROPYLBENZENE	91	120
Styrene	104	78
Tertiary-Amyl Methyl Ether	73	55, 87, 71
Tertiary-Butyl Alcohol	59	41, 43
1,1,1,2-Tetrachloroethane	131	133, 119
1,1,2,2-Tetrachloroethane	83	131, 85
Tetrachloroethene	164	129, 131, 166
Tetrahydrofuran	42	72, 71
Toluene	92	91
1,2,3-Trichlorobenzene	180	182, 145
1,2,4-Trichlorobenzene	180	182, 145
1,3,5-Trichlorobenzene	180	182, 145
1,1,1-Trichloroethane	97	99, 61
1,1,2-Trichloroethane	83	97, 85
Trichloroethene	95	97, 130, 132

TABLE 4 (cont.)

VOA COMPOUNDS AND CHARACTERISTIC IONS

COMPOUND	1° ION	2° ION
Trichlorofluoromethane	151	101, 153
1,2,3-Trichloropropane	75	77
1,2,3-Trimethylbenzene	105	120
1,2,4-Trimethylbenzene	105	120
1,3,5-Trimethylbenzene	105	120
Vinyl Acetate	43	86
Vinyl Chloride	62	64
Xylenes (Total)	106	91
1-Chlorohexane	91	55,43

TITLE: **ANALYSIS OF VOAs BY PURGE AND TRAP GC/MS: SW-846 METHOD 8260**

TABLE 5

ANALYTE QUANTITATION AND INTERNAL STANDARDS

Pentafluorobenze	**1,4-Difluorobenzene**	**Chlorobenzene - d5**	**1,4-Dichlorobenzene - d4**
Dichlorodifluoromethane	1,2-Dichloroethane	1,3-Dichloropropane	1,1,2,2-Tetrachloroethane
Chloromethane	1,1-Dichloropropene	Tetrachloroethene	1,2,3-Trichloropropane
Bromomethane	Carbon tetrachloride	Dibromochloromethane	Isopropylbenzene
Vinyl chloride	Benzene	Chlorobenzene	Bromobenzene
Chloroethane	1,2-Dichloropropane	1,1,1,2-Tetrachloroethane	2-Chlorotoluene
Trichlorofluoromethane	Trichloroethene	Ethylbenzene	4-Chlorotoluene
Methylene Chloride	Dibromomethane	Xylenes (total)	1,3,5-Trimethylbenzene
Acetone	Bromodichloromethane	Bromoform	Tert-Butylbenzene
1,1-Dichloroethene	cis -1,3-Dichloropropene	Styrene	1,2,4-Trimethylbenzene
1,1-Dichloroethane	4-Methyl-2-pentanone	2-Hexanone	Sec-Butylbenzene
cis-1,2-Dichloroethene	Toluene-d8 (surr.)	Bromoform	1,3-Dichlorobenzene
trans-1,2-Dichloroethene	Toluene		P-Isopropyltoluene
Chloroform	trans-1,3-Dichloropropene		1,4-Dichlorobenzene
2,2-Dichloropropane	1,1,2-Trichloroethane		1,2-Dichlorobenzene
2-Butanone	1,2-Dibromoethane		N-Propylbenzene
Methyl-tert-butylether (MTBE)	Vinyl Acetate		1,2-Dibromo-3-chloropropane
Tetrahydrofuran	Methyl Methacrylate		1,2,4-Trichlorobenzene
Bromochloromethane	Ethyl Methacrylate		Naphthalene
1,1,1-Trichloroethane	1,4-Dioxane		Hexachlorobutadiene
Tertiary-butyl alcohol (TBA)	2-Chloroethylvinyl ether		1,2,3-Trichlorobenzene
Di-isopropyl ether (DIPE)	Bromofluorobenzene (surr.)		cis-1,4-Dichloro-2-butene
Ethyl-tert-butylether (ETBE)			trans-1,4-Dichloro-2-butene
Tertiary-amyl methyl ether			Pentachloroethane
Diethyl Ether			n-Butylbenzene
Carbon Disulfide			1,3,5-Trichlorobenzene
Freon-113			1,2,3-Trimethylbenzene
Iodomethane			
Acrolein			
Isobutyl Alcohol			
Allyl Chloride			
Chloroprene			
Propionitrile			
Methacrylonitrile			
Acrylonitrile			
Cyclohexane			
Methyl Acetate			
Methylcyclohexane			
1-Chlorohexane			
Dibromofluoromethane (surr.)			
1,2-Dichloroethane-d4 (surr.)			

TITLE: **ANALYSIS OF VOAs BY PURGE AND TRAP GC/MS: SW-846 METHOD 8260**

FIGURE 1

EXAMPLE OF VOA RUNLOG PAGE

KATAHDIN ANALYTICAL SERVICES
GCMS-D INSTRUMENT RUNLOG

DATE/TIME OF BFB INJECTION: 040210
Reviewed by/Date:

SAMPLE NAME	DATAFILE	DF	ALS #	METHOD	PREP METHOD 5030	5035	1311	Y/N	MS/MSD	PH	ANALYST	COMMENTS
Rinse	D5399	—	—	—				—			TTC	
50 ng BFB	D8361	—	—	BFB288AQ				Y				
VSTD10D02A	D5400	1	1	D826.25mL09				N				
VSTD40D02A *	D5401	1	2	D826.25mL10				Y				
20 *	D5402	1	3					Y				
10 B *	D5403	1	4					Y				
5 *	D5404	1	5					Y				
2 *	D5405	1	6					Y				
1 *	D5406	1	7					Y				
LCSA WG75857-1	D5407	1	8					Y				
VBLKA	D5408	1	9					N				
VBLKB WG75857-2	D5409	1	10					Y				Target hits
SD1507-13 A	D5410	1	11					Y		<2		
-14 A	D5411	1	12					N				
-1 A	D5412	1	13					N				Gas off
-3 A	D5413	1	14					N				
-5 A	D5414	1	15					N				
-9 A	D5415	1	16					N				
-11 A	D5416	1	17					N				
-15 A	D5417	1	18					N				
-17 A	D5418	1	19					N				
-19 A	D5419	1	20					N				
Rinse	D5420	1	21					—	—	—		
	D5421	1	22					—	—	—		

Curve Ok

TTC 4/5/10

STANDARD	CODE
BFB	V3098
CAL. STD.	V3141
LCS/MS MIX	V3142
EXTRAS MIX	V3108

STANDARD	CODE
IS MIX	V3137
SS MIX	V3138

Circle Methods:

SW846 8260	OLM 04.2
EPA 624	OLM 03.1
EPA 524	OLC 02.1
SIM	OLC 03.2

QAMS423

00000072

TITLE: **ANALYSIS OF VOAs BY PURGE AND TRAP GC/MS: SW-846 METHOD 8260**

FIGURE 2

EXAMPLE OF GC/MS STANDARDS RECEIPT LOGBOOK PAGE

KATAHDIN ANALYTICAL SERVICES

STOCK STANDARDS RECEIVED

GCMS LABORATORY
REVIEWED BY/DATE:

AMP1518 1-Chlorohexane (EPA-1208) Rec'd 11/07/07
1519 Lot; CB-R341A Ultra
1520 Exp; 11/30/09
1521 1000µg/ml

AMP1522 Cat# 30434 MA VPH Standard 500-1500 ug/ml in Purge and Trap Methanol Lot# A040187 Exp: 11/12 Store: Freezer Restek Corporation - 110 Benner Circle - Bellefonte, PA 16823 Rec'd 11/7/07 EKL
1523
1524
1525

AMP1526 Catalog# 30465 RL Lot # A049252 Exp: 12/11 Store:Freezer Restek Corporation 110 Benner Circle - Bellefonte, PA 16823 FOR LABORATORY USE ONLY rec'd DMF 11/20/07
1527

AMP1528 AccuStandard 125 Market St. · New Haven, CT 06513 · USA Tel: 203-786-5290 · www.accustandard.com FOR LABORATORY USE ONLY rec'd DMF 11/21/07
1529
AS-E0285 Diethyl ether 5000 µg/mL in MeOH Lot: B4070099-1A Exp. Jan 19, 2010 1 mL STORAGE Ambient POISON

AMP1530 AccuStandard 125 Market St. · New Haven, CT 06513 · USA Tel: 203-786-5290 · www.accustandard.com FOR LABORATORY USE ONLY
1531
CLP-LC-IS-100X Laboratory Control Sample - Internal Standard Mix 2500 µg/mL in MeOH Lot: B2090027 Exp: Sep 6, 2012 1 mL 3 comps. STORAGE Ambient POISON

AMP1532 Catalog# 30624 RL Lot # A050631 Exp: 3/10 Store:Freezer Restek Corporation 110 Benner Circle - Bellefonte, PA 16823 FOR LABORATORY USE ONLY rec'd DMF 11/26/07
1533

TITLE: **ANALYSIS OF VOAs BY PURGE AND TRAP GC/MS: SW-846 METHOD 8260**

FIGURE 3

EXAMPLE OF VOA STANDARDS PREPARATION LOGBOOK PAGE

KATAHDIN ANALYTICAL SERVICES
GC/MS VOA STANDARD PREP LOG BOOK

	STOCK NAME	STOCK	STOCK CONC ug/mL	VOLUME ADD uL
CODE: V2809				
STANDARD: 8260 LCS	502.2 Cal Mix #1	AMP 2187	2000	150
FINAL CONC (ug/mL): 200	MTBE	AMP 2121	↓	↓
FINAL VOLUME (mL): 1.5	502.2 Cal Mega Mix	AMP 2143		
PREP DATE: 8/4/09 HCG 8/4/09	S-4575-10X	AMP 2147		
EXPIRATION DATE: 8/18/09	M-8260-ADD-10X	AMP 2180	↓	↓
MEOH VOLUME (uL): 150	1-Chlorohexane	AMP 2109	1000	300
MEOH LOT #: E2580	cyclohexane	AMP 2183	↓	↓
INITIALS: HCG				
				8/4/09 (HCG)
CODE: V2810	STOCK NAME	STOCK	STOCK CONC ug/mL	VOLUME ADD uL
STANDARD: 8260 IS "T"	Custom 8260 IS Mix	AMP 2071	5000	50
FINAL CONC (ug/mL): 50				
FINAL VOLUME (mL): 5				
PREP DATE: 8/5/09				
EXPIRATION DATE: 8/19/09				
MEOH VOLUME (uL): 4950				
MEOH LOT #: E2560				
INITIALS: HCG				
				(HCG) 8/5/09
CODE: V2811	STOCK NAME	STOCK	STOCK CONC ug/mL	VOLUME ADD uL
STANDARD: 8260 SS "T"	8260 Surrogate Mix	AMP 2223	2500	100
FINAL CONC (ug/mL): 50				
FINAL VOLUME (mL): 5				
PREP DATE: 8/5/09				
EXPIRATION DATE: 8/19/09				
MEOH VOLUME (uL): 4900				
MEOH LOT #: E2560				
INITIALS: HCG				
				(HCG) 8/5/09

Reviewed by/Date:

TITLE: **ANALYSIS OF VOAs BY PURGE AND TRAP GC/MS: SW-846 METHOD 8260**

FIGURE 4

STANDARD INFORMATION

VOA Standards

Standard	Concentration	Manufacturer	Catalog Number
1,2,3 Trimethylbenzene	2000 ug/mL	Restek	58733
1,2,3 Trichlorobenzene	2000 ug/mL	Accustandard	M-502-47-10X
1,2,4 Trimethylbenzene	2000 ug/mL	Accustandard	M-502-54-10X
1,3,5 Trichlorobenzene	neat	Supelco	44-2235
1,3.5 Trimethylbenzene	2000 ug/mL	Accustandard	M502-55-10X
2-CEVE	2000 ug/mL	Accustandard	M-601C-10X
502.2 Cal Mix #1 (gases)	2000 ug/mL	Restek	30042
502.2 Cal2000 Mega Mix	2000 ug/mL	Restek	30431
504.1 Cal Mix	200 ug/mL	Accustandard	M-504.1-CSS
Acrolein & Acrylonitrile	5000 ug/mL	Accustandard	M-603-M-5X
Appendix IX Volatiles Mix	various	Accustandard	M-8240C-R3-10X
Bromochloromethane	2000 ug/mL	Accustandard	M-502-03-10X
California Oxygenates Mix #1	2000 - 10,000 ug/mL	Restek	30465
Carbon Disulfide	2000 ug/mL	Restek	30258
Chloroprene	2000 ug/mL	Accustandard	APPX9-048-R1
Custom GC Std	2000 ug/mL	Accustandard	S-11160
Custom VOC mix	various	Accustandard	S-7920-R1
Custom Volatile GC/MS Std	2000 ug/mL	Accustandard	S-3432B
Custom Volatiles GC/MS	2000 ug/mL	Accustandard	S-3432A
Diethyl Ether	5000 ug/mL	Accustandard	AS E0285
Freon 113	2000 ug/mL	Supelco	4-7944
Method 8260 Additions	2000 ug/mL	Accustandard	M-8260-ADD-10X
Method 8260B-Revision	2000 ug/mL	Accustandard	M-8240B-R-10X
MTBE	2000 ug/mL	Supelco	4-8483
Napthalene	2000 ug/mL	Accustandard	M-502-40-10X
THF	2000 ug/mL	Accustandard	S-4575-10X
Vinyl Acetate	2000 ug/mL	Restek	30216
Vinyl Acetate	2000 ug/mL	Accustandard	APPX9-211-20X
VOA Calibration Mix #1 (Ketones)	5000 ug/mL	Restek	30006
TCL Ketone Mix	5000 ug/mL	Accustandard	CLP-022-25X
VOC Liquid Mix	2000 ug/mL	Accustandard	M-502A-R2-10X
Volatile Organic Compounds (gases)	2000 ug/mL	Accustandard	M-502B-10X
IS/SS/Tune			
Custom 8260 IS	5000 ug/mL	Restek	54577
Custom 8260 SS	5000 ug/mL	Restek	54578
4-BFB	2000 ug/mL	Supelco	48083
VOA Tuning Compound (BFB)	5000 ug/mL	Restek	30003
1,2 Dichlorobenzene-D4	2000 ug/mL	Supelco	48952-U
Fluorobenzene	2000 ug/mL	Supelco	
VOA IS (CLP)	2500 ug/mL	Restek	30004
VOA SS (CLP)	2000 ug/mL	Supelco	48943
624 IS	1500 ug/mL	Restek	30023
4-BFB/Fluorobenzene/Pentafl. (EPA 624)	20000 ug/mL	Accustandard	M-624-SS-M
8260A SS	2500 ug/mL	Restek	30240
CLP Only			
04.1 CLP VOA Cal 2000	2000 ug/mL	Restek	30456
LCS-IS	2500 ug/mL	Accustandard	CLP-LCS-IS-100X
LCS-Volatiles	200 ug/mL	Accustandard	CLP-LCS-V
CLP Volatiles DMC Stock Solution	deutrated compds	Cambridge Isotope	ES 5038
3.2 OLC mix	1000 - 2000 ug/mL	Restek	30492

TITLE: **ANALYSIS OF SEMIVOLATILE ORGANIC COMPOUNDS BY: SW 846 METHOD 8270 – Modified for Selected Ion Monitoring (SIM)**

Prepared By: GC/MS Department Date: 6/98

Approved By:

Group Supervisor: J Halay Date: 020101

Operations Manager: John C. Benton Date: 1/31/01

QA Officer: Deborah J. Nadeau Date: 1.31.01

General Manager: Dennis P. Lufan Date: 2/01/01

Revision History:

SOP Revision	Changes	Approval Initials	Approval Date	Effective Date
01 8270C Mod.	Format changes, added pollution prevention, added instrument and other calibration options. Other minor changes to sections 7,8 & QA Table.	DN	1.31.01	1.31.01
02 8270C	Many changes in formatting. Some additions to sections & Table 1 to comply with Navy.	DN	09.30.04	09.30.04
03 8270C	Sect. 7.2: Removed "K" Instrument & added "R" instrument. Added Pentafluorophenol surr. to Tables 3, 5 and Sect. 8.2. Removed all References to TIC's.	LAD	04/06	04/06
04 8270C	Sect. 8.2 - changed 5 to 4 and removed pentachlorophenol. Table 3 and 5 - removed pentachlorophenol. Changed linear regression correlation coefficient criteria. Added M1 SOP reference. Added LCS exceedance criteria. Added ICV requirement and criteria. Added RT window procedure.	LAD	06/07	06/07
05 8270C	Added "G" instrument, Removed "X" instrument Edited section 7.5.1 - initial cal. table	LAD	02/08	02/08

TITLE: **ANALYSIS OF SEMIVOLATILE ORGANIC COMPOUNDS BY: SW 846 METHOD 8270 – Modified for Selected Ion Monitoring (SIM)**

SOP Revision	Changes	Approval Initials	Approval Date	Effective Date
06	Section 5.3.2.3- Added calibration Mix B. Section 7.5.1- Edited to address diffent SIM compounds may need to be calibrated at different levels depending on the compound and project requirements.	LAD	04/09	04/09
07	Changes made for compliance with DoD QSM version 4.1	LAD	08/09	08/09
08	Updated Standard prep. Added compounds to Table 3 and 5. Updated references. Added DoD QSM QC requirements Table.	LAD	04/10	04/10

TITLE: ANALYSIS OF SEMIVOLATILE ORGANIC COMPOUNDS BY: SW 846 METHOD 8270 – Modified for Selected Ion Monitoring (SIM)

Please acknowledge receipt of this standard operating procedure by signing and dating both of the spaces provided. Return the bottom half of this sheet to the QA Department.

I acknowledge receipt of copy ___ of document SOP CA-213-08, titled "**ANALYSIS OF SEMIVOLATILE ORGANIC COMPOUNDS BY METHOD 8270 – Modified for Selected Ion Monitoring (SIM)**".

Recipient: _____ Date: _____

KATAHDIN ANALYTICAL SERVICES, INC.
STANDARD OPERATING PROCEDURE

I acknowledge receipt of copy ___ of document SOP CA-213-08, titled "**ANALYSIS OF SEMIVOLATILE ORGANIC COMPOUNDS BY METHOD 8270 – Modified for Selected Ion Monitoring (SIM)**".

Recipient: _____ Date: _____

TITLE: ANALYSIS OF SEMIVOLATILE ORGANIC COMPOUNDS BY: SW 846 METHOD 8270 – Modified for Selected Ion Monitoring (SIM)

1.0 SCOPE AND APPLICATION

The purpose of this SOP is to describe the procedures utilized by Katahdin Analytical Services, Inc. laboratory personnel to prepare and analyze water and soil sample extracts for semivolatile organics by EPA SW-846 Method 8270, current revision, modified for selected ion monitoring.

In order to maintain consistency in data quality, this SOP consolidates all aspects of the analyses in one working document, to be revised as necessary.

1.1 Definitions

ANALYTICAL BATCH: 20 or fewer samples which are analyzed together with the same method sequence and the same lots of reagents and with the manipulations common to each sample within the same time period or in continuous sequential time periods.

METHOD BLANK (laboratory reagent blank): An artificial sample designed to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus. For aqueous samples, reagent water is used as a blank matrix; for soil samples, baked organic-free sand is used as a blank matrix. The blank is taken through the appropriate steps of the process.

CALIBRATION CHECK: Verification of the ratio of instrument response to analyte amount, a calibration check is done by analyzing for analyte standards in an appropriate solvent. Calibration check solutions are made from a stock solution that is different from the stock used to prepare standards.

CALIBRATION STANDARD (WORKING STANDARD): A solution prepared from the stock standard solution that is used to calibrate the instrument response with respect to analyte concentration.

LABORATORY CONTROL SAMPLE (LCS): A blank that has been spiked with the analyte(s) from an independent source and is analyzed exactly like a sample. Its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements. The matrix used should be phase matched with the samples and well characterized.

MATRIX SPIKE/MATRIX SPIKE DUPLICATE (MS/MSD): Predetermined quantities of stock solutions of certain analytes are added to a sample matrix prior to sample extraction and analysis. Samples are split into duplicates, spiked and analyzed. Percent recoveries are calculated for each of the analytes detected. The relative percent difference between the samples is calculated and used to assess analytical precision.

STANDARD CURVE (CALIBRATION CURVE): A curve that plots concentration of known analyte standard versus the instrument response to the analyte.

STOCK STANDARD SOLUTION: A concentrated solution containing a single certified standard that is a method analyte, or a concentrated solution of a single analyte prepared in the laboratory with an assay reference compound. Stock standard solutions are used to prepare calibration standards.

SURROGATES: Organic compounds which are similar to analytes of interest in chemical composition, extraction and chromatography, but which are not normally found in environmental samples. These compounds are spiked into all blanks, standards, samples and spiked samples prior to analysis. Percent recoveries are calculated for each surrogate.

TARGET: A software system that combines full processing, reporting and comprehensive review capabilities, regardless of chromatographic vendor and data type.

TARGET DB: An oracle database used to store and organize all Target data files.

QUICKFORMS: A laboratory reporting software for Target and Target DB. The QuickForms report module for Target is preconfigured with generalized forms and US EPA CLP report forms and disk deliverables, which can be customized.

1.2 Responsibilities

This method is restricted to use by, or under the supervision of analysts experienced in the analysis of semivolatile organic compounds by EPA Method 8270. Each analyst must demonstrate and document their ability to generate acceptable results with this method. Refer to Katahdin SOP QA-805, "Personnel Training & Documentation of Capability," current revision.

It is the responsibility of all Katahdin technical personnel involved in analysis of semivolatiles by Method 8270 to read and understand this SOP, to adhere to the procedures outlined, and to properly document their data in the appropriate lab notebook. Any deviations from the test or irregularities with the samples should also be recorded in the lab notebook and reported to the Department Manager or designated qualified data reviewer responsible for this data.

It is the responsibility of the Department Manager to oversee that members of their group follow this SOP, to ensure that their work is properly documented and to initiate periodic review of the associated logbooks.

1.3 Safety

Users of this procedure must be cognizant of inherent laboratory hazards, proper disposal procedures for contaminated materials and appropriate segregation of hazardous wastes. The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical should be treated as a potential health hazard. A reference file of material safety data sheets is available to all personnel involved in the chemical analysis. Everyone involved with the procedure must be familiar with the MSDSs for all the materials used in this procedure.

Each qualified analyst or technician must be familiar with the Katahdin Analytical Health and Safety Manual including the Katahdin Hazardous Waste Management Plan and follow appropriate procedures. These include the use of appropriate personal protective equipment (PPE) such as safety glasses, gloves, and lab coats when working with chemicals or near an instrument and not taking food or drink into the laboratory. Each analyst should know the location of all safety equipment. Each analyst shall receive a safety orientation from their Department Manager, or designee, appropriate for the job functions they will perform.

1.4 Pollution Prevention/Waste Disposal

Whenever possible, laboratory personnel should use pollution prevention techniques to address their waste generation. Refer to the current revision of the Katahdin Hazardous Waste Management Program for further details on pollution prevention techniques.

After analysis, autosampler vials containing sample extracts in methylene chloride are returned to the SVOA hood, and the contents transferred to a labeled waste container. The contents of this container are disposed of in accordance with the Katahdin Hazardous Waste Management Plan and Safety Manual and SOP SD-903, "Sample Disposal," current revision. Expired standards are lab packed, placed in the Katahdin hazardous waste storage area, and disposed of in accordance with this SOP.

2.0 SUMMARY OF METHOD

The process involves the extraction of semivolatiles from a sample using an appropriate solvent followed by clean up steps (where applicable) and concentration of the extract (refer to Katahdin SOP CA-502, "Preparation of Aqueous Samples for Extractable Semivolatile Analyses", SOP CA-512, "Preparation of Sediment/Soil Samples by Sonication Using Method 3550 for Subsequent Extractable Semi-Volatiles Analysis" and SOP CA-526, "Preparation of Sediment/Soil Samples by Soxhlet Extraction Using Method 3540 for Subsequent Extractable Semivolatile Analysis"). An aliquot of the final extract is injected into the gas chromatograph

for compound separation by capillary column, followed by the electron impact mass spectrometer for identification and quantitation.

3.0 INTERFERENCES

Interfering contamination may occur when a sample containing low concentrations of SVOCs is analyzed immediately after a sample containing high concentrations of SVOCs. Any samples that have suspected carryover must be reanalyzed.

4.0 APPARATUS AND MATERIALS

4.1 GC: Hewlett Packard 5890 and/or 6890

4.2 Mass Spectrometers (MS): HP5973, HP5972 and/or HP5970

4.3 Helium: Carrier gas for routine applications. All carrier gas lines must be onstructed from stainless steel or copper tubing; non-polytetrafluoroethylene (non-PTFE) thread sealant or flow controllers with rubber component are not to be used.

4.4 Autosamplers: HP 7673As

4.5 Hamilton syringes: 2.00 uL to 10 mL

4.6 Volumetric glassware: Grade A or equivalent

4.7 Columns: DB-5MS 30m, 0.25mm I.D., 25um film thickness, columns (J&W Scientific) or equivalent.

4.8 Acquisition System: The acquisition system must be interfaced to the MS and allow continuous acquisition of data throughout the duration of the chromatographic program. It must permit, at a minimum, the output of time vs. intensity (peak height or peak area). Hewlett Packard Chemstation or equivalent.

4.9 Data System: The Target software is used for processing data and generating forms.

5.0 REAGENTS

5.1 J.T. Baker Ultra Resi-Analyzed methylene chloride (or equivalent)

5.2 Purge and trap grade methanol

5.3 Standards: Stock standards and working standards are received and recorded in accordance with SOP CA-106 "Standard Preparation and Documentation".

5.3.1 The expiration date for all standards is one year from date of opening the ampule. If the manufacturer's expiration date is before this one year date, the manufacturer's expiration must be followed. New standards must be opened if degradation is observed.

5.3.2 Secondary dilution standards

5.3.2.1 The standards are prepared on an as needed basis (or every 6 months) and stored in screw-cap amber bottles with Teflon liners in the BNA standards freezer between uses. Standards prepared from various stock solutions must always use the first expiration date of any of the solutions used for preparation.

5.3.2.2 Calibration Mix A – Prepare standards in methylene chloride containing the compounds listed in Table 3. The final concentration of each compound is 20 ug/mL.

5.3.2.3 Calibration Mix B - Some compounds must be calibrated at higher concentrations. For these compounds a secondary standard is prepared which will "boost" the concentration of these compounds in the initial calibration. The concentration of this standard is determined on a project to project basis.

5.3.2.4 Internal Standard Solution – Prepare standard in methylene chloride containing 1,4-dichlorobenzene-d4, naphthalene-d8, acenaphthene-d10, phenanthrene-d10, chrysene-d12, and perylene-d12 at a final concentration of 80 ug/mL.

5.3.2.5 DFTPP Solution – Prepare standard in methylene chloride containing DFTPP at a final concentration of 25 ug/mL.

5.3.2.6 Independent Calibration Verification (ICV) Standard – From a source independent of the calibration standards, prepare a standard in methylene chloride containing the compounds listed in Table 3. The final concentration of each compound is 2 ug/mL.

6.0 SAMPLE COLLECTION, PRESERVATION AND HANDLING

All semivolatile sample extracts must be analyzed within forty days following the date of extraction.

7.0 PROCEDURES

7.1 NAMING AND CODING CONVENTIONS FOR ANALYTICAL STANDARDS – Used in accordance with SOP CA-106 "Standard Preparation and Documentation".

7.2 COMPUTER (DATA SYSTEM) CONVENTIONS -

Conventions for all instruments are as follows:

Sub-Directory for data acquisition and storage: C:\HPCHEM\1\DATA
Tune file: DFTPP.U

Method files: LSPSIMXX.M (all samples and standards)
Where:
XX = the calibration number in chronological order
L = instrument ID (R, U, or G)
DFTPP390.M (DFTPP tuning acquisition)

NOTE: All acquisition parameters must be identical for LSPSIMXX.M and DFTPP2. M.

Data Files: L_ _ _ _.D, where _ _ _ _ is a number in chronological order from 0001 to 9999 and L is the instrument ID (R, U, or G). This file also contains the Quantitation output file.

Data Files for DFTPP: LD_ _ _.D, where _ _ _ is a number in chronological order from 001 to 999 and L is the instrument ID (R, U, or G).

7.3 INSTRUMENT SPECIFIC PROCEDURES

It is the policy of the GC/MS group that all data be acquired in the batch mode. The following items must be checked prior to data acquisition in the batch mode:

- Ensure that the proper sequence and tune files are being used.
- Check the autosampler syringe (Is it clean? Does the plunger move freely? etc.), its alignment and make sure the solvent rinse vial is full. Ensure that the knurled nut holding the top of the syringe plunger is tight.
- Look at the batch to be analyzed and check the following:

  -Make sure that the data files are in numerical order with no duplication and that the method file is the same as that used for ICAL or Continuing Calibration analysis.

-Bottle numbers match with the numbers on the autosampler tray.

After the batch has been deemed free of errors, start the batch by using the "Position and run" command under the SEQUENCE menu in MSTop.

7.4 INSTRUMENT TUNING - Prior to the analysis of any calibration standards, blanks or samples, the GC/MS system must be shown to meet the mass spectral key ion and ion abundance criteria for decafluorotriphenylphosphine (DFTPP) tabulated below. Pentachlorophenol, benzidine and DDT are also present in this standard.

DFTPP Key Ions and Ion Abundance Criteria	
Mass	**Criteria**
51	30.0-80.0 percent of mass 198
68	less than 2.0 percent of mass 69
69	present
70	less than 2.0 percent of mass 69
127	40.0 – 60.0 percent of mass 198
197	less than 1.0 percent of mass 198
198	base peak, 100 percent of mass 198
199	5.0-9.0 percent of mass 198
275	10.0-30.0 percent of mass 198
365	greater than 1.00 percent of mass 198
441	present, but less than mass 443
442	greater than 40.0 percent of mass 198
443	17.0-23.0 percent of mass 442

All ion abundances must be normalized to m/z 198, the nominal base peak.

The following are the GC/MS operating conditions for injection of DFTPP.

GC/MS OPERATING CONDITIONS - DFTPP	
Initial column temperature hold	140°C for 3 minutes
Column temperature program	140-275°C at 15 degrees/minute
Final column temperature hold	275°C
Injection port temperature	280°C
Transfer line/source temperature	285°C
Injector - splitless, valve time	0.18 minutes
EPC	inlet B
Constant flow	ON
Constant flow pressure	10psi

Constant flow temperature	30°C
Vacuum comp.	ON
Run time	10-12 minutes
Scan start time	5.0 minutes
Sample volume	2.0 uL of 25 ng/uL DFTPP solution
Carrier gas	helium at @ 1.0 mL/minute
Mass range	35 to 500 amu
Number of A/D samples	4
GC Peak threshold	500 counts
Threshold	10 counts

Set up the run on the Enviroquant system using "Edit Sample Log Table". For a more detailed explanation of the Enviroquant software, consult the appropriate manual, Organic Department Manager, or senior chemist within the GC/MS group.

The DFTPP solution must be analyzed once at the beginning of each twelve hour period during which standards and/or samples are analyzed. The 12 hour time period for GC/MS system begins at the moment of injection of the DFTPP analysis. The time period ends after twelve hours has elapsed according to the system clock. The last injection must be accomplished prior to the expiration of 12 hours; conceivably, the run-time of an injection could end after the twelve hours.

When the DFTPP has concluded, the run must be evaluated to determine if sample analysis can proceed. The chromatography and the ion ratios must be examined. The DFTPP run is processed using the current algorithms in the Target software.

If the results indicate the system does not meet acceptance criteria, the GC/MS must be manually tuned. Once the manual tune procedure is completed, DFTPP must be re-injected and reevaluated. If the instrument still does not meet criteria, notify your Department Manager. Under no circumstances should calibration proceed if the instrument DFTPP is not in criteria.

7.5 INSTRUMENT CALIBRATION

7.5.1 Initial Calibration for Method 8270-SIM

Prior to the analysis of samples and required method blanks, and after the instrument DFTPP tuning criteria have been met, the GC/MS system must be calibrated at six different concentrations, typically, 0.20, 0.50, 1.0, 2.0, 5.0 and 8.0 ng/uL. This is done to determine instrument sensitivity and the linearity of GC/MS response for the semivolatile target and surrogate compounds.

Some SIM compounds may need to be calibrated at higher concentrations. A second standard is prepared containing these compounds. The two

standards are combined as in the example below. A 100 uL aliquot of each of the standards above is spiked with 1 uL of internal standards and analyzed.

Example –
For a calibration at the following levels:
Calibration mix A would be prepared containing ALL analytes at 20 ng/ul
Calibration Mix B would be prepared containing phenols and phthalates at 20 ng/ul.

Final PAH conc. (ng/uL)	Final Conc. Phenols and phthalates (ng/ul)	Cal-Mix A Added (uL)	Cal-Mix B Added (uL)	$MeCl_2$ Added (uL)	Final Volume (uL)
0.20	1.0	10	40	950	1000
0.50	2.0	25	75	900	1000
1.0	3.0	50	100	850	1000
2.0	4.0	100	100	800	1000
5.0	5.0	250	0	750	1000
8.0	8.0	400	0	600	1000

Note: Calibration Mix B only is used to boost the phenols and phthalates concentrations in Cal. levels 1 through 4.

The GC/MS operating conditions for the calibration standards injections are the same as for the DFTPP with the following exceptions:

GC/MS OPERATING CONDITIONS – CALIBRATION and SAMPLES	
Column temperature program	40°C for 3 min. to 300°C at 10°/min.
Final column temperature hold	300°C
Run time	35 minutes (time may vary dependent upon column length)
Scan start time	2.0-6.0 minutes (time may vary dependent upon column length)
Sample volume	1 uL

The conditions are set up in the method file LSPSIMXX.M

After analysis of the five calibration points, they must be quantitated and evaluated for adherence to QC criteria. Minimum requirements of ID files are the use of specific quantitation ions and quantitating a specific set of targets and surrogates with a set internal standard. Of particular importance when performing SIM analysis are the ion ratios. These requirements are found in Tables 3 and 5.

7.5.2 Initial Calibration Criteria

Relative response factors (RRFs) must be calculated and evaluated for each target compound and surrogate. The RRF is defined as follows:

$$RRF = \frac{Ax}{A_{IS}} \times \frac{C_{IS}}{Cx}$$

where:
- Ax = area of the primary ion for the target compound
- A_{IS} = area of the primary ion for the corresponding istd
- C_{IS} = concentration of the istd (ng/uL)
- C_x = concentration of the target compound

After the calibration points have been quantitated, update the calibration curve points using the Target data processing software to generate the RRF's and %RSD's for all analytes. If information is needed concerning the use of these programs, consult the Organic Department Manager or a senior chemist within the group.

Response factor criteria have been established for the calibration of the semivolatile target and surrogate compounds. These criteria must be met in order for the calibration curve to be considered valid. The percent RSD for each calibration check compound (CCC) must be less than or equal to 30 percent. There are three CCC's: Acenaphthene, Fluoranthene, and Benzo(a)pyrene. There are no criteria for the SPCC compounds. This is also applicable to clients that request DOD criteria.

7.5.2.1 Linearity of Target Analytes (This is also applicable to clients that request DOD criteria.)

If the RSD of any target analyte is 15% or less, then the response factor is presumed to be constant over the calibration range, and the average response factor may be used for quantitation.

If the RSD of any target analyte exceeds 15%, then a calibration option outlined in section 7.0 of method 8000 will need to be employed.
Option 1 (Section 7.5.2 of method 8000 - Rev. 2, 12/96), is a linear regression of instrument response versus the standard concentration.

The correlation coefficient (r) for each target analyte and surrogate must be greater than or equal to 0.995. Target software calculates the

correlation coefficient squared (r^2). This must be equal to or greater than 0.990.

Option 2 (Section 7.5.3 of method 8000 - Rev. 2, 12/96), is a non-linear calibration model not to exceed a third order polynomial. The lab would use a quadratic model or second order polynomial. The use of a quadratic model requires six calibration points. In order for the quadratic model to be acceptable, the coefficient of determination must be greater than or equal to 0.990.
If time remains in the clock after meeting the initial calibration acceptance criteria, samples may be analyzed. The calibration must be verified each twelve hour time period (time period starts from the moment of the DFTPP injection) for Method 8270-SIM. The SSTD1.0 in the curve may be used as the continuing calibration standard as long as it meets the continuing calibration acceptance criteria. All sample results must be quantitated using the initial calibration response factors.

7.5.2.2 Immediately following calibration an Independent Calibration Verification Standard must be analyzed. For clients requiring DOD criteria, all project analytes must be within +/- 20% of true value.

7.5.3 Continuing Calibration

A check of the calibration curve must be performed once every twelve hours immediately following analysis of the tuning compound DFTPP. This check contains all target compounds and surrogates at a concentration of 1.0 ng/uL.

After quantitation of the 1.0 ng/uL continuing calibration check, response factors must be calculated and compared to the average response factors in the initial calibration. The Target program calculates the calibration check response factors and compares them to the average RFs in the calibration curve by calculating percent differences. The method 8270 CCC's must have a % difference of +/- 20%D in order to be considered in criteria. These conditions must be met before method blank and/or sample analysis can begin. For clients requiring DOD criteria, all project analytes and surrogates must be within +/- 20%.

If the continuing calibration check does not meet criteria, corrective action must be taken. Depending on the situation, corrective action may be as follows:

- Re-analyze the 1.0 ng/uL continuing calibration check.

- Change the septum; clean the injection port; install a clean, silanized quartz liner; cut off a small portion (1" to 3") of the front end of the capillary column. This is usually performed when chromatography is poor. Record any of these actions in the appropriate instrument maintenance logbook.

- Analyze a new initial calibration curve.

The last option, the generation of a new initial calibration curve, is usually chosen when percent difference are >30%. In these instances, there is little or no chance of a continuing calibration reanalysis meeting criteria. If there is any doubt concerning which corrective action to undertake, consult the Organic Department Manager or a senior chemist within the group.

If the continuing calibration does meet the criteria specified above then analysis may proceed using initial calibration response factors.

7.5.4. Retention Time Windows

Retention time windows are set at the midpoint standard of the calibration curve, following every ICAL. When a CV is analyzed (and not an ICAL), the retention time windows of the daily CV must be within 30 seconds of the midpoint calibration standard of the most recent ICAL. The samples analyzed following the daily CV must have retention times within 30 seconds of those for the daily CV. Each successive daily CV must be compared to the most recent ICAL midpoint standard.

7.6 SAMPLE ANALYSIS

Sample extracts may be analyzed only after the GC/MS system has met tuning criteria, initial calibration and continuing calibration requirements. Ensure that the same instrument conditions are being used for tuning, calibration and sample analysis by reviewing the GC parameters using the "Edit entire method" option under the Method menu in MSTOP. Note that you can not edit a method if the instrument is running.

Extracts are stored in the refrigerator in the organics extraction laboratory at 4°C ±2°C. Remove them from the refrigerator and place them in the GC/MS laboratory semivolatile hood when ready for analysis.

Prepare a 1.8 mL clear glass vial (crimp top) with a disposable insert (350 uL). Add 100 uL of sample extract and 1.0 uL of the 80 ng/uL IS stock to the vial and then cap. This gives a 0.8 ng/uL final concentration for the internal standard compounds. The samples are topped with Teflon lined crimp top caps.

7.7 FINAL DATA PACKAGE

7.7.1 Initial Data Review (IDR)

The initial data review is accomplished by the analyst who ran the samples and is a review of sufficient quality and detail to provide a list of samples that need to be reanalyzed or diluted and reanalyzed. The initial data review is performed on the detailed quantitation reports of the analyzed sample. This data review examines criteria that directly impact whether or not the sample needs to be reanalyzed:

- Surrogate Recoveries
- Internal Standard Area Stability
- Method Blank Acceptance
- Chromatography
- Target Compound Detection/Quantitation/Review for false positives
- Laboratory Control Sample Recoveries
- Matrix Spike/Matrix Spike Duplicate Recoveries

The analyst must evaluate all data using the QA Acceptance Criteria table found within this SOP (Table 1). This table gives acceptance criteria and corrective actions for criteria that are not met. In addition to evaluating QC elements, the chromatography and quantitation of target analytes must be reviewed. During this review, the analyst checks the integration of each individual peak. The hardcopy has false positives crossed out so they can be reviewed for appropriateness by the Organic Department Manager.

7.7.2 Chromatography

The chromatography should be examined for the presence or absence of any ghost peaks and can also be used as an indication of whether or not matrix interferences might be affecting surrogate recoveries and/or istd area recoveries. Whether or not the chromatography is acceptable is a judgment call on the part of the analyst and should be used in conjunction with other monitored QC (e.g. surrogate recoveries) to determine the necessity of reanalyzing.

Manual integrations are to be performed when chromatographic conditions preclude the computer algorithm from correctly integrating the peak of

concern. In no instance shall a manual integration be performed solely to bring a peak within criteria.

Each peak of concern is examined by the primary analyst to ensure that the peak was integrated properly by the computer algorithm. Should a manual integration be necessary (for instance, due to a split peak, peak tailing, or incomplete resolution of isomeric pairs), an "m" qualifier will automatically be printed on the quantitation report summary.

This manual integration package must then be submitted to the Department Manager or his/her designee, who will review each manual integration.

For specific manual integration procedures, refer to Katahdin SOP QA-812, "Manual Integration", current revision.

7.7.3 Target Compound Detection/Quantitation

The semivolatile ID files have been set up to err on the side of false positives; that is to identify and quantitate peaks as target compounds that may not necessarily be valid hits. It is the responsibility of the GC/MS analyst to use his/her technical judgment to determine if the identification of a target compound is correct or not.

If any target concentration exceeds the upper limit, a dilution must be made and analyzed. The dilution chosen should keep the concentration of the largest target compound hit in the upper half of the initial calibration range. LCS and MS/MSD samples need not be diluted to get spiked analytes within the calibration range.

The requirements for qualitative verification by comparison of mass spectra are as follows:

- All ions present in the standard mass spectra at a relative intensity > 10% must be present in the sample spectrum.
- The relative intensities of primary and secondary ions must agree within ±20% between the standard and sample spectra.
- Ions greater than 10% in the sample spectrum but not present in the standard spectrum must be considered and accounted for by the analyst.

If a compound cannot be verified by all three criteria above, but, in the technical judgment of the mass spectral interpretation specialist, the

identification is correct, then the laboratory shall report that compound on the Form 1 as a valid hit.

The GC/MS laboratory initial data review must be completed within twelve hours of batch completion; in the majority of instances, the initial review should be accomplished at the beginning of a work shift for the previous set of analyses.

7.7.4 Reporting

After the chromatograms have been reviewed and any target analytes have been quantitated using Target, the necessary files are brought into QuickForms. Depending on the QC label requested by the client, a Report of Analysis (ROA) and additional reports, such as LCS forms and chronology forms, are generated. The package is assembled to include the necessary forms and raw data. The data package is reviewed by the primary analyst and then forwarded to the secondary reviewer. The secondary reviewer validates the data and checks the package for any errors. When completed, the package is sent to the department manager for final review. A complete review checklist is provided with each package. The final data package from the Organics department is then processed by the Data Management department.

7.8 INJECTION PORT LINER CLEANING AND SILANIZING PROCEDURE

- Remove the rubber o-ring from the liner and place the liner in a large Erlenmeyer flask.
- In the hood, pour nitric acid into the flask until the liner is covered. Place the flask on a hotplate and boil for 2-3 hours.
- Let cool; drain nitric acid and thoroughly flush the liner with water.
- Bake briefly in the muffle oven until liner is dry and cool to room temperature.
- Place the liner in a beaker, fill with Sylon and let it soak for at least two hours.
- Take out the liner and rinse it thoroughly with toluene.
- Rinse the liner thoroughly with purge and trap grade methanol.
- Bake the liner in the muffle oven for a minimum of three hours.

7.9 Instrument Maintenance

Instrument preventative maintenance is performed on a semi-annual basis by GC/MS chemists. This maintenance includes a thorough inspection and cleaning of all parts, including changing rough and turbopump oils. GC/MS analysts perform other maintenance on an as-needed basis. Typically, routine maintenance involves clipping off the front end of the DB-5MS column, replacing the injection port septum, and installing a freshly silanized quartz liner after sample analysis.

All maintenance must be documented in the instrument-specific maintenance log, whether it is routine or not. The Department Manager must authorize any maintenance over and above a routine source cleaning.

8.0 QUALITY CONTROL AND ACCEPTANCE CRITERIA

Refer to Table 1 and to details in this section for a summary of QC requirements, acceptance criteria, and corrective actions. These criteria are intended to be guidelines for analysts. The criteria does not cover all possible situations. If any of the QC requirements are outside the recovery ranges listed in this section or in Table 1, all associated samples must be evaluated against all the QC. In some cases data may be reported, but may be reanalyzed in other cases. Making new reagents and standards may be necessary if the standardization is suspect. The corrective actions listed in this section and in Table 1 may rely on analyst experience to make sound scientific judgements. These decisions are based on holding time considerations, client and project specific Data Quality Objectives and on review of chromatograms. The supervisor, Operations Manager, and/or Quality Assurance Officer may be consulted to evaluate data. Some samples may not be able to be reanalyzed within hold time. In these cases "qualified" data with narration may be advisable after consultation with the client.

In some cases the standard QC requirements listed in this section and in Table 1 may not be sufficient to meet the Data Quality Objectives of the specific project. Much of the work performed at the lab is analyzed in accordance with specific QC requirements spelled out in a project specific Quality Assurance Project Plan (QAPP) or in a program specific Quality Systems Manual (QSM). The reporting limits, acceptance criteria and/or corrective actions may be different than those specified in this SOP. In these cases the appropriate information will be communicated to the Department Manager and/or senior chemists before initiation of the analyses so that specific product codes can be produced for the project. In addition, the work order notes for each project will describe the specific QAPP or QSM to be followed.

8.1 Method Blank Criteria

A method blank is defined as a volume of a clean reference material (deionized distilled water for water samples, baked organic-free sand for soil/sediment matrices)

that is carried through the entire analytical procedure. One method blank must be extracted with each group of samples of a similar matrix and must be analyzed on the GC/MS system that was used to analyze the samples.
An acceptable method blank must contain less than or equal to the PQL of any target compound. For clients requiring DOD criteria, no analytes detected at > ½ PQL and > 1/10 the amount measrued in any sample or 1/10 the regulatory limit.

If the method blank exceeds these contamination levels, the analytical system is considered out of control and corrective action must be taken before sample analysis.

Reanalysis of the blank is the first step of the corrective action; if that does not solve the problem, a Katahdin Corrective Action Report (CAR) will be initiated. Corrective action will be specified after consultation including the Department Manager, Operations Manager, and QA Officer.

8.2 Surrogate Recoveries

The four surrogates (2-Methylnaphthalene-d10, 2,4-Dibromophenol, Fluorene-d10 and Pyrene-d10) must meet the current statistically derived acceptance limits. If statistical limits have not been established then the surrogate recovery must meet the nominal limits of 30-150%. For clients requiring DOD criteria, use acceptance limits specified by DOD or use in-house limits where none are specified.

If specifications are not met, the sample (or blank) should be reanalyzed. If specifications are met in the reanalysis, this reanalysis should only be submitted. If surrogate specifications are not met in the sample or method blank reanalysis, a Corrective Action Report (CAR) should be initiated. Corrective action will be specified after consultation including the Department Manager and Operations Manager.

For further information regarding the acceptance of surrogate recoveries, consult the Organic Department Manager.

8.3 Internal Standard Responses

Internal standard responses and retention times (RT) in all samples and blanks must be evaluated as part of the technical data review. The method files have been set up to only detect compounds that fall within a set RT window. For Method 8270-SIM analysis, if the extracted ion current profile (EICP) area for any internal standard changes by more than a factor of two (-50% to +100%) as compared to the daily continuing calibration standard, reanalysis must occur. If the reanalysis meets criteria, only the in-criteria run should be reported. If the reanalysis is still out of criteria, both analyses should be included in the sample package set.
MS/MSD samples that do not meet the EICP area criteria above do not have to be reanalyzed.

8.4 Laboratory Control Sample (LCS)

An LCS must be performed for each group of samples of a similar matrix, for the following, whichever is more frequent:

- Every 20 samples of a similar matrix or similar concentration, or
- Every batch of samples extracted.

Statistical limits are compiled annually for LCS recoveries (archived in QA office). Statistical limits are only calculated when at least 20 usable data points are obtained for any given compound. If insufficient data points are available, nominal limits are set by the section supervisor, Laboratory Operations Manager and Quality Assurance Officer. Refer to Katahdin SOP QA-808, "Generation and Implementation of Statistical QC Limits and/or Control Charts", current revision.

The use of statistical limits versus nominal limits is dependent on the client and project. This information is communicated to the Organic Department Manager through the Katahdin project manager. It is standard practice to use statistical limits for reporting purposes and to evaluate any QC criteria exceedances. However, nominal limits of 30-150% may be used for some projects or states (i.e. South Carolina). For clients requiring DOD criteria, use acceptance limits specified by DOD or use in-house limits where none are specified.

The LCS recoveries for all analytes are evaluated. All of the compounds of interest must fall within the established statistical limits with the following sporadic exceedance allowances.

Number of Analytes	Number of Allowable Exceedances
> 90	5
71 – 90	4
51 – 70	3
31 – 50	2
11 – 30	1
<11	0

If less than the number of allowable exceedances fail the statistical limits, no corrective action is needed. If greater than the number of allowable exceedances fail the statistical limits, corrective action may be taken. Corrective actions may vary with each situation. However, in the case where the failures are high and the samples are non-detect for those compounds, then no corrective action is required. Otherwise, corrective action may involve reanalysis or recalibration. The specific corrective actions taken will rely on analyst experience to make sound scientific judgments while

considering client objectives, other quality control indicators and/or the ability to reanalyze a sample within holding time

Please note that for compounds with only nominal limits (i.e. insufficient data points were available to generate statistical limits), no corrective action is required for out-of-criteria recoveries until enough data points are established to generate statistical limits.

8.5 Matrix Spike/Matrix Spike Duplicate (MS/MSD) Criteria

Matrix Spike and Matrix Spike Duplicates must be extracted and analyzed for each group of up to 20 samples of a similar matrix or similar concentration. In the event insufficient sample volume is available an LCS/LCS Duplicate is extracted and analyzed in place of the MS/MSD.

Statistical limits are compiled annually for MS/MSD recoveries for a short list of the spiked compounds (Acenaphthene, Pentachlorophenol and Pyrene). Nominal limits of 30-130% are used for all other compounds. Generally, corrective action is only taken for the short list of the spiked compounds. The specific corrective actions will rely on analyst experience to make sound scientific judgments while considering client objectives, other quality control indicators and/or the ability to reanalyze a sample within holding time. For clients requiring DOD criteria, use acceptance limits specified by DOD or use in-house limits where none are specified.

A Corrective Action Report (CAR) must be filled out and filed if any criteria for percent recovery or relative percent difference are not met to document any decisions with reporting data.

9.0 METHOD PERFORMANCE

The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. The MDLs are determined annually per type of instrument and filed with the Organic Department Manager and with the QAO. Refer to the current revision of Katahdin SOP QA-806, Method Detection Limit, Instrument Detection Limit and Reporting Limit Studies and Verifications, for procedures on determining the MDL.

Refer to the current revision of Method 8270 for other method performance parameters and requirements.

TITLE: ANALYSIS OF SEMIVOLATILE ORGANIC COMPOUNDS BY: SW 846 METHOD 8270 – Modified for Selected Ion Monitoring (SIM)

10.0 APPLICABLE DOCUMENTS/REFERENCES

"Test Methods for the Evaluation of Solid Waste: Physical/Chemical Methods", SW-846, third Edition, Final Updates I, II, IIA, III, IIIA and IIIB, November 2004, Method 8270C.

"USEPA Contract Laboratory Program Statement of Work for Organics Analysis," Rev. 02/88.

Code of Federal Regulations (40 CFR), Part 136, Appendix A, Rev. June, 1998.

Katahdin SOP CA-101, Equipment Maintenance and Troubleshooting, current revision.

Department of Defense Quality Systems Manual for Environmental Laboratories (DoD QSM), Version 4.1, 04/22/09

The National Environmental Laboratory Accreditation Conference (NELAC) Standards, June 2003

Katahdin SOP QA-806, Method Detection Limit, Instrument Detection Limit and Reporting Limit Studies and Verifications, current revision.

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TABLE 1

QC REQUIREMENTS

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action
Check of mass spectral ion intensities using DFTPP	Prior to initial calibration and calibration verification	Refer to the criteria listed in Section 7.4	Retune instrument, and verify
Six-point initial calibration for all analytes	Initial calibration prior to sample analysis	RSD ≤30 for RFs of the CCCs; Average %RSD < 15% for all compounds. Refer to section 7.5.2.1 for more details.	Repeat calibration if criterion is not met
Independent calibration verification	Once after Initial calibration	± 20 % D	1) Reanalyze standard 2) Reprep standard 3) Reprep standard from fresh stock.
Continuing calibration verification	Once per each 12 hours, prior to sample analysis	CCCs ≤ 20%D	Repeat initial calibration and reanalyze all samples analyzed since the last successful calibration verification
ISs	Immediately after or during data acquisition of calibration check standard	Retention time ± 30 seconds; EICP area within -50% to +100% of last calibration verification (12 hours) for each IS	Inspect mass spectrometer or GC for malfunctions; mandatory reanalysis of samples analyzed while system was malfunctioning
Demonstration of ability to generate acceptable accuracy and precision	Once per analyst initially and annually thereafter	All recoveries within method QC acceptance limits.	Recalculate results; locate and fix problem; reextract/reanalyze P&A study for those analytes that did not meet criteria
Method blank	One per prep batch	No analytes detected > PQL	(1) Investigate source of contamination (2) Evaluate the samples and associated QC: i.e.If the blank results are above the PQL, report samples that are <PQL or > 10X the blank result. Reprep a blank and the remaining samples.
LCS for all analytes	One LCS per prep batch	Statistically derived from lab data or nominal limits depending on the project. . See also section 8.4 of this SOP for more information on allowable exceedances.	(1) Evaluate the samples and associated QC: i.e.If an MS/MSD was performed and acceptable, narrate. If an LCS/LCSD was performed and only one was unacceptable, narrate. If the surrogate recoveries in the LCS are low but are acceptable in the blank and samples, narrate. If the LCS rec. is high but the sample results are <PQL, narrate. Otherwise, reprep a blank and the remaining samples.

TABLE 1

QC REQUIREMENTS

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action
Surrogate spike	Every sample, control, standard, and method blank	Statistically derived limits.	(1) Check chromatogram for interference; if found, flag data (2) If not found, check instrument performance; if problem is found, correct and reanalyze (3) If still out reextract and analyze sample (4) If reanalysis is out, flag data
MS/MSD	One MS/MSD per every 20 samples	Statistically derived from lab data or nominal limits depending on the project. Nominal limits are used as default limits.	(1) Evaluate the samples and associated QC: i.e. If the LCS results are acceptable, narrate. (2) If both the LCS and MS/MSD are unacceptable reprep the samples and QC.
MDL and/or LOD/LOQ Verification study	Refer to KAS SOP QA-806, "Method Detection Limit, Instrument Detection Limit and Reporting Limit Studies and Verifications", current revision.		

TABLE 2

DoD QSM QC REQUIREMENTS

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 significant change in instrument type, personnel, test method, or sample matrix.	QC acceptance criteria published by DoD, if available; otherwise, method-specific 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.
LOD determination and verification	Refer to current revision of SOP QA-806				
LOQ establishment and verification	Refer to current revision of SOP QA-806				
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 Method 8270 only)	Correct problem then repeat breakdown check.	Degradation ≤ 20% for DDT. Benzidine and pentachlorophenol should be present at their normal responses, and should not exceed a tailing factor of 2.	At the beginning of each 12-hour period, prior to analysis of samples.	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 ≥ 0.050. 2. RSD for RFs for CCCs ≤ 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).	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.

TABLE 2 (cont)

DoD QSM QC REQUIREMENTS

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
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 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 ≥ 0.050. 2. %Difference/Drift for all target compounds and surrogates ≤ 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 failed standards.	Sample results are not acceptable without a valid IS verification.

TABLE 2 (cont)

DoD QSM QC REQUIREMENTS

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Method blank	One per preparatory batch.	No analytes detected > ½ RL (> RL for common lab contaminants) 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 the problem. Report sample results that are <LOD or >10x the blank concentration. Reprepare and reanalyze the method blank and all associated samples with results > LOD and < 10x the contaminated blank result. Contact Client if samples cannot be reprepped within hold time.	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.	The laboratory shall use laboratory control limits (CLs) or use DoD-generated LCS-CLs, if available depending on project requirements. In-house CLs may not be greater than ± 3 times the standard deviation of the mean LCS recovery. A number of analytes may fall outside the CL but within marginal exceedance limit depending on the total number of analytes in the LCS.	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. Refer to Table G-1 for number of marginal exceedences allowed. Contact Client if samples cannot be reprepped within hold time.	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 if sufficient sample is available.	For matrix evaluation, use LCS acceptance criteria.	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 there is a matrix effect or analytical error.
Matrix spike duplicate (MSD) or sample duplicate	One per preparatory batch per matrix if sufficient sample is available.	MSD: For matrix evaluation, use LCS acceptance criteria. MS/MSD: RPD ≤ 30%.	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 2 (cont)

DoD QSM QC REQUIREMENTS

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Surrogate spike	All field and QC samples.	The laboratory shall use laboratory surrogate CLs or use DoD-generated surrogate CLs, if available depending on project requirements. .	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. Contact Client if samples cannot be reprepped within hold time.	Apply Q-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 J-flag to all results between DL and LOQ.	

TABLE 3

SUMMARY OF METHOD MODIFICATIONS

TOPIC	KATAHDIN SOP CA-213-08	METHOD 8270, current revision
Apparatus/Materials	none	
Reagents	none	
Sample preservation/ handling	none	
Procedures	none	
QC - Spikes	none	
QC - LCS	none	
QC - Accuracy/Precision	none	
QC - MDL	none	

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TABLE 4

ANALYTE QUANITIATION AND INTERNAL STANDARDS

Internal Standard: 1,4-dichlorobenzene-d4	2,4-Dinitrotoluene
Target and Surrogates:	2,4-Dinitrophenol
1,4-Dioxane	2,3,4,6-Tetrachlorophenol
Benzaldehyde	Diethylphthalate
Phenol	4-Chlorophenyl-phenyl ether
bis(2-Chloroethyl)ether	4,6-Dinitro-2-methylphenol
2-Chlorophenol	N-nitrosodiphenylamine
2-Methylphenol	2-Nitroaniline
3&4-Methylphenol	3-Nitroaniline
2,2'-Oxybis(1-chloropropane)	4-Nitroaniline
Nitrobenzene	Dibenzofuran
Hexachloroethane	4-Nitrophenol
Acetophenone	**Internal Standard: Phenanthrene-d10**
N-nitroso-di-n-propylamine	Target and Surrogates:
Internal Standard: Naphthalene-d8	Pentachlorophenol
Target and Surrogates:	1-Methylphenanthrene (dredge)
Naphthalene	Phenanthrene
1-Methylnaphthalene (dredge)	Hexachlorobenzene (special)
2-Methylnaphthalene	Anthracene
2-Methylnaphthalene-D10 (surrogate)	Fluoranthene
Isophorone	Carbazole
2-Nitrophenol	Di-n-butylphthalate
2,4-Dimethylphenol	4-Bromophenyl-phenyl ether
bis(2-Chloroethoxy)methane	Atrazine
2,4-Dichlorophenol	**Internal Standard: Chrysene-d12**
4-Chloroaniline	Target and Surrogates:
Hexachlorobutadiene	Butylbenzylphthalate
Caprolactam	3,3'-Dichlorobenzidine
4-Chloro-3-methylphenol	Pyrene
Internal Standard: Acenaphthene-d10	Benzo(a)Anthracene
Target and Surrogates:	Chrysene
1,1'-Biphenyl (dredge)	Bis-(2-ethylhexyl)phthalate
2,6 Dimethylnapthalene (dredge)	Pyrene-d10 (surrogate)
Acenaphthylene	**Internal Standard: Perylene-d12**
Acenaphthene	Target and Surrogates:
Fluorene	Perylene (dredge)
2-Fluorene-d10 (surrogate)	Benzo(b)fluoranthene
2,4-Dibromophenol (surrogate)	Benzo(k)fluoranthene
2-Chloronaphthalene	Benzo(e)pyrene (dredge)
Hexachlorocyclopentadiene	Di-n-octylphthalate
2,4,6-Trichlorophenol	Benzo(a)pyrene
2,4,5-Trichlorophenol	Indeno(1,2,3-cd)pyrene
Dimethylphthalate	Dibenz(a,h)anthracene
2,6-Dinitrotoluene	Benzo(ghi)perylene

TABLE 5

PROCEDURE CONDENSATION

Clock

12 hours from injection of 50ng DFTPP.

Calibration Curve Criteria

<30% RSD for CCCS
<15% RSD average for all analytes in calibration standard

Continuing Calibration Check Criteria

<20% D for CCC compounds

Additional QC

LCS every extraction batch
MS/MSD every 20 samples

TABLE 6

SVOA COMPOUNDS AND CHARACERISTIC IONS

COMPOUND	PRIMARY ION	SECONDARY IONS
1,4-Dioxane	88	58
Benzaldehyde	77	105,106
Phenol	94	65,66
bis(2-Chloroethyl)ether	93	63,95
2-Chlorophenol	128	64,130
1,4-Dichlorobenzene-d4 (IS)	152	150,115
2,2'-Oxybis(1-choropropane)	45	77,121
2-Methylphenol	108	107,77
Acetophenone	105	77,51
N-nitroso-di-n-propylamine	70	52,101
Hexachloroethane	117	201,199
3&4-Methylphenol	108	107,77
Nitrobenzene	77	123,51
Isophorone	82	54,138
2-Nitrophenol	139	109,81
2,4-Dimethylphenol	107	122,121
bis(2-Chloroethoxy)methane	93	63,123
2,4-Dichlorophenol	162	164,98
Naphthalene-d8 (IS)	136	137,134
Naphthalene	128	129,127
4-Chloroaniline	127	129
Hexachlorobutadiene	225	223,227
Caprolactam	113	55,56
4-Chloro-3-methylphenol	107	77,142
2,4-Dibromophenol (surr)	252	63,143
2-Methylnaphthalene-d10 (surr)	152	150
2-Methylnaphthalene	142	141,115
1-Methylnaphthalene	142	141,115
Hexachlorocyclopentadiene	237	235,239
2,4,6-Trichlorophenol	196	198,200
2,4,5-Trichlorophenol	196	198,200
2-Chloronaphthalene	162	127,164
1,1'-Biphenyl	154	153,76
2-Nitroaniline	65	92,138
Dimethylphthalate	163	194,164
2,6-Dinitrotoluene	165	63,89
Acenaphthylene	152	151,153
Acenaphthene	152	154,152
Acenaphthene-d10 (IS)	164	162
3-Nitroaniline	138	65,92
2,4-Dinitrophenol	184	107
Dibenzofuran	168	139

TABLE 6 (cont.)

SVOA COMPOUNDS AND CHARACERISTIC IONS

COMPOUND	PRIMARY ION	SECONDARY IONS
2,4-Dinitrotoluene	165	63
4-Nitrophenol	109	139,65
2,3,4,6-Ttrachlorophenol	232	230
Diethylphthalate	149	177,176
Fluorene-d10 (surr)	176	174,178
Fluorene	166	165
4-Chlorophenyl-phenyl ether	204	206,141
4-Nitroaniline	138	108,65
4,6-Dinitro-2-methylphenol	198	121
N-nitrosodiphenylamine	169	168,167
4-Bromophenyl-phenyl ether	248	250,141
Hexachlorobenzene	284	142,249
Atrazine	200	173,215
Pentachlorophenol	266	264,268
Phenanthrene-d10 (IS)	188	189
Phenanthrene	178	179,176
Anthracene	178	179,176
Carbazole	167	166,139
Di-n-butylphthalate	149	150,104
Fluoranthene	202	200,203
Pyrene	202	200,201
Pyrene-d10 (surr)	212	210,106
Butylbenzylphthalate	149	91,206
Benzo(a)anthracene	228	229,226
Chrysene-d12 (IS)	240	236,120
3,3-Dichlorobenzidine	252	254,126
Chrysene	228	226,229
bis(2-Ethylhexyl)phthalate	149	167
Di-n-octylphthalate	149	150
Benzo(b)fluoranthene	252	253,125
Benzo(k)fluoranthene	252	253,125
Benzo(a)pyrene	252	253,250
Perylene-d12 (IS)	264	260
Indeno(1,2,3-cd)pyrene	276	277
Dibenzo(a,h)anthracene	278	279
Benzo(g,h,i)perylene	276	277

Primary ions must not be changed except in unusual instances where interference occurs with a co-eluting non-target analyte. In this case, a secondary ion may be used for quantitation with the following rules:
(1) The corresponding standard(s) (initial calibration curve and continuing calibration standard) must be re-quantitated with the secondary ion.

TABLE 6 (cont.)

SVOA COMPOUNDS AND CHARACERISTIC IONS

(2) Approval must be obtained from the Organic Department Manager or the laboratory Operations Manager.

The quantitation ion must then be changed back to the one specified in the table above after quantitation of the samples(s).

Secondary ions are recommended only and may be changed depending upon instrument conditions (sensitivity, etc.). However, it is Katahdin policy that a minimum of 2 ions (primary and one secondary) be used for all GC/MS analyses.

TITLE: **ANALYSIS OF SEMIVOLATILE ORGANIC COMPOUNDS BY: SW 846 METHOD 8270 – Modified for Selected Ion Monitoring (SIM)**

FIGURE 1

EXAMPLE OF RUNLOG LOGBOOK PAGE

KATAHDIN ANALYTICAL SERVICES
GC/MS SVOA INJ LOG INSTRUMENT: 5970-X

DATE OF DFTPP INJECTION: 03/009

JOB	SAMPLE	DATAFILE	DF	ALS #	METHOD	UL INJ	CHEMIST	COMMENTS
	50ng DFTPP	X0600	1	1	DFTPP390	2.0	JK	OK
	SSTD060X0316	X9437		2	X625A022	1.0		✓
	150	38		3				✓
	100	39		4				✓
	30	40		5				✓
	05	41		6				✓
	3560 MIX 1	42		7				OK
	2	43		8				
	3	44		9				
	4	45		10				
	5	46		11				
	6	47		12				
	7	48		13				
	8	49		14				
	9	50		15				
	BLANK 1	51		16				
	2	52		17				

STANDARD	CODE
DFTPP	50856
CAL. STD.	5089-30 5089-49
IS MIX	AMP0934

REVIEWED AND APPROVED BY: _____
DATE: _____

QAMS302

00000034

TITLE: ANALYSIS OF SEMIVOLATILE ORGANIC COMPOUNDS BY: SW 846 METHOD 8270 – Modified for Selected Ion Monitoring (SIM)

FIGURE 2

EXAMPLE OF GC/MS STANDARDS RECEIPT LOGBOOK ENTRY

KATAHDIN ANALYTICAL SERVICES

STOCK STANDARDS RECEIVED

GCMS LABORATORY
REVIEWED BY/DATE:

AMP0946

AccuStandard® 125 Market St. • New Haven, CT 06513 • USA Tel. 203-786-5290 • www.accustandard.com

APP-9-176-D-20X
Pentachlorophenol
2.0 mg/mL in CH2Cl2
Lot: B3010100
Exp. Jan 10, 2013.

1 mL

FOR LABORATORY USE ONLY

WARNING: This product contains a chemical(s) known to the State of California to cause cancer.

STORAGE Ambient

POISON

[redacted]

8/16/06
JLG

AMP0947

AccuStandard® 125 Market St. • New Haven, CT 06513 • USA Tel. 203-786-5290 • www.accustandard.com

APP-9-090-50X
4,6-Dinitro-o-cresol
5.0 mg/mL in MeOH
Lot: B1100296
Exp. Aug 16, 2012

1 mL

FOR LABORATORY USE ONLY

STORAGE Ambient

FLAMMABLE

[redacted]

AMP0948

AccuStandard® 125 Market St. • New Haven, CT 06513 • USA Tel. 203-786-5290 • www.accustandard.com

APP-9-145-50X
p-Nitrophenol
5.0 mg/mL in MeOH
Lot: B5050205
Exp. May 18, 2015

1 mL

FOR LABORATORY USE ONLY

STORAGE Ambient

POISON

[redacted]

TITLE: ANALYSIS OF SEMIVOLATILE ORGANIC COMPOUNDS BY: SW 846 METHOD 8270 – Modified for Selected Ion Monitoring (SIM)

FIGURE 3

EXAMPLE OF SVOA STANDARDS PREPARATION LOGBOOK ENTRY

GC/MS SVOA STANDARD PREP LOGBOOK

50863	8270 Stock (w/o MeOH)	3-15-06	7-7-06	JLM	AMP0844	8270 Mixes/Comp	300	2-22-07	4.2ml	150 ng/ml
					AMP0857	↓	300	3-15-07		
					AMP0911	APP IX #2	600	3-2-07		
					AMP0910	↓ 1	100	3-9-07		
					AMP0570	↓ 1	200	7-7-06		
					AMP0659	Organophosphorus	300	8-19-06		
					AMP0878	Benzoic Acid	↓	3-9-07		
					AMP0867	Hexachlorophene		2-22-07		
					AMP0806	Benzidine		3-9-07		
					AMP0836	3,3'-Dichlorobenzidine	↓	3-14-07		
					AMP0532	8270 Surr	150	3-9-07		
					50861	DEA	300	3-13-07		
					B43590	MeCl2	550	—		
50864	8270 level 1	3-15-06	7-7-06	JLM	50863	8270 Stock	70	7-7-06	1.05ml	10 ng/ml
					B43590	MeCl2	980			
50865	8270 level 2	3-15-06	7-7-06	JLM	50863	8270 Stock	150	7-7-06	0.90ml	25 ng/ml
					B43590	MeCl2	750			
50866	8270 level 3	3-15-06	7-7-06	JLM	50863	8270 Stock	600	7-7-06	1.8ml	50 ng/ml
					B43590	MeCl2	1200			
50867	8270 level 4	3-15-06	7-7-06	JLM	50864	8270 Stock	700	7-7-06	1.05ml	100 ng/ml
					B43590	MeCl2	350			

Reviewed by/Date:

KATAHDIN ANALYTICAL SERVICES, INC.
STANDARD OPERATING PROCEDURE

SOP Number: CA-214
Revision History
Cover Page
Page 1

TITLE: CLOSED-SYSTEM PURGE-AND-TRAP AND EXTRACTION FOR VOLATILE ORGANICS IN SOIL AND WASTE SAMPLES USING SW846 METHOD 5035

Prepared By: GC/MS Group Date: 7/98

Approved By:

Group Supervisor: J. Haley Date: 011201

Operations Manager: John C. Burton Date: 1/15/01

QA Officer: Deborah J. Madeau Date: 1·23·01

General Manager: Dennis P. Hughes Date: 1/16/07

Revision History:

SOP Revision	Changes	Approval Initials	Approval Date	Effective Date
01 5035	Format changes, added pollution prevention, minor changes throughout	DM	1·23·01	12301
02 5035	Reorganized sections 4, 5, 6, 7 and 8.	MRC	07.02.04	07.02.04
03 5035	Editted section 6.4.3 to include the addition of 5mL of H2O to sample	LAD	020305	020305
04 5035	Balance weighs to 0.1g grammatical corrections formatting corrections	LAD	04/06	04/06
05	Added 3585 Reference. Sections 6.1.2.3, 6.4.3 and 7.2.2: changed 20mL to 5mL.	LAD	09/08	09/08

TITLE: **CLOSED-SYSTEM PURGE-AND-TRAP AND EXTRACTION FOR VOLATILE ORGANICS IN SOIL AND WASTE SAMPLES USING SW846 METHOD 5035**

Please acknowledge receipt of this standard operating procedure by signing and dating both of the spaces provided. Return the bottom half of this sheet to the QA Department.

I acknowledge receipt of copy ___ of document **SOP CA-214-05**, titled **CLOSED-SYSTEM PURGE-AND-TRAP AND EXTRACTION FOR VOLATILE ORGANICS IN SOIL AND WASTE SAMPLES USING SW846 METHOD 5035.**

Recipient: _____ Date: _____

KATAHDIN ANALYTICAL SERVICES, INC.
STANDARD OPERATING PROCEDURE

I acknowledge receipt of copy ___ of document **SOP CA-214-05**, titled **CLOSED-SYSTEM PURGE-AND-TRAP AND EXTRACTION FOR VOLATILE ORGANICS IN SOIL AND WASTE SAMPLES USING SW846 METHOD 5035.**

Recipient: _____ Date: _____

TITLE: **CLOSED-SYSTEM PURGE-AND-TRAP AND EXTRACTION FOR VOLATILE ORGANICS IN SOIL AND WASTE SAMPLES USING SW846 METHOD 5035**

1.0 SCOPE AND APPLICATION

This method describes a closed-system purge-and-trap process for the analysis of volatile organic compounds (VOCs) in solid materials (e.g., soils, sediments, and solid waste). While the method is designed for use on samples containing low levels of VOCs, procedures are also provided for collecting and preparing solid samples containing high concentrations of VOCs and for oily wastes. For these high concentration and oily materials, sample collection and preparation are performed using the procedures described here, and sample introduction is performed using the aqueous purge-and-trap procedure in Method 5030. These procedures may be used in conjunction with any appropriate determinative gas chromatographic procedure, including, but not limited to, Methods 8015, 8021, and 8260.

The low soil method utilizes a hermetically sealed sample vial, the seal of which is never broken from the time of sampling to the time of analysis. Since the sample is never exposed to the atmosphere after sampling, the losses of VOCs during sample transport, handling, and analysis are negligible. The applicable concentration range of the low soil method is dependent on the determinative method, matrix, and compound. However, it will generally fall in the 5.0 to 200 µg/kg range.

Procedures are included for preparing high concentration samples for purging by Method 5030. High concentration samples are those containing VOC levels of >200 µg/kg.

Procedures are also included for addressing oily wastes that are soluble in a water-miscible solvent by method 3585. These samples are also purged using Method 5030.

Method 5035 can be used for most volatile organic compounds that have boiling points below 200°C and that 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 closed-system purge-and-trap equipment employed for low concentration samples is not appropriate for soil samples preserved in the field with methanol. Such samples should be analyzed using Method 5030 (see the note in Sec. 6.2.2).

1.1 Definitions

1.2 Responsibilities

This method is restricted to use by, or under the supervision of analysts experienced in the analyses using Methods 5030, 5035 and 3585. Each analyst must demonstrate and document their ability to generate acceptable results with this method. Refer to Katahdin SOP QA-805, current revision, "Personnel Training & Demonstration of Capability".

It is the responsibility of all Katahdin technical personnel involved in analysis of soils by method 5035 to read and understand this SOP, adhere to the procedures outlined, and to properly document their data in the appropriate lab notebook. Any deviations from the test or irregularities with the samples should also be recorded in the lab notebook and reported to the department manager or designated qualified data reviewer responsible for this data.

It is the responsibility of the Department Manager to oversee that members of their group follow this SOP, to ensure that their work is properly documented and to initiate periodic review of the associated logbooks.

1.3 Safety

Users of this procedure must be cognizant of inherent laboratory hazards, proper disposal procedures for contaminated materials and appropriate segregation of hazardous wastes. The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical should be treated as a potential health hazard. A reference file of material safety data sheets is available to all personnel involved in the chemical analysis. Everyone involved with the procedure must be familiar with the MSDSs (material safety data sheets) for all the materials used in this procedure.

Each qualified analyst or technician must be familiar with Katahdin Analytical safety procedures and the Katahdin Hazardous Waste Management Plan and must follow appropriate procedures. These include the use of appropriate personal protective equipment (PPE) such as safety glasses, gloves and lab coats when working with chemicals or near an instrument and not taking food or drink into the laboratory. Each analyst should know the location of a respirator and all safety equipment. Each analyst shall receive a safety orientation from their department manager, or designee, appropriate for the job functions they will perform.

1.4 Pollution Prevention/Waste Disposal

Whenever possible, laboratory personnel should use pollution prevention techniques to address their waste generation. Refer to the current revision of the Katahdin Hazardous Waste Management Plan for further details on pollution prevention techniques.

After analysis, partially-filled VOA vials and sample jars are returned to the appropriate refrigerators to be disposed of in adherence with the Katahdin Hazardous Waste Management Plan and Safety Manual and SOP SD-903, Sample Disposal, current revision. Expired standards are lab packed, placed in the Katahdin hazardous waste storage area, and disposed of in accordance with this SOP SD-903.

Sample aliquots used for analysis are disposed of in accordance with SOP SD-903 and the Katahdin Hazardous Waste Management Plan and Safety Manual. The soil samples must be decanted and the soil fraction disposed of separately in compliance with Katahdin's disposal policies.

2.0 SUMMARY OF METHOD

2.1 Low concentration soil method - generally applicable to and soils and other solid samples with VOC concentrations in the range of 5.0 to 200 µg/kg. Volatile organic compounds (VOCs) are determined by collecting an approximately 5-g sample, weighed in the field at the time of collection, and placing it in a pre-weighed vial with a septum-sealed screw-cap (see Sec. 4) that already contains a stirring bar and a sodium bisulfate or organic-free laboratory reagent grade water preservative solution. If the samples are sent to the laboratory in an Encore sampling device, the laboratory extrudes the sample into this vial containing a stirring bar and a sodium bisulfate or organic-free laboratory reagent grade water preservative solution. The entire vial is then placed, unopened, into the instrument carousel. Immediately before analysis, organic-free laboratory reagent grade water, surrogates, and internal standards (if applicable) are automatically added without opening the sample vial. The vial containing the sample is heated to 40° and the volatiles purged into an appropriate trap using an inert gas combined with agitation of the sample. Purged components travel via a transfer line to a trap. When purging is complete, the trap is heated and backflushed with helium to desorb the trapped sample components into a gas chromatograph for analysis by an appropriate determinative method.

2.2 High concentration soil method - generally applicable to soils and other solid samples with VOC concentrations greater than 200 µg/kg. The sample introduction technique in Sec. 2.1 is not applicable to all samples, particularly those containing high concentrations (generally greater than 200 µg/kg) of VOCs which may overload either the volatile trapping material or exceed the working range of the determinative instrument system (e.g., GC/MS, GC/FID, GC/EC, etc.). In such instances, this method describes two sample collection options and the corresponding sample purging procedures.

2.2.1 The first option is to collect a bulk sample in a vial or other suitable container without the use of the preservative solution described in Sec. 2.1. A portion of that sample is removed from the container in the laboratory and is dispersed in a water-miscible solvent (e.g., methanol) to dissolve the volatile organic constituents. An aliquot of the solution is added to 20 mL of laboratory reagent grade water in a purge tube. Surrogates and internal standards (if applicable) are added to the solution, then purged using

Method 5030, and analyzed by an appropriate determinative method. Because the procedure involves opening the vial and removing a portion of the soil, some volatile constituents may be lost during handling.

2.2.2 The second option is to collect an approximately 5-g sample in a pre-weighed vial with a septum-sealed screw-cap (see Sec 4) that contains a known aliquot of a water-miscible organic solvent (e.g., methanol). An aliquot of the solution is added to 20 mL of laboratory reagent grade water in a purge tube. Surrogates and internal standards (if applicable) are added to the solution, then purged using Method 5030, and analyzed by an appropriate determinative method.

2.3 High concentration oily waste method - generally applicable to oily samples with VOC concentrations greater than 200 µg/kg that can be diluted in a water-miscible solvent. Samples that are comprised of oils or samples that contain significant amounts of oil present additional analytical challenges. This procedure is generally appropriate for such samples when they are soluble in a water-miscible solvent.

2.3.1 After demonstrating that a test aliquot of the sample is soluble in methanol, a separate aliquot of the sample is diluted in the appropriate solvent. An aliquot of the solution is added to 20 mL of laboratory reagent grade water in a purge tube, taking care to ensure that a floating layer of oil is not present in the purge tube. Internal standards (if applicable) and surrogates are added to the solution that is then purged using Method 5030 and analyzed by an appropriate determinative method.

2.3.2 Samples that contain oily materials that are not soluble in water-miscible solvents must be prepared in n-hexandecane according to Method 3585.

3.0 INTERFERENCES

3.1 Impurities in the purge gas and from organic compounds out-gassing from the plumbing ahead of the trap account for the majority of contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running method blanks. The use of non-polytetrafluoroethylene (non-PTFE) plastic coating, non-PTFE thread sealants, or flow controllers with rubber components in the purging device must be avoided, since such materials out-gas organic compounds which will be concentrated in the trap during the purge operation. These compounds will result in interferences or false positives in the determinative step.

3.2 Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride and fluorocarbons) through the septum seal of the sample vial

during shipment and storage. A trip blank prepared from organic-free laboratory reagent grade water and carried through sampling and handling protocols serves as a check on such contamination.

3.3 Contamination by carryover can occur whenever high-concentration and low-concentration samples are analyzed in sequence. Where practical, samples with unusually high concentrations of analytes should be followed by an analysis of organic-free laboratory reagent grade water to check for cross-contamination. If the target compounds present in an unusually concentrated sample are also found to be present in the subsequent samples, the analyst must demonstrate that the compounds are not due to carryover. Conversely, if those target compounds are not present in the subsequent sample, then the analysis of organic-free laboratory reagent grade water is not necessary.

3.4 The laboratory where volatile analysis is performed should be free of solvents. The analytical and sample storage area should be isolated from all atmospheric sources of methylene chloride, otherwise random background levels will result. Since methylene chloride will permeate through PTFE tubing, all GC carrier gas lines and purge gas plumbing should be constructed of stainless steel or copper tubing. Laboratory workers' clothing previously exposed to methylene chloride fumes during common liquid/liquid extraction procedures can contribute to sample contamination. The presence of other organic solvents in the laboratory where volatile organics are analyzed will also lead to random background levels and the same precautions must be taken.

4.0 APPARATUS AND MATERIALS

4.1 Sample Containers

The specific sample containers required will depend on the purge-and-trap system to be employed (see Sec. 4.2). Our laboratory is equipped with Archon model 5100 purge and trap autosampler systems. A standard 40 ml VOA vial is used (e.g. ESS pre-cleaned certified 40 ml clear Type I borosilicate glass vials, open-top/polypropylene with 0.125 inch septa).

4.2 Purge-and-Trap System

The purge-and-trap system consists of a unit that automatically adds water, surrogates, and internal standards to a vial containing the sample, purges the VOCs using an inert gas stream while agitating the contents of the vial, and also traps the released VOCs for subsequent desorption into the gas chromatograph. The Archon systems at Katahdin meet the following criteria:

4.2.1 The purging device should be capable of accepting a vial sufficiently large to contain a 5-g soil sample plus a magnetic stirring bar and 10 mL of water. The device must be capable of heating a soil vial to 40°C and holding it at that temperature while the inert purge gas is allowed to pass through the sample. The device should also be capable of introducing at least 20 mL of organic-free laboratory reagent grade water into the sample vial while trapping the displaced headspace vapors. It must also be capable of agitating the sealed sample during purging, (e.g., using a magnetic stirring bar added to the vial prior to sample collection, sonication, or other means). The analytes being purged must be quantitatively transferred to an absorber trap. The trap must be capable of transferring the absorbed VOCs to the gas chromatograph (see 4.2.2).

4.2.2 A variety of traps and trapping materials may be employed with this method. The choice of trapping material may depend on the analytes of interest. Whichever trap is employed; it must demonstrate sufficient adsorption and desorption characteristics to meet the quantitation limits of all the target analytes for a given project and the QC requirements in Method 8000 and the determinative method. The most difficult analytes are generally the gases, especially dichlorodifluoromethane. The trap must be capable of desorbing the late eluting target analytes.

NOTE: Check the responses of the brominated compounds when using alternative charcoal traps (especially Vocarb 4000), as some degradation has been noted when higher desorption temperatures (especially above 240°C - 250°C) are employed. 2-Chloroethyl vinyl ether is degraded on Vocarb 4000 but performs adequately when Vocarb 3000 is used. The primary criterion, as stated above, is that all target analytes meet the sensitivity requirements for a given project.

4.2.2.1 The standard trap used in other EPA purge-and-trap methods is also acceptable. That trap is 25 cm long and has an inside diameter of at least 0.105 in. Starting from the inlet, the trap contains the equal amounts of the adsorbents listed below. It is recommended that 1.0 cm of methyl silicone-coated packing (35/60 mesh, Davison, grade 15 or equivalent) be inserted at the inlet to extend the life of the trap. If the analysis of dichlorodifluoromethane or other fluorocarbons of similar volatility is not required, then the charcoal can be eliminated and the polymer increased to fill 2/3 of the trap. If only compounds boiling above 35° are to be analyzed, both the silica gel and charcoal can be eliminated and the polymer increased to fill the entire trap.

4.2.2.1.1 2,6-Diphenylene oxide polymer - 60/80 mesh,

chromatographic grade (Tenax GC or equivalent).

4.2.2.1.2 Methyl silicone packing - OV-1 (3%) on Chromosorb-W, 60/80 mesh or equivalent.

4.2.2.1.3 Coconut charcoal - Prepare from Barnebey Cheney, CA-580-26, or equivalent, by crushing through 26 mesh screen.

4.2.2.2 Trapping materials other than those listed above also may be employed, provided that they meet the specifications in Sec. 4.2.3, below.

4.2.3 The desorber for the trap must be capable of rapidly heating the trap to the temperature recommended by the trap material manufacturer, prior to the beginning of the flow of desorption gas. Several commercial desorbers (purge-and-trap units) are available.

4.3 Syringe and Syringe Valves

4.3.1 25-mL glass hypodermic syringes with Luer-Lok (or equivalent) tip (other sizes are acceptable depending on sample volume used).

4.3.2 25-µL micro syringe with a 2 inch x 0.006 inch ID, 22° bevel needle (Hamilton #702N or equivalent).

4.3.3 Micro syringes - 10-, 100-µL.

4.3.4 Syringes - 0.5-, 1.0-, and 5-mL, gas-tight.

4.4 Miscellaneous

4.4.1 Glass vials

4.4.1.1 60-mL, septum-sealed, to collect samples for screening, dry weight determination.

4.4.1.2 40-mL, screw-cap, PTFE lined, septum-sealed. Examine each vial prior to use to ensure that the vial has a flat, uniform sealing surface.

4.4.2 Top-loading balance - Capable of accurately weighing to 0.1 g.

4.4.3 Glass scintillation vials - 20-mL, with screw-caps and PTFE liners, or glass culture tubes with screw-caps and PTFE liners, for dilution of oily waste samples.

4.4.4 Volumetric flasks - Class A, 10-mL and 100-mL, with ground glass stoppers.

4.4.5 2-mL glass vials, for GC autosampler - Used for oily waste samples extracted with methanol or PEG.

4.4.6 Spatula, stainless steel - narrow enough to fit into a sample vial.

4.4.7 Disposable Pasteur pipettes.

4.4.8 Magnetic stirring bars - PTFE- or glass-coated, of the appropriate size to fit the sample vials. Consult manufacturer's recommendation for specific stirring bars. Stirring bars may be reused, provided that they are thoroughly cleaned between uses. Consult the manufacturers of the purging device and the stirring bars for suggested cleaning procedures.

4.5 Field Sampling Equipment

4.5.1 EnCore™ sampler - (En Chem, Inc., 1795 Industrial Drive, Green Bay, WI 54302), or equivalent.

4.5.2 Alternatively, disposable plastic syringes with a barrel smaller than the neck of the soil vial may be used to collect the sample. The syringe end of the barrel is cut off prior to sampling. One syringe is needed for each sample aliquot to be collected.

4.5.3 Portable balance - For field use, capable of weighing to 0.01 g.

4.5.4 Balance weights - Balances employed in the field should be checked against an appropriate reference weight at least once daily, prior to weighing any samples, or as described in the sampling plan. The specific weights used will depend on the total weight of the sample container, sample, stirring bar, laboratory reagent grade water added, cap, and septum.

5.0 REAGENTS

5.1 Organic-free laboratory reagent grade water - All references to water in this method refer to organic-free laboratory reagent grade water.

5.2 Methanol, CH_3OH - purge-and-trap quality or equivalent. Store away from other solvents.

5.3 Sodium bisulfate, $NaHSO_4$ - ACS reagent grade or equivalent.

5.4 Polyethylene glycol (PEG), $H(OCH_2CH_2)_nOH$ – free of interferences at the detection limit of the target analytes.

5.5 See the determinative method for guidance on internal standards and surrogates to be employed in this procedure.

6.0 SAMPLE COLLECTION, PRESERVATION AND HANDLING

The low concentration portion of this method employs sample vials that are filled and weighed in the field and never opened during the analytical process. As a result, sampling personnel should be equipped with a portable balance capable of weighing to 0.01 g.

6.1 Preparation of sample vials

The specific preparation procedures for sample vials depend on the expected concentration range of the sample, with separate preparation procedures for low concentration soil samples and high concentration soil and solid waste samples. Sample vials should be prepared in a fixed laboratory or other controlled environment, sealed, and shipped to the field location. Gloves should be worn during the preparation steps.

Because volatile organics will partition into the headspace of the vial from the aqueous solution and will be lost when the vial is opened, surrogates, matrix spikes, and internal standards should only be added to the vials back in the laboratory, either manually by puncturing the septum with a small-gauge needle or automatically by the sample introduction system, just prior to analysis.

6.1.1 Low concentration soil samples

Sodium bisulfate preservation is used in the preparation of vials used in the collection of low concentration soil samples to be analyzed by the closed-system purge-and-trap equipment described in Method 5035.
Water and subsequent freezing preparation of vials is used in the collection of low concentration soil samples known to contain carbonate minerals which may effervesce upon contact with an acidic preservation solution and which are to be analyzed by the closed-system purge-and-trap equipment

described in Method 5035. This type of preservation is typically done in the lab after Encore samplers are received from the field

6.1.1.1 Add a clean magnetic stirring bar to each clean vial.

6.1.1.2 The preservative is added to each vial prior to shipping the vial to the field. Add 20 mL of 20% sodium bisulfate solution or 20 mL of water to the vial and seal the vial with the screw-cap and septum seal.

6.1.1.3 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). It is important that labels and tape not cover the junction of the screw top and vial. Labels and tape must also be applied smoothly (i.e. no wrinkles) to prevent autosampler failures.

6.1.1.4 Weigh the prepared vial to the nearest 0.1 g and record it on the label.

6.1.2 High concentration soil samples in methanol:

6.1.2.1 When high concentration samples are collected without a preservative, a variety of sample containers may be employed, including 40-mL glass vials with septum seals (see Sec. 4.4).

6.1.2.2 The following steps apply to the preparation of vials used in the collection of high concentration soil samples to be preserved in the field with methanol and analyzed by the aqueous purge-and-trap equipment described in Method 5030.

6.1.2.3 Add 5 mL of methanol to each vial.

6.1.2.4 Seal the vial with the screw-cap and septum seal.

6.1.2.5 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).

6.1.2.6 Weigh the prepared vial to the nearest 0.01 g and record it on the label.

NOTE: Vials containing methanol should be weighed a second time on the day that they are to be used. Vials found to have lost methanol (reduction in weight of >0.01 g) should not be used for sample collection.

6.1.3 Oily waste samples

When oily waste samples are known to be soluble in methanol, sample vials may be prepared as described in Sec. 6.1.2.2, using the appropriate solvent. However, when the solubility of the waste is unknown, the sample should be collected without the use of a preservative, in a vial such as that described in Sec. 6.1.2.1.

6.2 Sample collection

Collect the sample according to the procedures outlined in the sampling plan. As with any sampling procedure for volatiles, care must be taken to minimize the disturbance of the sample in order to minimize the loss of the volatile components. Several techniques may be used to transfer a sample to the relatively narrow opening of the low concentration soil vial. These include devices such as the EnCore™ sampler, the Purge-and-Trap Soil Sampler™ , and a cut plastic syringe. Always wear gloves whenever handling the tared sample vials.

6.3 Sample handling and shipment

All samples for volatiles analysis should be cooled to approximately 4°C, packed in appropriate containers, and shipped to the laboratory on ice, as described in the sampling plan. Samples should be shipped on the day of sampling if at all possible.

6.4 Sample storage

6.4.1 Once in the laboratory, store samples at 4°C until analysis. The sample storage area should be free of organic solvent vapors.

6.4.2 All samples should be analyzed as soon as practical, and within the designated holding time from collection. Samples not analyzed within the designated holding time must be noted and the data are considered minimum values.

6.4.3 When the low concentration samples are strongly alkaline or highly calcareous in nature, the sodium bisulfate preservative solution may not be strong enough to reduce the pH of the soil/water solution to below 2. Therefore, when low concentration soils to be sampled are known or suspected to be strongly alkaline or highly calcareous, additional steps may

be required to preserve the samples. Such steps include: addition of larger amounts of the sodium bisulfate preservative to non-calcareous samples, or the addition of 5 mL of water and storage at -10° (taking care not to fill the vials so full that the expansion of the water in the vial breaks the vial), or significantly reducing the maximum holding time for low concentration soil samples.

7.0 PROCEDURES

This section describes procedures for the low concentration soil method, the high concentration soil method, and the procedure for oily waste samples. High concentration samples are to be introduced into the GC system using Method 5030. Oily waste samples are to be introduced into the GC system using Method 5030 if they are soluble in a water-miscible solvent, or using Method 3585 if they are not.

For the high concentration soil and oily waste samples, the surrogate compounds may either be spiked into the solvent at the time of extraction or the laboratory reagent grade water containing an aliquot of the extract prior to analysis.

7.1 Low concentration soil method (Approximate concentration range of 5 to 200 µg/kg -the concentration range is dependent upon the determinative method and the sensitivity of each analyte.)

7.1.1 Archon Operation

Prior to using this introduction technique for any GC or GC/MS method, the system must be calibrated by the analytical method to be used. When a GC/MS method is used, internal standard calibration is employed.

7.1.1.1 Establish the purge-and-trap instrument operating conditions. Adjust the instrument to inject 10 mL of water, to heat the sample to 40°C, and to hold the sample at 40°C for 1.5 minutes before commencing the purge process, or as recommended by the instrument manufacturer.

7.1.1.2 Carry out the purge-and-trap procedure as outlined in Secs. 7.1.2. to 7.1.4.

7.1.2 Sample purge-and-trap
This method is designed for a 5-g sample size, but smaller sample sizes may be used. The soil vial is hermetically sealed at the sampling site, and MUST remain sealed in order to guarantee the integrity of the sample.

Gloves must be worn when handling the sample vial since the vial has been tared. If any soil is noted on the vial or cap, it must be carefully removed prior to weighing. Weigh the vial and contents to the nearest 0.01 g, even if the sample weight was determined in the field, and record this weight. This second weighing provides a check on the field sampling procedures and provides additional assurance that the reported sample weight is accurate. Data users should be advised on significant discrepancies between the field and laboratory weights.

7.1.2.1 Remove the sample vial from storage and allow it to warm to room temperature. Shake the vial gently, to ensure that the contents move freely and that stirring will be effective. Place the sample vial in the instrument carousel according to the manufacturer's instructions.

7.1.2.2 Without disturbing the hermetic seal on the sample vial, add 10 mL of organic-free laboratory reagent grade water, the internal standards, and the surrogate compounds. This is carried out either manually or using the automated sampler. Other volumes of organic-free laboratory reagent grade water may be used. However, it is imperative that all samples, blanks, and calibration standards have exactly the same final volume of organic-free laboratory reagent grade water. Prior to purging, heat the sample vial to 40°C for 1.5 minutes, or as described by the manufacturer.

7.1.2.3 For the sample selected for matrix spiking, add the matrix spiking solution described in Sec. 5.0 of Method 5000, either manually, or automatically, following the manufacturer's instructions.

7.1.2.4 Purge the sample with helium or another inert gas at a flow rate of up to 40 mL/minute (the flow rate may vary from 20 to 40 mL/min, depending on the target analyte group) for 11 minutes while the sample is being agitated with the magnetic stirring bar or other mechanical means. The purged analytes are allowed to flow out of the vial through a transfer line to a trap packed with suitable sorbent materials.

7.1.3 Sample Desorption

7.1.3.1 Non-cryogenic interface - After the 11 minute purge, place the purge-and-trap system in the desorb mode and preheat the trap to 245°C without a flow of desorption gas. Start the flow of desorption gas at 10 mL/minute for about four minutes. Begin the temperature program of the gas chromatograph and start data acquisition.

7.1.4 Trap Reconditioning

After desorbing the sample for 4 minutes, recondition the trap by returning the purge-and-trap system to the purge mode. Maintain the trap temperature at 245°C (or other temperature recommended by the manufacturer of the trap packing materials). After approximately 10 minutes, turn off the trap heater and halt the purge flow through the trap. When the trap is cool, the next sample can be analyzed.

7.2 High concentration method for soil samples with concentrations generally greater than 200 µg/kg.

The high concentration method for soil is based on a solvent extraction. A solid sample is either extracted or diluted, depending on sample solubility in a water-miscible solvent. An aliquot of the extract is added to organic-free laboratory reagent grade water containing surrogates, internal and matrix spiking standards (added manually or by the autosampler), purged according to Method 5030, and analyzed by an appropriate determinative method. The specific sample preparation steps depend on whether or not the sample was preserved in the field. Samples that were not preserved in the field are prepared using the steps below, beginning at Sec. 7.2.1. If solvent preservation was employed in the field, then the preparation begins with Sec. 7.2.4.

7.2.1 When the high concentration sample is not preserved in the field, the sample consists of the entire contents of the sample container. Do not discard any supernatant liquids. Remove a representative aliquot with a spatula.

7.2.2 For soil and solid waste samples that are soluble in methanol, add 5.0 g (wet weight) of sample to a tared 40-mL VOA vial using a calibrated (refer to Katahdin SOP, CA-102, Balance Calibration) top loading balance. Record the weight to 0.1 g. Add 5 mL of methanol to the vial containing the sample and shake for two minutes.

NOTE: The steps in Secs. 7.2.1, 7.2.2, and 7.2.3 must be performed rapidly and without interruption to avoid loss of volatile organics. These steps must be performed in a laboratory free from solvent fumes.

7.2.4 For soil and solid waste samples that were collected in methanol or PEG, weigh the vial to 0.01 g as a check on the weight recorded in the field.

7.2.5 For each new lot of methanol, add an appropriate aliquot of the methanol to 20 mL of organic-free laboratory reagent grade water and analyze by Method 5030 in conjunction with the appropriate determinative method.

Proceed to Sec. 7.0 in Method 5030 and follow the procedure for purging high concentration samples.

7.3 High concentration method for oily waste samples

This procedure for the analysis of oily waste samples involves the dilution of the sample in methanol or PEG. However, care must be taken to avoid introducing any of the floating oil layer into the instrument. A portion of the diluted sample is then added to 5.0 mL of organic-free laboratory reagent grade water, purged according to Method 5030, and analyzed using an appropriate determinative method.
The specific sample preparation steps depend on whether or not the sample was preserved in the field. Samples that were not preserved in the field are prepared using the steps below, beginning at Sec. 7.3.2. If methanol preservation was employed in the field, then the preparation begins with Sec. 7.3.4.

7.3.1 For oily samples that are not soluble in methanol or PEG (including those samples consisting primarily of petroleum or coking waste), dilute or extract with hexadecane and shake for two minutes.

7.3.2 For oily samples that are soluble in methanol if the waste was not preserved in the field, tare a 10-mL volumetric flask, or a VOA vial, weigh 1 g (wet weight) of the sample into the tared vessel and add 10.0 mL methanol or PEG with a calibrated syringe. If a vial is used instead of a volumetric flask, it must be calibrated prior to use. This operation must be performed prior to opening the sample vial and weighing out the aliquot for analysis. Invert the vial a minimum of three times to mix the contents.

7.3.4 If the sample was collected in the field in a vial containing methanol or PEG, weigh the vial to 0.1 g as a check on the weight recorded in the field, and proceed with Sec. 7.3.5.

7.3.5 Regardless of how the sample was collected, the target analytes are extracted into the solvent along with the majority of the oily waste (i.e., some of the oil may still be floating on the surface). If oil is floating on the surface, transfer 1 to 2 mL of the extract to a clean GC vial using a Pasteur pipet. Ensure that no oil is transferred to the vial.

7.3.6 Add an appropriate aliquot of the methanol or PEG to 5.0 mL of organic-free laboratory reagent grade water and analyze by Method 5030 in conjunction with the appropriate determinative method. Proceed to Sec. 7.0 in Method 5030 and follow the procedure for purging oily waste samples.

7.4 Determination of % Dry Weight

If results are to be reported on a dry weight basis, it is necessary to determine the dry weight of the sample. Refer to Katahdin SOP, CA-717, for determination of % dry weight.

NOTE: It is highly recommended that the dry weight determination only be made after the analyst has determined that no sample aliquots will be taken from the 60-mL vial for high concentration analysis. This is to minimize loss of volatiles and to avoid sample contamination from the laboratory atmosphere. There is no holding time associated with the dry weight determination. Thus, this determination can be made any time prior to reporting the sample results, as long as the vial containing the additional sample has remained sealed and properly stored.

8.0 QUALITY CONTROL AND ACCEPTANCE CRITERIA

8.1 Before processing any samples, the analyst should demonstrate through the analysis of an organic-free laboratory reagent grade water method blank that all glassware and reagents are interference free. Each time a set of samples is extracted, or there is a change in reagents, a method blank should be processed as a safeguard against chronic laboratory contamination. The blank samples should be carried through all stages of the sample preparation and measurement.

8.2 Initial Demonstration of Proficiency - Each laboratory must demonstrate initial proficiency with each sample preparation and determinative method combination it utilizes, by generating data of acceptable accuracy and precision for target analytes in a clean matrix. The laboratory must also repeat this demonstration whenever new staff are trained or significant changes in instrumentation are made.

8.3 Sample Quality Control for Preparation and Analysis - See the appropriate analytical method to follow to demonstrate acceptable continuing performance on each set of samples to be analyzed. These include the method blank, either a matrix spike/matrix spike duplicate or a matrix spike and duplicate sample analysis, a laboratory control sample (LCS), and the addition of surrogates to each sample and QC sample.

9.0 METHOD PERFORMANCE

Refer to appropriate analytical method.

TITLE: **CLOSED-SYSTEM PURGE-AND-TRAP AND EXTRACTION FOR VOLATILE ORGANICS IN SOIL AND WASTE SAMPLES USING SW846 METHOD 5035**

10.0 APPLICABLE DOCUMENTS/REFERENCES

"Test Methods for the Evaluation of Solid Waste: Physical/Chemical Methods," Method 5035, SW-846, USEPA, Revision III, June, 1997.

"Test Methods for the Evaluation of Solid Waste: Physical/Chemical Methods," Method 5035A, SW-846, USEPA, Revision III, June, 1997.

"Test Methods for the Evaluation of Solid Waste: Physical/Chemical Methods," Method 3585, SW-846, USEPA, Revision IIIB, Nov., 2004.

Archon Operator's Manual

LIST OF TABLES AND FIGURES

Table 1 Summary of Method Modifications

TITLE: **CLOSED-SYSTEM PURGE-AND-TRAP AND EXTRACTION FOR VOLATILE ORGANICS IN SOIL AND WASTE SAMPLES USING SW846 METHOD 5035**

TABLE 1

SUMMARY OF METHOD MODIFICATIONS

TOPIC	KATAHDIN SOP CA-214-05	METHOD 5035, current revision
Apparatus/Materials		
Reagents		
Sample preservation/ handling		
Procedures	(1) Use methanol prep for all high concentration soils. (2) For high concentration soils, leave all extract in the vial with the soil for storage.	(1) For high concentration soils from an unknown source, perform a solubility test. (2) For high concentration soils, pipet approximately 1 mL of extract into a GC vial for storage.

KATAHDIN ANALYTICAL SERVICES, INC.
STANDARD OPERATING PROCEDURE

SOP Number: CA-302
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Page 1

TITLE: ANALYSIS OF PESTICIDES BY GAS CHROMATOGRAPHY/ELECTRON CAPTURE DETECTOR (GC/ECD): SW-846 METHOD 8081

Prepared By: Peter Lemay Date: 7/96

Approved By:

Group Supervisor: Peter Lemay Date: 1/15/01

Operations Manager: John C. Burton Date: 1/15/01

QA Officer: Deborah J. Nadeau Date: 1.22.01

General Manager: Dennis P. Kufok Date: 1/16/01

Revision History:

SOP Revision	Changes	Approval Initials	Approval Date	Effective Date
02 8081A	Format changes, added pollution prevention, minor changes to sections 7, 8 and Table 1.	DN	1.22.01	1/22/01
03 8081A	Changes to comply with South Carolina requirements – added linear calibration option, retention time window criteria & other minor changes to surrogate criteria.	DN	5.21.01	5.21.01
04 8081A	Changed to practice of reporting higher value. Other minor changes to Table 1 + 2, section 7.5.3 and section 7.4.3.	DN	5.21.02	5.21.02
05 8081A	Added definitions and information for the new data processing system. Replaced several figures with updated ones.	MRC	05.04.04	05.04.04
06 8081A	added alternative CV Conc. changed data checklist minor changes throughout added wording to section 8	LAD	03/05 LAD	03/05 6-13-06

TITLE: **ANALYSIS OF PESTICIDES BY GAS CHROMATOGRAPHY/ELECTRON CAPTURE DETECTOR (GC/ECD): SW-846 METHOD 8081**

SOP Revision	Changes	Approval Initials	Approval Date	Effective Date
07	Added retention time window criteria. Sect. 7.4.2 - added to shake samples before vialing.	LAD	03/06	03/06
08	Sect. 1.4 - Updated to include waste streams. Sect. 4.5 - removed balance Changed makeup gas from N2 to Ar Me. Changed T.C. from 5 to 2 peaks. Updated column confirmation. Changed corr. coef. to coeff. of determination	LAD	06/07	06/07
09	Added extraction method 3535 for AQ samples Updated method references. Added Katahdin Analytical Environmental Health and Safety Manual. Changed number of peaks quantitated for Toxaphene to 3 of 5. Added S.C. clarification on marginal exceedences.	LAD	02/09	02/09
10	Changes made to sections 4.1, 7.4, 7.5, 8.0 and 10.0 for compliance with DoD QSM version 4.1	LAD	08/09	08/09
11	Added Table 2 with DoD QSM version 4.1 QC Requirements. Updated Figure 1 and 2.	LAD	04/10	04/10

TITLE: ANALYSIS OF PESTICIDES BY GAS CHROMATOGRAPHY/ELECTRON CAPTURE DETECTOR (GC/ECD): SW-846 METHOD 8081

Please acknowledge receipt of this standard operating procedure by signing and dating both of the spaces provided. Return the bottom half of this sheet to the QA Department.

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STANDARD OPERATING PROCEDURE

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TITLE: ANALYSIS OF PESTICIDES BY GAS CHROMATOGRAPHY/ELECTRON CAPTURE DETECTOR (GC/ECD): SW-846 METHOD 8081

1.0 SCOPE AND APPLICATION

This SOP describes all aspects of the analysis of extracts of solid and aqueous samples for Pesticides by EPA Method 8081B, as performed by Katahdin Analytical Services, Inc. including sample analysis, data review, standard preparation and instrument calibration.

It is applicable to the following compounds: aldrin, alpha-BHC, beta-BHC, gamma-BHC, delta-BHC, chlordane, 4,4'-DDT, 4,4-DDE, 4,4'-DDD, dieldrin, endosulfan I, endosulfan II, endosulfan sulfate, endrin, endrin aldehyde, heptachlor, heptachlor epoxide, toxaphene, endrin ketone, and methoxychlor. Extracts are analyzed by Gas Chromatography-Electron Capture Detector (GC-ECD).

1.1 Definitions

ANALYTICAL BATCH: 20 or fewer samples which are analyzed together with the same method sequence and the same lots of reagents and with the manipulations common to each sample within the same time period or in continuous sequential time periods.

METHOD BLANK (laboratory reagent blank): An artificial sample designed to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus. For aqueous samples, laboratory reagent grade water is used as a blank matrix; however a universal blank matrix does not exist for solid samples, and therefore, no matrix is used. The blank is taken through the appropriate steps of the process.

INDEPENDENT CALIBRATION VERIFICATION (ICV): A verification of the ratio of instrument response to analyte amount. ICV solutions are prepared from stock solutions which are independent from the stock solutions used to prepare the calibration standards.

CALIBRATION STANDARD (WORKING STANDARD): A solution prepared from the stock standard solution, which is used to calibrate the instrument response with respect to analyte concentration.

LABORATORY CONTROL SAMPLE (LCS): A blank that has been spiked with the analyte(s) from an independent source and is analyzed exactly like a sample. Its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements. The matrix used should be phase matched with the samples and well characterized.

MATRIX SPIKE/MATRIX SPIKE DUPLICATE (MS/MSD): Predetermined quantities of stock solutions of certain analytes are added to a sample matrix prior to sample extraction and analysis. Samples are split into duplicates, spiked and analyzed. Percent recoveries are calculated for each of the analytes detected. The relative percent difference between the samples is calculated and used to assess analytical precision.

STANDARD CURVE (CALIBRATION CURVE): A curve that plots concentration of known analyte standard versus the instrument response to the analyte.

STOCK STANDARD SOLUTION: A concentrated solution containing a single certified standard that is a method analyte, or a concentrated solution of a single analyte prepared in the laboratory with an assay reference compound. Stock standard solutions are used to prepare calibration standards.

SURROGATES: Organic compounds which are similar to analytes of interest in chemical composition, extraction and chromatography, but which are not normally found in environmental samples. These compounds are spiked into all blanks, standards, samples and spiked samples prior to analysis. Percent recoveries are calculated for each surrogate.

KATAHDIN INFORMATION MANAGEMENT SYSTEM (KIMS) : A complete multi-user system with the capabilities of integrating laboratory instrumentation, generating laboratory worksheets, providing complete Lab Order status and generating reports. KIMS utilizes these features through a database.

PE NELSON TURBOCHROM: A data acquisition system that is used to collect chromatographic data. The system can also be used to archive raw data files.

HP ENVIROQUANT: A data acquisition system that is used to collect chromatographic data.

TARGET: A software system that combines full processing, reporting and comprehensive review capabilities, regardless of chromatographic vendor and data type.

TARGET DB: An oracle database used to store and organize all Target data files.

QUICKFORMS: A laboratory reporting software for Target and Target DB. The QuickForms report module for Target is preconfigured with generalized forms and US EPA CLP report forms and disk deliverables, which can be customized.

1.2 Responsibilities

This method is restricted to use by, or under the supervision of analysts experienced in the analysis of pesticides by method 8081, current revision. Each analyst must demonstrate the ability to generate acceptable results with this method.

It is the responsibility of all Katahdin technical personnel involved in analysis by method 8081, current revision, to read and understand this SOP, adhere to the procedures outlined, and to properly document their data in the appropriate lab notebook. Any deviations from the test or irregularities with the samples should also be

recorded in the lab notebook and reported to the Department Manager or designated qualified data reviewer responsible for this data.

It is the responsibility of the Department Manager to oversee that members of their group follow this SOP, to ensure that their work is properly documented and to initiate periodic review of the associated logbooks.

1.3 Health and Safety

Users of this procedure must be cognizant of inherent laboratory hazards, proper disposal procedures for contaminated materials and appropriate segregation of hazardous wastes. The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical should be treated as a potential health hazard. A reference file of material safety data sheets is available to all personnel involved in the chemical analysis. Everyone involved with the procedure must be familiar with the MSDSs (material safety data sheets) for all the materials used in this procedure.

Each qualified analyst or technician must be familiar with Katahdin Analytical Environmental Health and Safety Manual including the Katahdin Hazardous Waste Plan and must follow appropriate procedures. These include the use of appropriate personal protective equipment (PPE) such as safety glasses, gloves and lab coats when working with chemicals or near an instrument and not taking food or drink into the laboratory. Each analyst should know the location of all safety equipment. Each analyst shall receive a safety orientation from their Department Manager, or designee, appropriate for the job functions they will perform.

1.4 Pollution Prevention/Waste Disposal

Whenever possible, laboratory personnel should use pollution prevention techniques to address their waste generation. Refer to the current revision of the Katahdin Hazardous Waste Management Program for further details on pollution prevention techniques.

Wastes generated during the preparation of samples must be disposed of in accordance with the Katahdin Analytical Environmental Health and Safety Manual and SOP SD-903, “Sample Disposal,” current revision. Expired standards are lab packed, placed in the Katahdin hazardous waste storage area, and disposed of in accordance with this SOP.

Wastes generated during standards preparation are disposed of in the Mixed Flammable Waste (O). After the extracts have been analyzed, the autosampler vials and any expired standard vials or ampules are disposed of in the Organic Vial Waste (P).

TITLE: ANALYSIS OF PESTICIDES BY GAS CHROMATOGRAPHY/ELECTRON CAPTURE DETECTOR (GC/ECD): SW-846 METHOD 8081

2.0 SUMMARY OF METHOD

2.1 Method 8081 provides gas chromatographic conditions for the detection of ppb concentrations of certain organochlorine pesticides. Prior to the use of this method, appropriate sample extraction techniques must be used. Both neat and diluted organic liquids (Method 3580, waste dilution) may be analyzed by direct injection. A 2-5 ul aliquot of sample is injected into a gas chromatograph (GC) using the direct injection technique, and compounds in the GC effluent are detected by an electron capture detector (ECD).

2.2 The sensitivity of Method 8081 usually depends on the concentration of interferences rather than on instrumental limitations. If interferences prevent detection of the analytes, Method 8081 may also be performed on samples that have undergone cleanup. Method 3660, Sulfur Cleanup, by itself or in conjunction with Method 3620, Florisil Column Cleanup, may also be used to eliminate interferences in the analysis.

3.0 INTERFERENCES

3.1 Interferences by phthalate esters can pose a problem in pesticide determinations when using the electron capture detector. Common flexible plastics contain various amounts of phthalates. Care has to be taken to avoid using any plastic materials during the extraction process. Exhaustive cleanup of reagents and glassware may be required to eliminate background phthalate contamination.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph

4.1.1 GC Hewlett Packard 6890 or 5890 series I or II or 6890 connected to the Turbochrom or Enviroquant data system,or equivalent.

4.1.2 Columns: Instruments are configured with a pre-column originating from the injection port which is connected to deactivated glass Y splitter that connects two different columns to two detectors. The most commonly used columns are: RTX-35 30M x 0.53 mm ID, RTX-5 30M x 0.53 MM ID, or RTX-1701 30M x 0.53 mm ID. Equivalent columns can be used.

4.1.3 Detectors: Electron capture detectors (ECD).

4.2 Volumetric flasks, class A: sizes as appropriate with the ground-glass stoppers.

4.3 Syringes: various sizes for preparing standards and injecting samples on the instrument.

4.4 Vials: various sizes and types including crimp tops.

4.6 Refrigerator for storage of extracts and standards.

5.0 REAGENTS

5.1 Solvents

5.1.1 Hexane: pesticide quality or equivalent for diluting samples and standards.

5.2 Standards

5.2.1 Stock standard solutions: Solutions purchased from suppliers like Restek or other acceptable retailers. Expiration dates are one year from date of opening vial or sooner if manufacturers date is less. Upon receipt, all standards are logged into the appropriate logbook with the date of receipt, expiration date, source, lot number, solvent and concentration of compounds.

5.2.2 Calibration standards: Prepared through the dilution of the stock standards with hexane. Expiration date is 6 months or sooner. Information is documented in a separate logbook.

5.2.3 Pesticide Working standards: Prepared by diluting the stock mix of 2000 ug/ml that contains all single component pesticides into hexane to give final concentrations of: 0.005, 0.01, 0.025, 0.05, 0.10, and 0.25 ug/ml. The mix, referred to as INDAB, also contains two surrogates: Tetrachloro-m-xylene and Decachlorobiphenyl, which are at the same concentrations as the pesticides.

5.2.4 Independent Calibration Verification Standard: Prepared as above using a standard independent of the calibration standards.

5.2.5 Multicomponent Pesticide Working standards: Toxaphene is prepared by diluting the Toxaphene stock solution to a concentration of 1.0 ug/ml. Technical chlordane is prepared similarly except to a concentration of 0.50 ug/ml.

5.2.6 Evaluation Mix: Prepared by diluting the stock solution to a concentration of 0.20 ug/mL.

6.0 SAMPLE COLLECTION, PRESERVATION AND HANDLING

Extracts must be stored under refrigeration and analyzed within 40 days of extraction.

7.0 PROCEDURES

EXTRACTION - Refer to the appropriate SOP for the correct extraction procedure. In general, water samples are extracted using methods 3510, 3520 or 3535 while solid samples use methods 3540, 3545 or 3550.

7.1 INSTRUMENT CONDITIONS

Refer to the instrument logbook for the current column and conditions.

Typical conditions are:	Makeup flow:	60 ml/min Nitrogen or Ar/Methane
	Column flow:	3.75 ml/min
	Injector Temp:	200
	Detector Temp:	300
	Oven Ramp:	160(0) - 5/min - 260(10)
	Run time:	24 min
	Injection size:	2 uL

7.2 CALIBRATION

7.2.1 The GC system is calibrated using the external standard calibration procedure. A six-point calibration standard mix of the INDAB mix listed in Reagents Section 5.2.2 is prepared along with a single point standard of Toxaphene and Technical Chlordane.

If the sample contains Toxaphene, a six-point calibration curve is analyzed. If the sample contains Chlordane and the analysis request is for Technical Chlordane, a six-point calibration curve is analyzed. If the analytical request is for the two components alpha-Chlordane and gamma-Chlordane, these two compounds are quantitated from the INDAB mix.

Toxaphene is calibrated using the 5 to 10 major peaks of the standard. The Target system will calculate a peak height for all 5 to 10 peaks. A calibration curve is prepared in Target using the peak heights of the 5 to 10 peaks against the concentration of the standard.
Technical Chlordane is calibrated using 3 to 5 major peaks of the standard. The Target system will calculate a peak height for all three to five peaks. A separate calibration curve for each of the 3 to 5 peaks is prepared in Target using the peak height against the concentration of the standard.

Each calibration standard is injected using the technique that is used to introduce the actual samples into the GC. The Target system will calculate a peak height for each compound. A calibration curve can be prepared in Target using the peak height against the concentration of the standard. A non-linear calibration applying a second order polynomial (quadratic fit) equation is used

to prepare the curve. In order to be used for quantitative purposes, the Coefficient of Determination must be greater than or equal to 0.990. The quadratic equation is:

$$y = ax^2 + bx + c$$

where: y = Instrument response
b = Slope of the line
x = Concentration of the calibration standard
c = The intercept

Please note that a non-linear calibration model may not be allowable for certain states, federal programs, or clients. South Carolina does not allow non-linear calibration for compliance work originating in their state. In these cases, a linear calibration model must be used. The linear equation is

$$y = bx + c$$

where: y = Instrument response
b = Slope of the line
x = Concentration of the calibration standard
c = The intercept

The calibration curve is calibrated the same way as the second order polynomial equation except that a five-point calibration standard mix is used.

7.2.2 The INDAB mix calibration curve must be checked initially by analyzing a standard containing the same analytes as the curve but prepared from another source. If the response of the analytes from the independent source varies by more than ± 20%, a new independent source standard must be analyzed or a new calibration curve must be prepared and/or analyzed.

7.2.3 The working calibration curve must be verified on each 12-hour shift that samples are to be analyzed by injecting the mid-point calibration standard.

7.3 RETENTION TIME WINDOWS

7.3.1 Three injections of all single component standard mixtures and multiresponsive products throughout the course of a 72-hour period.

7.3.2 The standard deviation of the three retention times is calculated for each single component standard. For multiresponsive products, a major peak from the envelope is chosen and a standard deviation is calculated using the three retention times for that peak.

7.3.3 Plus or minus three times the standard deviation of the retention times for each standard is used to define the retention time window; however, the experience of the analyst should weight heavily in the interpretation of chromatograms. For multiresponsive analytes, the analyst should use the retention time window, but should primarily rely on pattern recognition.

7.3.4 Retention time windows are calculated for each standard on each GC column and whenever a new GC column is installed. The data is kept on file in the laboratory.

7.3.5 If the calculated retention time window results in a value of 0.03 minutes or less, the laboratory will apply nominal windows. This is done in order to avoid any false negative hits because of the window being too narrow. The windows are: ± 0.05 for Heptachlor, Aldrin and all BHC compounds, ± 0.07 for all other target analytes. By utilizing these windows, a false positive hit may be initially indicated, but an experienced analyst could determine a false positive by carefully evaluating the chromatograms. Please note that the use of nominal retention time windows may not be allowable for certain states, federal programs, or clients. South Carolina does not allow the use of nominal limits for compliance work originating in their state. In these cases, a window of ± 0.03 minutes must be used if the established retention time window is less than 0.03 minutes.

7.4 GAS CHROMATOGRAPHIC ANALYSIS

7.4.1 Before calibration is performed, and at the beginning of each 12 hour shift, the system is evaluated for analyte degradation by the analysis of a standard mix containing only endrin and 4,4'-DDT, often called an evaluation mix (EVAL):

COMPOUND	CONCENTRATION
Endrin	0.20 ng/uL
DDT	0.20 ng/uL

The % breakdown of DDT and the % breakdown of Endrin is calculated using the following formulas (PH = Peak Height):

$$\%\ \text{Breakdown DDT} = \frac{(PH\ [DDD] + PH\ [DDE])}{(PH\ [DDD] + PH\ [DDE] + PH\ [DDT])} * 100$$

$$\%\ \text{Breakdown Endrin} = \frac{(PH\ [\text{Endrin Aldehyde}] + PH\ [\text{Endrin Ketone}])}{(PH\ \text{of}\ [\text{Endrin Aldehyde}] + PH\ \text{of}\ [\text{Endrin Ketone}] + PH\ \text{of}\ [\text{Endrin}]} * 100$$

The breakdown of either DDT or Endrin in the evaluation mix cannot exceed 15%. If there is breakdown of either compound exceeding 15% before starting a calibration, instrument maintenance must be performed. A calibration can not be run until the

evaluation mix meets the acceptance criteria. If the exceeding breakdown occurs during the analysis sequence, then any samples analyzed after a failing evaluation mix must be reanalyzed. Reanalysis can not resume until after an acceptable evaluation mix.

7.4.2 Gently shake sample extracts before vialing for analysis.

7.4.3 All instrument injections are performed using the direct injection technique with an autosampler set for 2-5 uL injection volumes.

7.4.4 Samples are analyzed in a set referred to as an analysis sequence. The sequence begins with instrument calibration as listed in section 7.2 followed by sample extracts interspersed with mid-concentration calibration standards. Before any samples are analyzed the instrument must be calibrated by analyzing a six-point calibration or a 0.05ppm concentration standard (calibration verification standard). If a CV is run, the calculated concentration must not exceed a difference of ± 15%. DoD allows a difference of ± 20%. Each sample analysis must be bracketed with an acceptable initial calibration and closing CV or an opening CV and a closing CV for each 12-hour shift. The closing CV standard is at 0.25ppm. The calibration standard must also be injected at intervals of not less than once every ten samples and at the end of the analysis sequence. If the CV fails, the instrument is checked for any obvious problems and maintenance is performed if deemed necessary. All samples that were injected after the last standard that last met the QC criteria must be evaluated to prevent mis-quantitations and possible false negative results, and re-injection of the sample extracts may be required. However, if the standard analyzed <u>after</u> a group of samples exhibits a response for an analyte that is <u>above</u> the acceptance limit, i.e. >15%, and the analyte was not detected in the specific samples analyzed during the analytical shift, then the extracts for those samples do not need to be reanalyzed, as the CV standard has demonstrated that the analyte would have been detected were it present. In contrast, if an analyte above the QC limits <u>was</u> detected in a sample extract, then re-injection is necessary to ensure accurate quantitation. If an analyte was not detected in the sample and the standard response is more than 15% below the initial calibration response, then re-injection is necessary to ensure that the detector response has not deteriorated to the point that the analyte would not have been detected even though it was present.

7.4.5 The center of the retention time window for each analyte and surrogate is established by using the absolute retention time for each analyte and surrogate from the daily opening calibration verification or initial calibration.

7.4.6 The identification of Pesticides is based on agreement between the retention times of peaks in the sample chromatogram with the retention time windows established through the analysis of standards of the target analytes. An analyte

is tentatively identified when a peak from a sample falls within the absolute retention time window. Each tentative identification must be confirmed using a second GC column of dissimilar stationary phase or using another technique such as GC/MS. If the retention times of the peaks on both columns fall within the retention time windows on the respective columns, then the target analyte identification has been confirmed.

7.4.7 If the response for an analyte exceeds the calibration range of the system, the sample must be diluted and reanalyzed.

7.4.8 If peak detection and identification are prevented due to interferences, the hexane extract may need to undergo a cleanup. The extract may be subjected to a florisil cleanup (method 3620) and/or a sulfur cleanup (method 3660). Whenever a sample receives a cleanup, the associated QC must also be subjected to the same cleanup(s) and reanalyzed.

7.4.9 When a GC system is determined to be out of control because either a CV can not pass or a six point calibration does not meet the coefficient of determination criteria, instrument maintenance is likely necessary. Routine instrument maintenance may involve changing the septum, replacing the liner, clipping the pre-column, replacing the Y connector, or replacing the column. This information is recorded in the instrument run log (Figure 1). When an instrument requires more severe maintenance like replacing the ECD or an electronic board, this information is written in the instrument maintenance logbook. Refer to Katahdin SOP CA-101, Equipment Maintenance.

7.4.10 The concentration of an analyte is calculated by using the calibrated curve that is prepared in Target. When an analyte is identified, Target displays a concentration after the file is processed through the appropriate calibrated method.

7.4.11 The concentrations from the reports are then incorporated with the extraction data to arrive at a final concentration.

7.4.11.1 Water: Concentration (ug/L) = (C) (Vt)/(Vs)

7.4.11.2 Soil / Sediment:Concentration (mg/kg) = (C) (Vt)/(Ws) (D)

where, C = concentration calculated by Target in ug/ml
Vt = Volume of total extract including any instrument dilutions
Vs = Volume of sample extracted
Ws = Weight of sample extracted
D = Decimal total solids

7.5 Data Review

7.5.1 Initial Data Review

The initial data review is accomplished by the analyst who ran the samples. This review is of sufficient quality and detail to provide a list of samples that need to be reanalyzed or diluted and reanalyzed. The initial data review is performed on the detailed quantitation reports of the analyzed samples. This data review examines criteria that directly impact whether or not the sample needs to be reanalyzed and/or extracted. These criteria include:

- QC criteria for method blank, LCS, MS/MSD, and calibration – refer to section 8.0.
- Surrogate recovery
- Chromatography: cleanups, manual integration.
- Target compound detection: quantitation, confirmation, false positives.

The requirement of the GC laboratory is that this initial data review be completed no later than the end of the next workday. After the analyst has completed his or her initial data review, the information is then ready to be processed for reporting. Refer to section 7.7.

7.5.2 Surrogate recovery

All recoveries must meet the most recently laboratory established acceptance limits, which are listed on the Laboratory Surrogate Acceptance Limit sheet. For DoD work, the surrogates must meet the acceptance limits in the DoD QSM.

The sample is evaluated for recoveries of the two surrogates. The recoveries of both surrogates are evaluated on both the primary and secondary column. The higher recovery from both columns is reported on the analytical report for both surrogates. The sample chromatogram is reviewed for any interferences before determining whether to accept a sample based on the surrogate recoveries. If the surrogate recovery is affected by matrix interference, the sample result may be accepted with narration. If the recovery of one surrogate is outside of the laboratory established acceptance limit on one or both columns, and the second is acceptable, the data is narrated. If the recoveries for both surrogates are not acceptable because the recoveries are high and the sample does not contain any analytes above the PQL, the data is narrated. If the recoveries for both surrogates are low and there is no apparent matrix effect, the sample is reextracted.

For method blanks, if the recoveries of both surrogates are low or high, and the blank does not contain any target analytes above the PQL, and the

recoveries of both surrogates in the sample(s) are acceptable, the data is narrated. If the recoveries in the blank are low and it does not contain any target analytes above the PQL, and the recoveries in the samples are acceptable but the sample contains one or more target analytes above the PQL, the sample may be reextracted.

For laboratory control samples (LCS), if the only discrepancy in the extraction batch is with the LCS, and the analyte spike recoveries are acceptable, the data is narrated. If the recoveries of both the surrogates and the analyte spikes are low, the samples may need to be reextracted.

For DoD work, Q-flag all detected analytes in the sample if the surrogates fail the acceptance criteria.

7.5.3 Chromatography

The chromatography should be examined for the presence of any non-target peaks, which can be used as an indication of whether or not matrix interference might be influencing surrogate recoveries. If the chromatogram indicates interferences, then a cleanup may be needed. See section 7.4.7.

Manual integrations are to be performed when chromatographic conditions preclude the computer algorithm from correctly integrating the peak of concern. In no instance shall a manual integration be performed solely to bring a peak within criteria.

Each peak of concern is examined by the primary analyst to ensure that the peak was integrated properly by the computer algorithm. Should a manual integration be necessary (for instance, due to a split peak, peak tailing, or incomplete resolution of isomeric pairs), an “m” qualifier will automatically be printed on the quantitation report summary. The analyst will date and initial the “m” on the quanitation report summary and assign a code that indicates the reason for the manual integration. Refer to Katahdin SOP QA-812 “Manual Integration on GC/MS, GC, HPLC and IC Datasystems” for more information.

7.5.4 Target Compound Detection

GC analysis relies heavily on the experience of the analyst. Sample chromatograms must be evaluated focusing on scientific judgment, knowledge of the column behavior and matrix effects. The chromatogram from channel A is evaluated with that from channel B. If a target analyte is present on both channels and the concentration is within the calibration range, and the quantitation from both chromatograms agrees within ±40%, the analyte is considered to be present in the sample. In cases where the

RPD is greater than 40% and the analyte is reported, the analyte must be J-flagged indicating that the result is an estimated value. The higher of the two concentrations is reported unless matrix interference is causing erroneously high results. In this case report the lower result and narrate. Sometimes interference on one column (i.e. sulfur) will prevent a target analyte from detection and it is present on the conformational column. In this scenario, the result would be reported from one column and need to be "Q" flagged to indicate that it was not confirmed on a second column.

All flagged data must be discussed in the narrative

In order to avoid reporting false positives, identified peaks on a chromatogram may need to be undetected electronically in Target. The possible scenarios are: If an analyte is present on one column but its concentration is below the PQL, if an analyte is present on one column but does not confirm on the other channel, or if an analyte is present but its retention time is ±0.04 minutes or more than the retention time of the analyte in the preceding CV.

The GC Analyst must rely on technical experience in reviewing chromatograms in determining if a hit is an actual analyte or a false positive.

7.6 Reporting

After the chromatograms have been reviewed and any target analytes have been quantitated using Target, the necessary files are brought into QuickForms. Depending on the QC level requested by the client, a Report of Analysis (ROA) and additional reports, such as LCS forms and chronology forms, are generated. The package is assembled to include the necessary forms and raw data. The data package is reviewed by the primary analyst and then forwarded to the secondary reviewer. The secondary reviewer validates the data and checks the package for any errors. When completed, the package is sent to the department manager for final review. A completed review checklist (Figure 2) is provided with each package. The final data package from the Organics department is then processed by the Data Management department.

8.0 QUALITY CONTROL AND ACCEPTANCE CRITERIA

Refer to Table 1 and to details in this section for a summary of QC requirements, acceptance criteria, and corrective actions. These criteria are intended to be guidelines for analysts. The criteria does not cover all possible situations. If any of the QC requirements are outside the recovery ranges listed in this section or in Table 1, all associated samples must be evaluated against all the QC. In some cases data may be reported, but may be reanalyzed in other cases. Making new reagents and standards may be necessary if the standardization is

suspect. The corrective actions listed in this section and in Table 1 may rely on analyst experience to make sound scientific judgments. These decisions are based on holding time considerations, client and project specific Data Quality Objectives and on review of chromatograms. The Department Manager, Operations Manager, and/or Quality Assurance Officer may be consulted to evaluate data. Some samples may not be able to be reanalyzed within hold time. In these cases "qualified" data with narration may be advisable after consultation with the client.

In some cases the standard QC requirements listed in this section and in Table 1 may not be sufficient to meet the Data Quality Objectives of the specific project. Much of the work performed at the lab is analyzed in accordance with specific QC requirements spelled out in a project specific Quality Assurance Project Plan (QAPP) or in a program specific Quality Systems Manual (QSM). The reporting limits, acceptance criteria and/or corrective actions may be different than those specified in this SOP. In these cases the appropriate information will be communicated to the Department Manager and/or senior chemists before initiation of the analyses so that specific product codes can be produced for the project. In addition, the work order notes for each project will describe the specific QAPP or QSM to be followed.

8.1 For each analytical batch (up to 20 samples), a method blank, laboratory control sample (LCS), matrix spike and matrix spike duplicate are analyzed. They are carried through all stages of the sample preparation and analysis steps.

8.2 Spike concentrations: The LCS and the MS/MSD are spiked with the twenty single component pesticides at the same concentration. The spike concentrations are:

	WATER ug/L	SOILS ug/Kg
Pesticides	0.50	16.7

The surrogate spike concentrations in the final extract are:

	WATER ug/L	SOILS ug/Kg
Tetrachloro-m-xylene(TCX)	1.0	33.3
DCB	1.0	33.3

8.3 LCS and MS/MSD acceptance criteria and Corrective Action: All QC samples are calculated for percent recovery of the spiked analyte(s). The recoveries are compared to laboratory established acceptance limits. Refer to Katahdin SOP QA-808, "Generation and Implementation of Statistical QC Limits and/or Control Charts," current revision. For DoD work, the recoveries are compared to DoD QSM acceptance limits.

The LCS recoveries for all analytes are evaluated. All of the compounds of interest must fall within the established statistical limits with the following sporadic exceedance allowances. **South Carolina does not allow for marginal exceedances for compliance work originating in their state.**

Number of Analytes	Number of Allowable Exceedances
> 90	5
71 – 90	4
51 – 70	3
31 – 50	2
11 – 30	1
<11	0

If less than the number of allowable exceedances fail the statistical limits, no corrective action is needed. If greater than the number of allowable exceedances fail the statistical limits, corrective action may be taken. Corrective actions may vary with each situation. However, in the case where the failures are high and the samples are non-detect for those compounds, then no corrective action is required. Otherwise, corrective action may involve reanalysis or recalibration. The specific corrective actions taken will rely on analyst experience to make sound scientific judgments while considering client objectives, other quality control indicators and/or the ability to reanalyze a sample within holding time.

If a spike compound is outside of the acceptance limits in the matrix spike sample but is acceptable in the LCS, the data is considered acceptable. The cause of the failure is possibly attributable to matrix interference. However, if the compound fails in both the LCS and the MS/MSD, the result for that analyte is suspect and may not be reported for regulatory compliance purposes.

Please note that established acceptance limits that are wider than 70-130% may not be allowable for certain states, federal programs, or clients. For South Carolina, the acceptance limits for the spiked analytes will be 70-130% or narrower.

DoD work requires Q-flagging the specific LCS analytes that fail and are detected in the associated samples. MS/MSD failures require a J-flag in the parent sample for the analytes that fail the acceptance criteria.

8.4 Surrogate acceptance criteria and Corrective Action: Surrogate recoveries are calculated on all samples, blanks and spikes. The recoveries are compared to laboratory established acceptance limits.

When a sample has a surrogate that falls outside of the laboratory established acceptance limit window, the problem should be investigated. If the recovery looks like it is affected by the sample matrix, the sample may be reinjected to confirm matrix interference. When a sample has no detectable surrogate recovery, the sample should be reextracted.

For DoD work, Q-flag all detected analytes in the sample if the surrogates fail the acceptance criteria.

8.5 CAR: Whenever data is not acceptable because of a failing LCS or surrogate recovery, a corrective action report (CAR) must be initiated as soon as possible.

9.0 METHOD PERFORMANCE

The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. The MDLs are determined prior to sample analysis per type of instrument and filed with the Organic Department Manager and with the QAO. Refer to the current revision of Katahdin SOP QA-806, Method Detection Limit, Instrument Detection Limit and Reporting Limit Studies and Verifications, for procedures on determining the MDL.

Refer to the current revision of Method 8081 for other method performance parameters and requirements.

10.0 APPLICABLE DOCUMENTS/REFERENCES

Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition. Final Update IV, dated February, 2007, Method 8081B.

Department of Defense Quality Systems Manual for Environmental Laboratories (DoD QSM), Version 4.1, 04/22/09.

The National Environmental Laboratory Accreditation Conference (NELAC) Standards, June 2003.

Katahdin Analytical Services, Inc., SOP CA-106, Standard Preparation, Documentation and Traceability.

Katahdin Analytical Services, Inc., SOP CA-515, Preparation of Aqueous Samples for Pesticides/PCBs Analysis-Methods 3510 and 3520.

Katahdin Analytical Services, Inc., SOP CA-500, Preparation of Soil/Sediment Samples by Sonication Using Method 3550 for Subsequent Pesticides/PCBs Analysis.

Katahdin Analytical Services, Inc., SOP CA-524, Preparation of Soil/Sediment Samples by Soxhlet Extraction Using Method 3540 for Subsequent Pesticides/PCBs Analysis.

Katahdin SOP CA-101, Equipment Maintenance and Troubleshooting, current revision.

TITLE: ANALYSIS OF PESTICIDES BY GAS CHROMATOGRAPHY/ELECTRON CAPTURE DETECTOR (GC/ECD): SW-846 METHOD 8081

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TABLE 1

QC REQUIREMENTS

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action
Method blank	One per prep batch of twenty or fewer samples	No analyte detected >PQL DoD: no analyte detected >1/2 PQL and >1/10 the amount measured in sample	(1) Investigate source of contamination (2) Evaluate the samples and associated QC:i.e. If the blank results are above the PQL, report sample results which are < PQL or > 10X the blank concentration. Otherwise, reprep a blank and the remaining samples.
LCS	One per prep batch of twenty or fewer samples	Statistically derived limits. Note that limits wider than 70-130% are not allowable for some states, programs or clients, i.e. South Carolina. See also section 8.4 of this SOP for more information on allowable exceedances	(1) Evaluate the samples and associated QC: i.e. If an MS/MSD was performed and acceptable, narrate. If an LCS/LCSD was performed and only one of the set was unacceptable, narrate. If the surrogate recoveries in the LCS are low but are acceptable in the blank and samples, narrate. If the LCS recovery is high but the sample results are < PQL, narrate. Otherwise, reprep a blank and the remaining samples.
CCV	If calibration curve previously analyzed, analyze daily before samples and after every 10 samples.	± 15% D	(1) Evaluate the samples: If the %D>+15% and sample results are <PQL, narrate. If %D>±15% only on one channel, narrate. If %D>±15% for the closing CV, and is likely a result of matrix interference, narrate. Otherwise, reanalyze all samples back to last acceptable CV.
Matrix Spike\ Matrix Spike Duplicate	One for every set of 20 samples	Same as for LCS	(1) Evaluate the samples and associated QC: i.e. If the LCS results are acceptable, narrate. (2) If both the LCS and MS/MSD are unacceptable, reprep the samples and QC.
6 pt of INDAB mix with mid-pt cal of Toxaphene and Chlordane	Initial cal prior to sample analysis	6pt calibration coefficient of determination ≥ 0.990	(1) Repeat Initial calibration (2) If single pt cal Toxaphene, or Chlordane is identified in analysis of sample, 6 pt calibration run of identified compound with reanalysis of sample.
Independent calibration verification	Once after Initial calibration	± 20 % D	Reanalyze standard Reprep standard Reprep standard from fresh stock.
Demonstrate ability to generate acceptable P & A using 4 replicate analyses of a QC check standard	One time per analyst initially and annually thereafter.	All recoveries within method QC acceptance limits	Recalculate results; locate and fix problem; rerun P & A study for those analytes that did not meet criteria prior to sample analysis
MDL study	Refer to KAS SOP QA-806, “Method Detection Limit, Instrument Detection Limit and Reporting Limit Studies and Verifications”, current revision.		

TABLE 2

DoD QSM VERSION 4.1 QC REQUIREMENTS

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 significant 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.	Not Applicable (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.
LOD determination and verification	Refer to current revision of SOP QA-806				
LOQ establishment and verification	Refer to current revision of SOP QA-806				
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.	
Breakdown check (Endrin / DDT Method 8081 only)	At the beginning of each 12-hour period, prior to analysis of samples.	Degradation ≤ 15% for both DDT and Endrin.	Correct problem then repeat breakdown check.	Flagging criteria are not appropriate.	No samples shall be run until degradation ≤ 15% for both DDT and Endrin.
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 regression: r ≥ 0.995; Option 3: non-linear regression: coefficient of determination (COD) r2 ≥ 0.99 (6 points shall be used for second order). Mid point calibration of toxaphene and chlordane; if detected in sample, 6-point calibration is performed.	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, or toxaphene 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. On days when ICAL is not performed, the initial CCV is used.	NA.	NA.	

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TABLE 2

DoD QSM VERSION 4.1 QC REQUIREMENTS

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
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.
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 methods: 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 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. Retention time windows are updated per the method.
Method blank	One per preparatory batch.	No analytes detected > ½ RL (> RL for common lab contaminants) 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 the problem. Report sample results that are <LOD or >10x the blank concentration. Reprepare and reanalyze the method blank and all associated samples with results > LOD and < 10x the contaminated blank result. Contact Client if samples cannot be reprepped within hold time.	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.
Laboratory control sample (LCS) containing all analytes to be reported, including surrogates	One per preparatory batch.	The laboratory shall use laboratory control limits (CLs) or use DoD-generated LCS-CLs, if available depending on project requirements. In-house CLs may not be greater than ± 3 times the standard deviation of the mean LCS recovery. A number of analytes may fall outside the CL but within marginal exceedance limit depending on the total number of analytes in the LCS.	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. Refer to Table G-1 for number of marginal exceedences allowed. Contact Client if samples cannot be reprepped within hold time.	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.

TABLE 2

DoD QSM VERSION 4.1 QC REQUIREMENTS

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Matrix spike (MS)	One per preparatory batch per matrix if sufficient sample is available.	For matrix evaluation, use laboratory LCS CLs or use DoD-generated LCS-CLs, if available depending on project requirements.	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 there is a matrix effect or analytical error.
Matrix Spike duplicate (MSD)	One per preparatory batch per matrix if sufficient sample is available.	MSD: For matrix evaluation, use laboratory LCS CLs or use DoD-generated LCS-CLs, if available depending on project requirements. MS/MSD: RPD ≤ 30%.	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.	The laboratory shall use laboratory surrogate CLs or use DoD-generated surrogate CLs, if available depending on project requirements.	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. Contact Client if samples cannot be reprepped within hold time.	Apply Q-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 as for initial or primary column analysis. Results between primary and second column RPD ≤ 40%.	NA.	Apply J-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 (see Box D-16).
Results reported between DL and LOQ	NA.	NA.	NA.	Apply J-flag to all results between DL and LOQ.	

TABLE 3

SUMMARY OF METHOD MODIFICATIONS

TOPIC	KATAHDIN SOP CA-302-11	METHOD 8081, current revision
Apparatus/ Materials	None	
Reagents	None	
Sample preservation/ handling	None	
Procedures	7.3.5 If the calculated retention time window results in a value of 0.03 minutes or less, the laboratory will apply nominal windows. This is done in order to avoid any false negative hits because of the window being to narrow. The windows are: ± 0.05 for Heptachlor, Aldrin and all BHC compounds, ± 0.07 for all other target analytes. By utilizing these windows, a false positive hit may be initially indicated, but an experienced analyst could determine a false positive from scrutinizing the chromatograms. Please note that the use of nominal retention time windows may not be allowable for certain states, federal programs, or clients. South Carolina does not allow the use of nominal limits for compliance work originating in their state. In these cases, a window of ± 0.03 minutes must be used if the established retention time window is less than 0.03 minutes.	7.6.3 If the standard deviation of the retention times for a target compound is 0.000 (i.e., no difference between the absolute retention times), then the laboratory may either collect data from additional injections of standards or use a default standard deviation of 0.01 minutes. (Recording retention times to three decimal places rather than only two should minimize the instances in which the standard deviation is calculated as 0.000).
QC - Continuing Calibration	None	
QC - LCS	None	
QC - Accuracy/Precision	None	
QC - MDL	PQL – Practical Quantitation Level – three to ten times the MDL.	EQL – Estimated Quantitation Level – five to ten times the MDL

TITLE: ANALYSIS OF PESTICIDES BY GAS CHROMATOGRAPHY/ELECTRON CAPTURE DETECTOR (GC/ECD): SW-846 METHOD 8081

FIGURE 1

EXAMPLE OF INSTRUMENT RUN LOG

Katahdin Analytical Services, Inc.
Instrument: GC01
Amount Injected 2 µl
Reviewed by/ Date:

GC Laboratory Instrument Runlog
Method: SW846 8081 / 8082 / 8151
(circle) EPA 504.1 / 556 / 608
OLC03.2 / SOM01.2
OLM03.2 / OLM04.3

Date	Init.	Result File	Sample ID	Y/N	Method	Column	Comments
042110	RCT	1DD00251	WG76497-3 3550	Y	PEST035	327/328	
		252	WG76282-3 3510				↑meth B
		253	-4				
		254	SD1976-1				
		255	-2				
		256	-3				
		257	-4				
		258	SD2108-1 3550				
		259	Hexane	N			
		260	INDAB 0.025	Y			3↑B, 2↑A P5755
042210		261	Hexane	N			
		262	eval	Y			P5594
		263	INDAB 0.05	Y			↑methA&B P5754
		264	TC 0.5	Y	PEST035C		
		265	0.05				
		266	0.1				
		267	0.25				
		268	1				
		269	2.5				
		270	WG76373-1 3550	Y			
		271	-2				↓ES II A, ↓ES I Both
		272	SD1976-5 3510	Y			
		273	-8				
		274	-9				↓DCBA&B
		275	-10				↓DCBA&B
		276	-11				
		277	SD1789-3DL 3550				1:5 500/1000 ↑DCBA, ↓DCBB
		278	-8DL				1:2 500/1000 ↑DCBA
		279	SD1837-4RA				
		280	Hexane	N			

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TITLE: ANALYSIS OF PESTICIDES BY GAS CHROMATOGRAPHY/ELECTRON CAPTURE DETECTOR (GC/ECD): SW-846 METHOD 8081

FIGURE 2

DATA REVIEW CHECKLIST

PRIMARY REVIEW CHECKLIST

Verbal Due Date _____ (☐ **Verbals turned in**). **DueDate**_____

Client:		Primary	Secondary
Method:		Date:	Date:
SDG No:	Level:	Initials:	Initials:
KAS No:			Approved : ☐ Yes

DODQSM 3.0 ☐ **DODQSM 4.1** ☐ **WITH LAB. LIMITS** ☐
QUAPP ☐ **LAB** ☐ (*REPORT* ***ND's*** *to* ***MDL*** ☐)

List all curves that are scanned. _____ _____

_____ _____ _____ _____

Narrate which QC limits were used for (Surr., LCS,s MS/MSDs.) _____

All needed forms are present . _____

Correct Work Order Number or SDG name (all forms). _____

Correct project name and spelling (all forms). (Truncated ☐). _____

Correct file numbers (all forms). _____

Analysis Date Correct. _____

Extraction Method & Analysis Method Correct. _____

Product list compared to ROAs (compounds & PQLs). _____

Chromatogram reviewed for unlabeled peaks (check product list). _____

Flagging of all ROAs correct (Florida Flagging ☐). _____

All tunes included (level IV) . _____

All log book pages included (Soil weights,TCLP & SPLP). _____

Verify DOD QSM criteria. _____

Narrate any method deviations. (Blanks, LCS,s etc.) _____

Sign & Date Manual integration **(Narrate as needed).** _____

Sample I.D's Truncated (**NARRATED**). YES ☐ Please list KAS # below :

_____

QA-044 – Revision 1 – 04/05/2010

TITLE: ANALYSIS OF PESTICIDES BY GAS CHROMATOGRAPHY/ELECTRON CAPTURE DETECTOR (GC/ECD): SW-846 METHOD 8081

FIGURE 3

PQLS FOR METHOD 8081

Parameter/Method	Analyte	Practical Quantitation Level (PQL)	
		Waters (ug/L)	Soils (ug/kg)
Organochlorine	Aldrin	0.05	1.7
Pesticides	Alpha BHC	0.05	1.7
	Beta BHC	0.05	1.7
SW3510/SW8081B (W)	Delta BHC	0.05	1.7
SW3520/SW8081B (W)	Gamma BHC (Lindane)	0.05	1.7
SW3550/SW8081B (S)	Chlordane	0.50	17
	alpha-Chlordane	0.05	1.7
	gamma-Chlordane	0.05	1.7
	4,4'-DDD	0.10	3.3
	4,4'-DDE	0.10	3.3
	4,4'-DDT	0.10	3.3
	Dieldrin	0.10	3.3
	Endosulfan I	0.05	1.7
	Endosulfan II	0.10	3.3
	Endosulfan Sulfate	0.10	3.3
	Endrin	0.10	3.3
	Endrin Aldehyde	0.10	3.3
	Endrin Ketone	0.10	3.3
	Heptachlor	0.05	1.7
	Heptachlor Epoxide	0.05	1.7
	Methoxychlor	0.50	17
	Toxaphene	1.00	33

KATAHDIN ANALYTICAL SERVICES, INC.
STANDARD OPERATING PROCEDURE

SOP Number: CA-312
Revision History
Cover Page
Page 1

TITLE: METHOD FOR THE DETERMINATION OF VOLATILE PETROLEUM HYDROCARBONS (MADEP - VPH)

Prepared By: Peter Lemay Date: 4/98

Approved By:

Group Supervisor: [signature] Date: 2/15/01

Operations Manager: John C. Burton Date: 2/14/01

QA Officer: Deborah J. Nadeau Date: 2.14.01

General Manager: [signature] Date: 2/14/01

Revision History:

SOP Revision	Changes	Approval Initials	Approval Date	Effective Date
01	Format changes, added pollution prevention, other updated changes to all sections.	DN	2.14.01	2/14/01
02	minor changes to sections 5,6 + 7. Grammatical errors corrected	DN	4.9.02	4.9.02
03	added definitions modified Sections 5,7,8 and 9 modified table to include extra cmpds	LAD	01-31-05	01-31-05
04	Added pollution control and waste disposal to Sect. 14. Added kims definition to sect. 1.1 and 7.9.1. Removed all references to 60mL vials. Edited AQ LCS prep. minor changes throughout to reflect current practice. Fixed numbering and formatting	LAD	09/07	09/07
05	Corrected references in text to Tables 1,3 & 4. Reworded Sect.s 8.14.4, 8.1.5, 8.4.2.3 and 8.4.3 for clarity. Changed Lab fortified blank to LCS and lab fortified Matrix to MS	LAD	03/08	03/08

TITLE: METHOD FOR THE DETERMINATION OF VOLATILE PETROLEUM HYDROCARBONS (MADEP - VPH)

SOP Revision	Changes	Approval Initials	Approval Date	Effective Date
06	Removed references to obsolete method CA - 320 (method 5030)	LAN	09/08	09/08
07	Sect. 7: Added calibration procedure using CFs and % RSD, removed calibration procedure using linear regression, corrected soil calculation. Sect. 8: Clarified MS/D frequency. Removed annual RL verification and added non-conformance report criteria. Sect 9 & 10: Added references. Added ICV criteria.	LAN	04/10	04/10

TITLE: METHOD FOR THE DETERMINATION OF VOLATILE PETROLEUM HYDROCARBONS (MADEP - VPH)

Please acknowledge receipt of this standard operating procedure by signing and dating both of the spaces provided. Return the bottom half of this sheet to the QA Department.

I acknowledge receipt of copy ___ of document **SOP CA-312-07** titled **METHOD FOR THE DETERMINATION OF VOLATILE PETROLEUM HYDROCARBONS (MADEP - VPH).**

Recipient: _____ Date: _____

KATAHDIN ANALYTICAL SERVICES, INC.
STANDARD OPERATING PROCEDURE

I acknowledge receipt of copy ___ of document **SOP CA-312-07** titled **METHOD FOR THE DETERMINATION OF VOLATILE PETROLEUM HYDROCARBONS (MADEP - VPH).**

Recipient: _____ Date: _____

TITLE: METHOD FOR THE DETERMINATION OF VOLATILE PETROLEUM HYDROCARBONS (MADEP - VPH)

1.0 SCOPE AND APPLICATION

This method is designed to measure the collective concentrations of volatile aliphatic and aromatic petroleum hydrocarbons in water and soil. Volatile aliphatic hydrocarbons are collectively quantitated within two ranges: C_5 through C_8, and C_9 through C_{12}. Volatile aromatic hydrocarbons are collectively quantitated within the C_9 to C_{10} range. These aliphatic and aromatic hydrocarbon ranges correspond to a boiling point range between approximately 36°C and 220°C.

This method is based on a purge-and-trap, gas chromatography (GC) procedure using in-series Photoionization and Flame Ionization Detectors (PID/FID). This method should be used by, or under the supervision of, analysts experienced in the use of purge-and-trap systems and gas chromatographs. The analysts should be skilled in the interpretation of gas chromatograms and their use as a quantitative tool.

This method is also able to measure the individual concentrations of the VPH Target Analytes benzene, toluene, ethylbenzene, xylenes (BTEX), naphthalene, and methyl-tert-butylether (MTBE) in water and soil. Use of this method to identify and quantitate these Target Analytes is optional.

Petroleum products suitable for evaluation by this method include gasoline, mineral spirits, and certain petroleum naphthas. This method, in and of itself, is not suitable for the evaluation of kerosene, jet fuel, heating oils, lubricating oils, and/or other petroleum products that contain a significant percentage of hydrocarbons heavier than C_{12}.

This method includes a series of data manipulation steps to determine the concentrations of aliphatic and aromatic ranges of interest.

Like all GC procedures, this method is subject to a "false positive" bias in the reporting of Target Analytes, in that non-targeted hydrocarbon compounds eluting or co-eluting within a specified retention time window may be falsely identified and/or quantitated as a Target Analyte. Confirmatory analysis by a GC/MS procedure or other suitable method is recommended in cases where a Target Analyte reported by this method exceeds an applicable reporting or cleanup standard, and/or where co-elution of a non-targeted hydrocarbon compound is suspected.

This is a performance-based method. Modifications to this method are permissible, provided that adequate documentation exists, or has been developed, to demonstrate an equivalent or superior level of performance. MADEP encourages methodological innovations which (a) better achieve method and/or data quality objectives, (b) increase analytical precision and accuracy, (c) reduce analytical uncertainties and expenses, and/or (d) reduce the use of toxic solvents and generation of hazardous wastes. Laboratories that modify this method must achieve all required performance and acceptance standards, and must have on file a Standard Operating Procedure which thoroughly describes the revised

or alternative method, and documentation which demonstrates an equivalent or superior level of performance. All significant modifications to the method must be disclosed and described on the data report form.

1.1 Definitions

Analytical Batch is defined as a group of field samples with similar matrices which are processed as a unit. For Quality Control purposes, if the number of samples in such a group is greater than 20, then each group of 20 samples or less are defined as separate analytical batches.

Calibration Check Standard is defined as a calibration standard used to periodically check the calibration state of an instrument. The calibration check standard is prepared from the same stock solution as calibration standards, and is generally one of the mid-level range calibration standard dilutions.

Calibration Standards are defined as a series of standard solutions prepared from dilutions of a stock standard solution, containing known concentrations of each analyte and surrogate compound of interest.

C_5 through C_8 Aliphatic Hydrocarbons are defined as all aliphatic hydrocarbon compounds which elute on the FID chromatogram from n-pentane (C_5) to just before n-nonane (C_9).

C_9 through C_{12} Aliphatic Hydrocarbons are defined as all aliphatic hydrocarbon compounds which elute on the FID chromatogram from n-nonane (C_9) to just before naphthalene.

C_9 through C_{10} Aromatic Hydrocarbons are defined as all aromatic hydrocarbon compounds which elute on the PID chromatogram from just after o-xylene to just before naphthalene. Although it is an aromatic compound with 10 carbon atoms, naphthalene is excluded from this range because it is evaluated as a separate (Target) analyte.

Field Duplicates are defined as two separate samples collected at the same time and place under identical circumstances and managed the same throughout field and laboratory procedures. Analyses of field duplicates give a measure of the precision associated with sample collection, preservation, and storage, as well as laboratory procedures.

Laboratory Control Sample (LCS) is defined as a laboratory reagent grade water blank or clean sand blank fortified with a matrix spiking solution.

Laboratory Duplicates are defined as split samples taken from the same sampling container and analyzed separately with identical procedures. The analysis of laboratory duplicates give a measure of the precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

Matrix Spike (MS) Sample is defined as an environmental sample which has been spiked with a matrix spiking solution containing known concentrations of method analytes. The MS sample is treated and analyzed exactly as a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined through the separate analyses of a laboratory or field duplicate, and the measured values in the MS sample corrected for background concentrations.

Laboratory Method Blank (LMB) is defined as an aliquot of laboratory reagent grade water or clean sand spiked with a surrogate standard. The laboratory method blank is treated exactly as a sample, exposed to all glassware, solvents, reagents, and equipment. A laboratory method blank is analyzed with every batch of samples, to determine if method analytes or other interferences are present in the laboratory environment, reagents, or equipment.

Matrix Spiking Solution is defined as a solution prepared independently from the calibration standards, containing known concentrations of method analytes.

System Solvent Blank is defined as an aliquot of method solvent (e.g., methanol) that is directly purged into the GC system. The purpose of the Solvent Blank is to determine the level of noise and baseline rise attributable solely to the GC system, in the absence of any other analytes or contaminants.

Target VPH Analytes are defined as benzene, toluene, ethylbenzene, m-xylene, p-xylene, o-xylene, naphthalene, and methyl-tert-butylether.

Unadjusted C_5 through C_8 Aliphatic Hydrocarbons are defined as all hydrocarbon compounds which elute on the FID chromatogram from n-pentane (C_5) to just before n-nonane (C_9).

Unadjusted C_9 through C_{12} Aliphatic Hydrocarbons are defined as all hydrocarbon compounds which elute on the FID chromatogram from n-nonane (C_9) to just before naphthalene.

Volatile Petroleum Hydrocarbons (VPH) are defined as collective fractions of hydrocarbon compounds eluting from n-pentane to naphthalene, excluding Target VPH Analytes. VPH is comprised of C_5 through C_8 Aliphatic Hydrocarbons, C_9 through C_{12} Aliphatic Hydrocarbons, and C_9 through C_{10} Aromatic Hydrocarbons.

Volatile Petroleum Hydrocarbon (VPH) Component Standard is defined as a 15 component mixture of the aliphatic and aromatic compounds listed in Table 3. The compounds comprising the VPH Component Standard are used to (a) define the individual retention times and chromatographic response factors for each of the Target VPH Analytes, (b) define and establish the windows for the collective aliphatic and aromatic hydrocarbon ranges of interest, and (c) determine average chromatographic response factors that can in turn be used to calculate the collective concentration of hydrocarbons within these ranges.

KATAHDIN INFORMATION MANAGEMENT SYSTEM (KIMS): A complete multi-user system with the capabilities of integrating laboratory instrumentation, generating laboratory worksheets, providing laboratory status reports, and generating final reports. KIMS utilizes these features through a database.

PE NELSON TURBOCHROM: A data acquisition system that is used to collect chromatographic data. The system can also be used to archive raw data files.

TARGET: A software system that combines full processing, reporting and comprehensive review capabilities, regardless of chromatographic vendor and data type.

TARGET DB: An oracle database used to store and organize all Target data files.

QUICKFORMS: A laboratory reporting software for Target and Target DB. The QuickForms report module for Target is preconfigured with generalized forms and US EPA CLP report forms and disk deliverables, which can be customized.

1.2 Responsibilities

This method is restricted to use by, or under the supervision of analysts experienced in the analysis of VPH by MADEP VPH-04-1.1. Analysts should be skilled in the interpretation of gas chromatograms and their use as a quantitative tool. Each analyst must demonstrate and document their ability to generate acceptable results with this method. Refer to Katahdin SOP QA-805, current revision, "Personnel Training & Documentation of Capability".

It is the responsibility of all Katahdin technical personnel involved in analysis of VPH by MADEP VPH-04-1.1 to read and understand this SOP, to adhere to the procedures outlined, and to properly document their data in the appropriate lab notebook. Any deviations from the test or irregularities with the samples should also be recorded in the lab notebook and reported to the Department Manager or designated qualified data reviewer responsible for this data.

It is the responsibility of the Department Manager to oversee that members of their group follow this SOP, to ensure that their work is properly documented and to initiate periodic review of the associated logbooks.

1.3 Safety

Users of this procedure must be cognizant of inherent laboratory hazards, proper disposal procedures for contaminated materials and appropriate segregation of hazardous wastes. The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical should be treated as a potential health hazard. A reference file of material safety data sheets is available to all personnel involved in the chemical analysis. Everyone involved with the procedure must be familiar with the MSDSs (material safety data sheets) for all the materials used in this procedure.

Each qualified analyst or technician must be familiar with Katahdin Analytical Environmental Health and Safety Manual including the Katahdin Hazardous Waste Plan and must follow appropriate procedures. These include the use of appropriate personal protective equipment (PPE) such as safety glasses, gloves and lab coats when working with chemicals or near an instrument and not taking food or drink into the laboratory. Each analyst should know the location of all safety equipment. Each analyst shall receive a safety orientation from their Department Manager, or designee, appropriate for the job functions they will perform.

1.4 Pollution Prevention/Waste Disposal

Whenever possible, laboratory personnel should use pollution prevention techniques to address their waste generation. Refer to the current revision of the Katahdin Hazardous Waste Management Plan for further details on pollution prevention techniques.

Wastes generated during the preparation of samples must be disposed of in accordance with the Katahdin Hazardous Waste Management Plan and Safety Manual and SOP SD-903, "Sample Disposal," current revision. Expired standards are lab packed, placed in the Katahdin hazardous waste storage area, and disposed of in accordance with this SOP. Purge vial and methanol waste are disposed of in the "A" waste satellite accumulation area located between GC04 and GC09.

2.0 SUMMARY OF METHOD

2.1 Samples are analyzed using purge-and-trap sample concentration. The gas chromatograph is temperature programmed to facilitate separation of organic

compounds. Detection is achieved by a Photoionization detector (PID) and flame ionization detector (FID) in series. Quantitation is based on comparing the PID and FID detector response of a sample to a standard comprised of aromatic and aliphatic hydrocarbons. The PID chromatogram is used to determine the individual concentrations of targeted analytes and collective concentration of aromatic hydrocarbons within the C_9 through C_{10} range. The FID chromatogram is used to determine the collective concentration of aliphatic hydrocarbons within the C_5 through C_8 and C_9 through C_{12} ranges.

2.2 This method is suitable for the analysis of waters, soils, and sediments. Water samples may be analyzed directly for volatile petroleum hydrocarbons by purge-and-trap concentration and gas chromatography. Soil samples are dispersed in methanol to dissolve the volatile organic constituents. A portion of the methanol solution is then analyzed by purge-and-trap GC.

2.3 This method is based on (1) USEPA Methods 5030, 8000, 8020, and 8015, SW-846, "Test Methods for Evaluating Solid Wastes", 3rd Edition, 1986; (2) Draft "Method for Determination of Gasoline Range Organics", EPA UST Workgroup, November, 1990; and (3) "Method for Determining Gasoline Range Organics", Wisconsin Department of Natural Resources, PUBL-SW140, 1992.

3.0 INTERFERENCES

3.1 Samples can become contaminated by diffusion of volatile organics through the sample container septum during shipment and storage or by dissolution of volatiles into the methanol used for preservation. Trip blanks prepared from both laboratory reagent grade water and methanol should be carried through sampling and subsequent storage and handling to serve as a check on such contamination.

3.2 Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. To reduce carryover, the sample syringe and/or purging device must be rinsed between samples with laboratory reagent grade water or solvent. For volatile samples containing high concentrations of water-soluble materials, suspended solids, high boiling-point compounds or organohalides, it may be necessary to wash the syringe or purging device with a detergent solution, rinse with distilled water, and then dry in an oven at 105°C between analyses. The trap and other parts of the system are also subject to contamination, therefore, frequent bake-out and purging of the entire system may be required. A screening step is recommended to protect analytical instrumentation. Whenever an unusually concentrated sample is encountered, it must be followed by the analysis of a system solvent blank or laboratory method blank to check for cross-contamination.

3.3 Certain organic compounds not associated with releases of petroleum products, including chlorinated solvents, ketones, and ethers, will be quantitated as Volatile Petroleum Hydrocarbons. If necessary and/or desirable, additional sample cleanup and/or analytical procedures may be employed to minimize or document the presence of such compounds.

3.4 The response selectivity of a photoionization detector (PID) is used in this method to differentiate aromatic hydrocarbons from aliphatic hydrocarbons. All compounds eluting on the PID chromatogram after o-xylene are identified by the method as aromatic hydrocarbons. This will lead to an overestimation of aromatic hydrocarbons within samples, as certain aliphatic compounds will elicit a response on the PID, particularly unsaturated compounds such as alkenes. The significance and implications of this overestimation will vary from sample to sample; where less conservative data are desired, additional actions should be considered to minimize the detection of non-aromatic compounds, including the use of a lower energy PID lamp, different chromatographic columns, and/or addition of a pre-analysis sample cleanup step.

4.0 APPARATUS AND MATERIALS

4.1 The following glassware is used in this method:

4.1.1 VOC Vials: 40 mL VOC vials with Teflon/ silicone septa for waters and soils.

4.1.2 Class "A" Volumetric flasks: 10 mL, 50 mL, 100 mL, and 1,000 mL with a ground-glass stopper.

4.1.3 Disposable pipettes: Pasteur.

4.2 Analytical balance: An analytical balance capable of accurately weighing 0.0001 g must be used for weighing standards. A top-loading balance capable of weighing to the nearest 0.1 g must be used for weighing soil samples.

4.3 Gas Chromatography

4.3.1 Gas Chromatograph: An analytical system complete with temperature programmable gas chromatograph and purge-and-trap concentrator. The data station must be capable of storing and reintegrating chromatographic data and must be capable of determining peak areas using a forced baseline projection.

4.3.2 Chromatographic Column: The required column is: 105M x 0.53 mm I.D. Restek RTX 502.2 with 3 micron film thickness, or column with equivalent chromatographic properties.

NOTE: Based upon data obtained from the Round Robin testing programs, the choice of chromatographic column may have a significant impact on the apportionment and quantitation of aliphatic and aromatic compounds within the fractional ranges specified in this method. Substitution of the required column is not allowed, unless it can be demonstrated that the selected column has equivalent chromatographic properties and retention times for the aliphatic and aromatic compounds and ranges of interest. To demonstrate equivalency of column chromatography, a neat gasoline standard must be analyzed on both the required column and the proposed substitute column, with all other run and system parameters held constant. The concentrations of C_5-C_8 and C_9-C_{12} Aliphatic Hydrocarbons must be determined for each column (in which the concentration of the Target/aromatic analytes have been subtracted from the GC/FID response). The Relative Percent Difference between the concentrations of each fraction obtained for each column must be equal to or less than 25%.

4.3.3 Detectors: The method requires the use of a Photoionization Detector (PID) in series with a Flame Ionization Detector (FID); the PID first in the series. The method is based upon the use of a 10.0 +/- eV PID lamp, although lower energy lamps are permissible in order to minimize PID response to aliphatic compounds. In lieu of an in-series arrangement, in-parallel PID and FID units may be also used.

4.3.4 Purge-and-trap device: The purge-and-trap device consists of a sample purger, a trap, and a desorber. Several complete devices are commercially available.

4.3.4.1 The purging chamber must be designed to accept 5 mL samples with a water column at least 3 cm deep. Purging devices larger than 5 mL have a reduced purging efficiency and should not be used. The gaseous headspace between the water column and the top of the vessel should be at least 3 cm deep. The gaseous headspace between the water column and the trap must have a total volume of less than 15 mL. The purge gas must pass through the water column as finely divided bubbles with a diameter of less than 3 mm at the origin. Fritted glass or needle sparge cells may be used. If needle sparge cells are used, the purge gas must be introduced no more than 5 mm from the base of the water column. Alternate sample

purge devices may be used, provided equivalent performance is demonstrated.

4.3.4.2 The trap should be at least 25 cm long and have an inside diameter of at least 0.105 inches. The trap should be packed with 400 mg of Carbopack B (Supelco Cat. No. 209273). Alternative trap packing materials include: Tenax GC (or equivalent); 7.6 cm Carbopack B and 1.3 cm Carbosieve S-III (Supelco Cat No. 2-0321); 7 cm Carbopack C and 1.2 cm Carbopack B (Supelco Cat No. 2-1064); or equal volumes of Tenax, silica gel, and charcoal as described in EPA SW-846 Method 5030. In general, Carbopack trap packing materials are recommended because they have less of a tendency to retain methanol, which could interfere with the elution of pentane and quench the FID flame. The trap length and packing materials may be varied as long as equivalent performance has been verified.

4.3.4.3 Prior to initial use, the Carbopack B trap should be conditioned overnight at 270°C by backflushing with an inert gas flow of at least 20 mL/min. Vent the trap effluent to a hood, not to the analytical column. Prior to daily use, the trap should be conditioned for 10 min. at 260°C with backflushing. The trap may be vented to the analytical column during daily conditioning, however, the column must be run through the temperature program prior to analysis of samples. Devices other than the traps recommended in Section 4.3.4.2 should be conditioned and desorbed according to the manufacturer's guidelines.

4.3.4.4 The desorber should be capable of rapidly heating the trap to 240°C for desorption.

4.4 Data System: A data system which allows the continuous acquisition of data throughout the duration of the chromatographic program must be interfaced to the GC. The data system must be capable of storing and re-integrating chromatographic data and must be capable of determining peak areas using a forced baseline projection. All data editing will be reviewed by the Department Manager or qualified designee before samples are reported.

4.5 Ultrasonic bath.

4.6 Syringes: 5 mL Luerlock glass hypodermic and 5 mL gas-tight syringe with shutoff valve.

4.7 Syringe valve: Two-way, with luer ends.

4.8 Microsyringes: 1 µL, 5 µL, 10 µL, 25 µL, 100 µL, 250 µL, 500 µL, and 1,000 µL.

4.9 Spatula: Stainless steel.

5.0 REAGENTS

5.1 Reagents

5.1.1 Organic-free water: carbon filtered ASTM Type II water (laboratory reagent grade water)

5.1.2 Methanol: purge-and-trap grade or equivalent; store away from other solvents to prevent cross-contamination

5.1.3 Organic-free sand: sand baked in an oven at 400°C for four hours to remove organic contaminants

5.2 Stock Standard Solution

5.2.1 The stock standard solution consists of the 15 VPH component standards and a surrogate standard that is purchased from vendors like ULTRA Scientific at a concentration of 1000 µg/mL. The solution is stored at -10°C to -20°C and protected from light.

5.2.2 The stock standard solution must be replaced after six months from the date of opening or sooner if the manufacture's date is less.

5.3 Primary Dilution Standard

5.3.1 The primary dilution standards are prepared in methanol at concentrations listed in Table 3. These standards are stored at -10°C to -20°C.

5.3.2 The primary dilution standards should be replaced at least monthly.

5.4 VPH Calibration Standards

VPH calibration standards are prepared by injecting an aliquot of either the primary dilution standard or the stock standard directly into the 5 mL syringe. The volumes added are listed in Table 3.

5.5 Surrogate Standard

5.5.1 The analyst must monitor both the performance of the analytical system and the effectiveness of the method in dealing with sample matrices by spiking each sample, blank, and matrix spike with a surrogate standard. The

surrogate standard is also added to the VPH calibration standard solutions. The recommended surrogate standard is 2,5-dibromotoluene, which elutes after all aliphatic and aromatic compounds of interest. The use of another surrogate compound is permissible.

5.5.2 Surrogate Spiking Solution

5.5.2.1 For aqueous samples, from a stock standard solution prepare a surrogate spiking solution at 50 µg/mL in methanol. Add 5 µL of this surrogate spiking solution directly into the 5 mL syringe with every aqueous sample, method blank, and matrix spike. This will correlate to a concentration of 50 µg/L in the sample.

5.5.2.2 For soil samples, using a 200 µg/mL stock solution add 1 mL to every soil sample, method blank, and matrix spike during the extraction step. This will correlate to a concentration of 50 µg/L in the sample for a 15 g extraction.

5.6 Matrix Spiking Solution

5.6.1 The matrix spiking solution consists of the Targeted VPH analytes.

5.6.1.1 For aqueous samples, using a stock standard solution at a concentration of 50 µg/mL in methanol, add 10 µL directly into the 5 mL syringe with every aqueous laboratory control sample (LCS) and matrix spike sample (MS). This will correlate to a concentration of 100 µg/L in the sample.

5.6.1.2 For soil samples, using a stock solution at a concentration of 500/1000/1500 µg/mL in methanol, add 500 µL to every LCS and MS.

6.0 SAMPLE COLLECTION, PRESERVATION AND HANDLING

6.1 Aqueous Samples

6.1.1 Aqueous samples should be collected in duplicate (or the number of vials directed by the laboratory) without agitation and without headspace in contaminant-free glass VOC vials with Teflon-lined septa screw caps. The Teflon liner must contact the sample. Samples must be acidified to a pH of 2 or less at the time of collection. This can generally be accomplished by adding 3 or 4 drops (0.1 to 0.2 mL) of 1:1 HCl (1 part laboratory reagent

grade water and 1 part concentrated HCl) to a 40 mL sample vial. Samples must be cooled to 4°C immediately after collection.

6.1.2 A chain of custody form must accompany all sampling vials and must document the date and time of sample collection and acid preservation. The pH of all water samples must be determined by the laboratory unless sample vials containing acid for field preservation were supplied by the laboratory (this must be noted on the chain of custody). The pH measurement may be performed on left over sample. Any sample found to contain a pH above 2 must be so noted on the laboratory/data report sheet.

6.1.3 A laboratory reagent grade water trip blank should accompany each batch of water samples.

6.1.4 Any sample received by the laboratory that is not packed in ice or cooled to 4°C must be so noted on the laboratory/data report sheet.

6.1.5 Aqueous samples must be analyzed within 14 days of collection.

6.2 Soil Samples

6.2.1 Soil samples must be collected in a manner that minimizes sample handling and agitation. The use of specially designed air-tight collection samplers or a 30 mL plastic syringe with the end sliced off is recommended. All sediment must be removed from the glass threads of the vial to ensure an adequate seal. Samples must be cooled to 4°C immediately after collection.

6.2.2 **Methanol preservation of soil samples is mandatory.** Methanol (purge-and-trap grade) must be added to the sample vial before or immediately after sample collection. In lieu of the in-field preservation of samples with methanol, soil samples may be obtained in specially-designed air-tight sampling devices, provided that the samples are extruded and preserved in methanol within 48 hours of collection. Additional details and recommendations on soil sampling may be found in method MADEP VPH-04-1.1.

6.2.3 The desired ratio of methanol-to-soil is 1 mL methanol/1 gram soil, ± 25%. The exact weight of the soil sample and volume of methanol must be known or ascertained by the laboratory when calculating and reporting soil concentration data. A recommended practice is for a laboratory to provide to a field sampling technician labeled, pre-weighed sampling vials with a measured volume of methanol, and a scribed mark indicating the level of methanol that should exist in the vial when the required quantity of soil sample has been added. This requires an estimate on the density and

moisture content of the soil sample; a good estimate for most soils is 8-10 mL of displaced volume for 15 grams soil. **In all cases, the soil sample in the vial must be completely covered by methanol.**

6.2.4 Samples for VPH analysis should be collected in duplicate 40 mL vials. An additional sample of the soil must also be obtained (without methanol) to allow for a determination of soil moisture content and VPH dry weight correction factors.

6.2.5 A methanol trip blank should accompany each batch of soil samples.

6.2.6 A chain of custody form must accompany all sampling vials and must document the date and time of sample collection and, where appropriate, the volume of methanol added. Observations of vial leakage must be so noted on the laboratory/data report sheet.

6.2.7 Soil samples must be analyzed within 28 days of collection.

6.3 A summary of sample collection, preservation and holding times is provided in Table 4.

7.0 PROCEDURES

7.1 Sample Preparation and Purging

7.1.1 It is highly recommended that all samples be screened prior to analysis. This screening step may be analysis of a soil sample's methanol extract (diluted) or the hexadecane extraction and screening method (SW-846 Method 3820).

7.1.2 Water Samples - Introduce volatile compounds into the gas chromatograph using a purge-and-trap concentrator.

7.1.2.1 Remove the plunger from a 5 mL syringe. Open the sample or standard bottle, which has been allowed to come to ambient temperature, and carefully pour the sample into the syringe barrel to just short of overflowing. Replace the syringe plunger and compress the sample and vent any residual air while adjusting the sample volume to 5 mL. This process of taking an aliquot destroys the validity of the liquid sample for future analysis; therefore, if a second analysis is needed an alternate vial will be used. If an alternate vial is not available then the compromised vial will be used and notated.

7.1.2.2 If necessary, samples should be diluted prior to injection into the purge chamber. In such cases, all steps must be performed without delay until the diluted sample is in a gas-tight syringe.

7.1.2.2.1 Dilutions may be made in volumetric flasks (10 mL to 100 mL). Select the volumetric flask that will allow for the necessary dilution. Intermediate dilutions may be necessary for highly concentrated samples.

7.1.2.2.2 Calculate the approximate volume of laboratory reagent grade water to be added to the volumetric flask selected and add slightly less than this volume of laboratory reagent grade water to the flask.

7.1.2.2.3 Inject the proper aliquot of sample from the syringe prepared in Paragraph 7.1.2.1 into the flask. Aliquots of less than 1 mL are not recommended. Dilute the sample to the mark with laboratory reagent grade water. Cap the flask, invert, and shake three times. Repeat the above procedure for additional dilutions. Alternatively the dilutions can be made directly in the glass syringe to avoid further loss of volatiles.

7.1.2.2.4 Fill a 5 mL syringe with diluted sample as in Paragraph 7.1.2.1.

7.1.2.3 Add 5 µL of the surrogate spiking solution through the valve bore of the syringe.

7.1.2.4 Attach the syringe to the syringe valve on the purging device. Open the syringe valve and inject the sample into the purging chamber.

7.1.2.5 Close the valve and start the LSC 3000 sample concentrator. Refer to the instrument maintenance logbook for the current purge-and-trap operating parameters.

7.1.2.6 If the concentration of an analyte or hydrocarbon fraction in a sample exceeds the calibration range, a dilution of the sample is required. If a sample analysis results in a saturated detector response for a compound, the analysis must be followed by a blank laboratory reagent grade water analysis. If the blank analysis is not free of interferences, the system must be decontaminated. Sample analysis may not resume until a blank can be analyzed that is free of interferences.

7.1.2.7 All dilutions should keep the detector response of the major constituents (previously saturated peaks) in the upper half of the linear range of the curve.

7.1.3 Soil/Sediments - Soil and sediment samples are extracted with methanol. An aliquot of the extract is added to laboratory reagent grade water and introduced into the gas chromatograph using a purge-and-trap concentrator.

7.1.3.1 Weigh the sample vial to 0.1 g in a top loading balance and determine the weight of the soil/sediment sample; this determination requires knowledge of the empty/tarred weight of the sample vial and volume/weight of methanol preservative that was added to the sample vial.

7.1.3.2 Add 1 mL of the surrogate spiking solution. The concentration and/or volume of the surrogate spiking compound may need to be increased for samples that are highly contaminated (based upon screening and/or visual/olfactory evidence), to prevent dilution to below detectable limits. Shake the sample for 2 minutes and sonicate for 20 minutes.

7.1.3.3 Allow sediment to settle until a layer of methanol is apparent.

7.1.3.4 Using a microliter syringe, withdraw a 20 uL aliquot of the methanol extract for sparging. Sample screening data can be used to determine the volume of methanol extract to add to the 5 mL of laboratory reagent grade water for analysis. All dilutions must keep the response of the major constituents in the upper half of the linear range of the calibration curve.

7.1.3.5 Remove the plunger from one 5 mL Luerlock type syringe and fill until overflowing with laboratory reagent grade water. Replace the plunger and compress the water to vent trapped air. Pull the plunger to 5 mL for addition of the sample extract. Add the volume of methanol extract (20 µL maximum).

7.1.3.6 Attach the syringe to the syringe valve on the purging device. Open the syringe valve and inject the sample into the purging chamber.

7.1.4 Proceed with the analysis as described in Sections 7.1.2.5 through 7.1.2.7. Analyze all laboratory method blanks and QC samples under the same conditions as that used for samples.

7.1.5 If the responses exceed the calibration or linear range of the system, use a smaller aliquot of methanol.

7.2 GC Conditions

7.2.1 Refer to instrument maintenance logbook for the current oven conditions. The typical oven temperature program is: Oven temperature 35°C, hold for 8 min, then to 90°C at 3°C/min, to 140°C at 5°C/min, to 230°C at 45°C/min; hold for 10.5 min. Conditions may be altered to improve resolution of volatile petroleum hydrocarbons.

7.2.2 Gas Flows: The recommended carrier gas is helium.

7.2.2.1 Carrier gas flow: 10 mL/min.

7.2.2.2 Air: 160 mL/min

7.2.2.3 Hydrogen: 30 mL/min

7.2.2.4 Make up gas flow: 15 mL/min

7.2.3 Miscellaneous:

7.2.3.1 FID temperature: 220°C

7.2.3.2 PID temperature: 220°C

7.2.3.3 Injection port temperature: 200°C

7.2.3.4 Column head pressure: 30 psi

7.3 Retention Time Windows

7.3.1 Before establishing retention time windows, make sure the GC system is within optimum operating conditions. Make three injections of the VPH Component Standard throughout the course of a 72 hr period. Serial injections over less than a 72 hr period may result in retention time windows that are too tight.

7.3.2 Calculate the standard deviation of the three absolute retention times for each individual compound in the VPH Component Standard.

7.3.3 The retention time window is defined as plus or minus three times the standard deviation of the absolute retention times for each standard. However, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

7.3.4 In those cases where the standard deviation for a particular standard is zero, the laboratory should substitute the standard deviation of a closely eluting structurally similar compound to develop a valid retention time window.

7.3.5 The laboratory must calculate retention time windows for each standard on each GC column and whenever a new GC column is installed. This data must be retained by the lab.

7.3.6 VPH retention time (Rt) windows of the aliphatic ranges are defined as beginning 0.1 minutes before the Rt of the beginning marker compound and ending 0.1 before the Rt of the ending marker compound, except for C_9, which is both a beginning and ending marker compound for two different ranges.

The C_5-C_8 Aliphatic Hydrocarbon range ends immediately (0.1 min) before the elution of the n-C_9 peak. The C_9-C_{12} Aliphatic Hydrocarbon range begins 0.1 min before the elution of n-C_9, therefore there is no overlap of the two ranges and the n-C_9 peak is only included in the C_9-C_{12} Aliphatic Hydrocarbon range.

The VPH retention time (Rt) window for the C_9-C_{10} Aromatic Hydrocarbons is defined as beginning 0.1 minutes after the Rt of the beginning marker compound and ending 0.1 before the Rt of the ending marker compound, VPH marker compounds and windows are summarized below.

VPH Marker Compounds

Hydrocarbon Range	Beginning Marker Compound	Ending Marker Compound
C_5 - C_8 Aliphatic Hydrocarbons (FID)	0.1 min before Pentane	0.1 min before n-Nonane
C_9 - C_{12} Aliphatic Hydrocarbons (FID)	0.1 min before n-Nonane	0.1 min before Naphthalene[1]
C_9 -C_{10} Aromatic Hydrocarbons (PID)	0.1 min after o-xylene	0.1 min before Naphthalene[1]

[1]The retention time for Dodecane (C_{12}) is approximately 2 minutes less than the retention time for naphthalene, using the column and chromatographic conditions recommended for this method. For simplicity, naphthalene is used as the ending marker for the C_9-C_{12} Aliphatic Hydrocarbon range.

7.4 External Standard Calibration Procedure

7.4.1 Analyze each of the six VPH Calibration standards following the procedure outlined in section 7.5. Tabulate the area responses against the concentration injected. The ratio of area response to the concentration

injected, defined as the calibration factor (CF), may be calculated for target VPH analytes using the equation below.

Calibration Factor (CF) = area of peak/concentration purged (µg/L)

The percent relative standard deviation (%RSD) of the calibration factor must be equal to or less than 25% over the working range for the analyte of interest, as determined using the equation below. When this condition is met, linearity through the origin may be assumed, and the average calibration factor is used in lieu of a calibration curve.

%RSD = (stand dev of 6 CFs/mean of 6 CFs) x 100

7.4.2 A collective calibration factor must also be established for each hydrocarbon range of interest: C_5-C_8 Aliphatic Hydrocarbons, C_9-C_{12} Aliphatic Hydrocarbons and the C_9-C_{10} Aromatic Hydrocarbons. Calculate the collective CFs for C_5-C_8 Aliphatic Hydrocarbons and C_9-C_{12} Aliphatic Hydrocarbons using the FID chromatogram. Calculate the collective CFs for the C_9-C_{10} Aromatic Hydrocarbons using the PID chromatogram. Tabulate the summation of the peak areas of all components in that fraction against the total concentration injected. The results can be used to calculate the ratio of the peak area response summation to the concentration injected, defined as the CF, for the hydrocarbon ranges using the equation below. The %RSD of the calibration factor must be equal to or less than 25% over the working range for the hydrocarbon range of interest, as determined using the equation in 7.4.1.1.

CF = area summation of range components/total conc. purged (µg/L)

7.4.3 At a minimum, the working calibration curve or calibration factor must be verified on each working day, after every 20 samples and at the end of the analytical sequence by the injection of a mid-level continuing calibration standard to verify instrument performance and linearity. If the percent difference (%D) for any analyte varies from the predicted response by more than ± 25%, as determined using the equation below, a new calibration curve must be prepared for that analyte. Greater differences are permissible for n-nonane (±30%).

$\%D = (CF_{AVG} - CF_{CC})/((CF_{AVG}) \times 100$

where:

CF_{AVG} = Average calibration factor calculated from initial calibration.
CF_{CC} = Calibration factor calculated from continuing calibration.

7.4.4 Target VPH Analytes and C_9 to C_{10} Aromatic Hydrocarbons are quantitated on the PID chromatogram.

7.4.5 C_5 through C_8 and C_9 through C_{12} Aliphatic Hydrocarbons are quantitated on the FID chromatogram.

7.4.6 Independent Calibration Verification

Immediately following an initial calibration, an independent calibration standard must be analyzed. This standard contains all target compounds, and surrogates at mid-calibration range concentration and is obtained from a source independent of the initial calibration source. Please refer to Table 1 for acceptance criteria and corrective action for this standard. When analyzed after a initial calibration and directly before samples, this standard also doubles as an LCS sample.

7.5 GC Analysis

7.5.1 Samples are analyzed in a set referred to as an analysis sequence. The sequence begins with instrument calibration followed by samples interspersed with blanks and QC samples. The sequence ends when the set of samples has been analyzed or when qualitative and/or quantitative QC criteria are exceeded.

7.5.2 Samples are introduced into the gas chromatograph using a purge-and-trap concentrator.

7.5.3 Water samples are directly injected into the purging chamber using a 5 mL syringe. Soil samples are extracted in methanol, the methanol extract is mixed with laboratory reagent grade water, and the methanol/water mixture is injected into the purging chamber using a 5 mL syringe.

7.5.4 Establish daily retention time windows for each analyte of interest using the absolute retention time for each analyte as the midpoint of the window for that day **if** after analyzing the midpoint it is determined that one or more analytes falls outside of the previously established absolute retention time window. The daily retention time window equals the midpoint ± three times the standard deviation determined in Section 7.3.

7.5.4.1 Tentative identification of an analyte occurs when a peak from a sample falls within the daily retention time window. Confirmation on a second GC column or by GC/MS analysis may be necessary.

7.5.4.2 Coelution of the m- and p- Xylene isomers may occur.

7.5.4.3 Validation of GC system qualitative performance must be accomplished by the analysis of mid-level standards within the analysis sequence. If any of the standards fall outside their daily retention time window, the system is out of control. In such cases, the cause of the problem must be determined and corrected.

7.5.5 Aliphatic and aromatic ranges of interest are determined by the collective integration of all peak elutions between specified range "marker" compounds. Due to the variability in software approaches and applications to collective peak area integration, it is recommended that a manual check be initially performed, to document proper integration functions.

7.5.6 **When quantifying on a peak area basis by external calibration, collective peak area integration for the fractional ranges must be from baseline (i.e. must include the unresolved complex mixture "hump" areas).** For the integration of individual Target Analytes, surrogate compounds, a valley-to-valley approach should typically be used, though this approach may be modified on a case-by-case basis by an experienced analyst.

7.5.7 Baseline correction using a system solvent blank is permissible, if conducted in accordance with the procedures and requirements specified in Section 7.7.4.

7.5.8 If the VPH Target Analytes are to be quantitated using this method, and the response for an individual analyte exceeds the linear range of the system, dilute the extract and reanalyze. It is recommended that extracts be diluted so that all peaks are on scale. Overlapping peaks are not always evident when peaks are off scale.

7.5.9 For non-target analytes and target analytes eluting in the aliphatic or aromatic fractions, the upper linear range of the system is based on the highest calibration standard. Refer to Table 3 for concentrations.

7.6 Calculations (external standard)

The concentration of targeted analytes and hydrocarbon ranges in a sample may be determined by calculating the amount of analyte or hydrocarbon range purged, from the peak response using the calibration curve.

7.6.1 The concentration of an analyte is calculated by using the calibrated curve that is prepared in Target. When an analyte is identified, Target displays a concentration when the file is processed through the appropriate calibration method.

The concentrations from the reports are then incorporated with the purge and/or extraction data to arrive at a final concentration.

Water: Concentration (µg/L) = (C) (0.005L)/(V_s)

Soil: Concentration (mg/Kgdrywt) =
(C) (((((V_t+((M/100)(V_o)))(0.005L)/(V_o)(V_p)(100/100-M)(1/1000)

Where:
- C = Concentration calculated by Target in µg/L.
- V_s = Volume of sample purged in L.
- V_o = Weight of sample extracted in Kg.
- V_t = Volume of methanol in L.
- V_p = Total volume of extract purged in L.
- M = Moisture in %.

7.6.2 Required Adjustment of Range Concentration Data: In order to minimize the "double counting" of the same hydrocarbon compounds on both the FID and PID chromatograms, the collective concentrations of MTBE, benzene, toluene, ethylbenzene, and m-, p- and o-Xylene identified on the PID chromatogram must be subtracted from the collective C_5 through C_8 and C_9 through C_{12} Aliphatic Hydrocarbon concentration value determined using the FID chromatogram.

7.7 Sample Analysis

7.7.1 PID Chromatogram

7.7.1.1 If desired, determine the peak area count for the Target VPH Analytes.

7.7.1.2 Determine the peak area count for the surrogate 2,5-dibromotoluene.

7.7.1.3 Determine the total area count for all peaks eluting 0.1 minutes after the retention time (Rt) for o-Xylene and 0.1 minutes before the retention time for naphthalene.

7.7.1.4 Using the equations contained in Section 7.6.1, calculate the concentrations of the surrogate standard 2,5-dibromotoluene, and C_9 through C_{10} Aromatic Hydrocarbons. Optionally, calculate the individual concentrations of the Target VPH Analytes.

7.7.2 FID Chromatogram

7.7.2.1 Determine the total area count for all peaks eluting 0.1 minutes before the retention time (Rt) for n-pentane and 0.1 minutes before

the Rt for n-nonane. It is not necessary to identify or quantitate individual aliphatic compounds within this range.

7.7.2.2 Determine the total area count for all peaks eluting 0.1 minutes before the Rt for n-nonane and 0.1 before the Rt for naphthalene. It is not necessary to identify or quantitate individual aliphatic compounds within this range.

7.7.2.3 Determine the peak area count for the surrogate standard 2,5-dibromotoluene.

7.7.2.4 Using the equations contained in Section 7.6.1, calculate the concentrations of C_5 through C_8 Aliphatic Hydrocarbons, C_9 through C_{12} Aliphatic Hydrocarbons, and the surrogate standard 2,5-dibromotoluene.

7.7.3 Data Manipulations

7.7.3.1 By definition, the collective concentrations of aliphatic and aromatic fractions of interest **exclude** the individual concentrations of VPH Target Analytes. Accordingly, a series of data manipulation steps are necessary to adjust the collective range concentrations calculated in 7.7.1.4 and 7.7.2.4, to eliminate "double counting" of analytes.

7.7.3.2 Subtract the collective concentration of C_9-C_{10} Aromatic Hydrocarbons from the collective concentration of C_9-C_{12} Aliphatic Hydrocarbons.

7.7.3.3 Subtract the individual concentrations of the VPH Target Analytes from the appropriate aliphatic range (i.e., C_5-C_8 or C_9-C_{12} Aliphatic Hydrocarbons) in which they elute. If the individual concentrations of Target Analytes have not been quantitated, report the values as Unadjusted C_5-C_8 Aliphatic Hydrocarbons and Unadjusted C_9-C_{12} Aliphatic Hydrocarbons, and indicate "Not Determined" for C_5-C_8 Aliphatic Hydrocarbons and C_9-C_{12} Aliphatic Hydrocarbons.

7.7.4 Baseline Correction for Instrument Noise Level

7.7.4.1 Range integration areas may be corrected by the automatic subtraction of the baseline established by the injection of a system solvent blank.

7.7.4.2 Instrument baseline shall be established by the purging of a system solvent blank, an air blank, or by activation of a programmed run

without the injection of any material. All system and run elements and parameters must be identical to those of the sample run.

7.7.4.3 If baseline correction is used, instrument baseline must be established for every batch of samples, and after the analysis of samples that are suspected to be highly contaminated.

7.8 Data Review

7.8.1 Initial Data Review

The initial data review is accomplished by the analyst who ran the samples. This review is of sufficient quality and detail to provide a list of samples that need to be reanalyzed or diluted and reanalyzed. The initial data review is performed on the detailed quantitation reports of the analyzed samples. This data review examines criteria that directly impact whether or not the sample needs to be reanalyzed and/or extracted. These criteria include:

- QC criteria for method blank, LCS/LCSD, MS/MSD, and calibration – refer to section 8.0.
- Surrogate recovery.
- Chromatography: manual integration.
- Target compound detection: quantitation, false positives.

The requirement of the GC laboratory is that this initial data review be completed no later than the end of the next work day. After the analyst has completed his or her initial data review, the information is then ready to be processed for reporting. Refer to section 7.9.

7.8.2 Surrogate recovery

All recoveries must meet the method acceptance limits of 70-130%.

The sample is evaluated for recoveries of the surrogate. If the surrogate recovery is outside of the method acceptance limits on one channel but acceptable on the other channel, narrate. If the recovery is high and the sample results are less than the PQL, narrate. If the recovery is low and may be attributable to matrix interference, reanalyze to confirm a matrix effect and narrate. If the recovery is low and there is no apparent matrix effect, the sample should be reanalyzed. If the soil % moisture is >25% and the surrogate recovery is >10%, narrate. If the soil reanalysis is still low, re-extract.

7.8.3 Chromatography

Manual integrations are to be performed when chromatographic conditions preclude the computer algorithm from correctly integrating the peak of concern. In no instance shall a manual integration be performed solely to bring a peak within criteria.

Each peak of concern is examined by the primary analyst to ensure that the peak was integrated properly by the computer algorithm. Should a manual integration be necessary (for instance, if the sample contains a concentration of the aliphatic range C_5 through C_8 which was integrated "valley to valley" instead of a "baseline to baseline"), it will be done in Target Review. For specific procedures on how to manually integrate, refer to Katahdin SOP QA-812, "Manual Integration," current revision.

7.8.4 Target Compound Detection

In order to avoid reporting false positives, identified peaks on a chromatogram may need to be crossed out and a GC lab code applied adjacent to its concentration. The possible scenarios are: If an analyte is present on one channel but its concentration is below the PQL, then the analyte and its concentration are crossed out and the GC lab code BDL is written next to the concentration. If an analyte is present but its retention time is ±0.04 minutes or more than the retention time of the analyte in the preceding CV, then the analyte and its concentration are crossed out and the GC lab code RTW is written next to the concentration.

The GC lab codes are:

BDL - Below Detection Limit
RTW - Retention Time Window

7.9 Reporting

7.9.1 After the chromatograms have been reviewed and any target analytes have been quantitated using Target, the necessary files are brought into QuickForms. Depending on the QC level requested by the client, reports, such as chronology or calibration forms, are generated. Reports of Analysis (ROA), LCS/LCSD, MS/MSD and surrogate forms are generated in KIMS. The package is assembled to include the necessary forms and raw data. The data package is reviewed by the primary analyst and then forwarded to the secondary reviewer. The secondary reviewer validates the data and checks the package for any errors. When completed, the package is sent to the department manager for final review. A completed review checklist is

provided with each package. The final data package from the Organics department is then processed by the Data Management department.

7.9.2 The VPH reporting form contains an attestation that indicates whether significant modifications were made to the VPH method, a clear affirmation on whether the QA/QC procedures and standards specified in the method were followed and achieved.

7.9.3 Significant modifications may include the use of alternative detectors, the use of other than a purge-and-trap sample preparation, the use of solvents other than those recommended, and the use of a different surrogate than recommended. Any modifications which were made along with any QA/QC deviations are mentioned in the case narrative.

8.0 QUALITY CONTROL AND ACCEPTANCE CRITERIA

See below or refer to Table 1 for a summary of QC requirements, acceptance criteria, and corrective actions. These criteria are intended to be guidelines for analysts. The table does not cover all possible situations. If any of the QC requirements are outside the recovery ranges listed in Table 1, all associated samples must be evaluated against all the QC. In some cases data may be reported, but may be reanalyzed in other cases. Making new reagents and standards may be necessary if the standardization is suspect. The corrective actions listed in Table 1 may rely on analyst experience to make sound scientific judgments. These decisions are based on holding time considerations, client and project specific Data Quality Objectives and on review of chromatograms. The Department Manager, Operations Manager and/or Quality Assurance Officer may be consulted to evaluate data. Samples may not be able to be reanalyzed within hold time. In these cases "qualified" data with narration may be advisable after consultation with the client.

8.1 General Requirements and Recommendations

8.1.1 Each laboratory that uses this method is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and an ongoing analysis of spiked samples to evaluate and document the quality of data. The laboratory must maintain records to document the quality of the data generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance standards for the method. When results of sample spikes indicate atypical method performance, a quality control check standard must be analyzed to confirm that the measurements were performed in an in-control mode of operation.

8.1.2 A methanol trip blank or acidified laboratory reagent grade water blank should continually accompany each soil sample or water sample batch, respectively, over the course of sampling, storage, and analysis.

8.1.3 A Laboratory Method Blank must be run after samples suspected of being highly contaminated to determine if sample carryover has occurred.

8.1.4 At a minimum, for each analytical batch (up to 20 samples), an Initial Calibration or opening and closing Calibration Check Standard, Laboratory Method Blank, Laboratory Control Sample (LCS) and LCS duplicate (LCSD) must be run. A duplicate sample (if client requested) and Matrix Spike (MS) and/or MS duplicate (MSD) should be analyzed, at the discretion of the analyst, based upon the nature of the sample. For analytical batches with more than 10 samples, the analysis of an additional mid-range calibration check standard should also be considered. The blank and spiked samples should be carried through all stages of the sample preparation and measurement process.

8.1.5 The recommended sequence of analysis is as follows:

(1) Calibration Standards (initial) or mid-range Calibration Check Standard (daily check of initial calibration) **[REQUIRED]**
(2) Laboratory Method Blank **[REQUIRED]**
(3) Laboratory Control Sample and Duplicate **[REQUIRED]**
(4) Samples
(5) Duplicate sample [if client requested]
(6) Matrix Spike/Duplicate [As appropriate]
(7) Mid-range Calibration Check Standard [consider after 10 samples, as appropriate]

8.1.6 At a minimum, when surrogate recovery from a sample, blank, or QC sample is less than 70% or more than 130%, check calculations to locate possible errors, the fortifying solution for degradation, and changes in instrument performance. If the cause cannot be determined, reanalyze the sample.

8.2 Minimum Instrument QC

8.2.1 The n-pentane (C_5) and MTBE peaks must be adequately resolved from any solvent front that may be present on the FID and PID chromatograms, respectively. This is achievable using the recommended trap and purge-and-trap procedures. Coelution of the m- and p- xylene isomers is permissible. Any surrogates used must be adequately resolved from individual compounds in the VPH Component Standard.

8.2.2 Retention time windows must be established for each analyte of interest each time a new GC column is installed, and must be verified and/or adjusted on a daily basis. (See Section 7.3)

8.2.3 Calibration factors must be developed based upon the analysis of calibration standards prepared at a minimum of 5 concentration levels. The linearity of the calibration factors may be assumed if the %RSD over the working range of the curve is less than or equal to 25%. (See Section 7.4)

8.3 Initial and Periodic Method QC Demonstrations

The procedures specified in Section 8.3.1.1 through 8.3.1.3 must be conducted as an initial demonstration of laboratory capability, prior to the analysis of any samples. Subsequent to this initial demonstration, additional evaluations of this nature should be conducted on a periodic basis, in response to changes in instrumentation or operations, and/or in response to confirmed or suspected systems, method, or operational problems.

8.3.1 Accuracy and Precision

To demonstrate initial laboratory capability, analyze a minimum of four replicate laboratory reagent grade water and/or clean sand blanks spiked with each analyte of interest at approximately half of the highest calibration standard (100 µg/L water and 16.7-50 mg/Kg soil).

8.3.1.1 Add an appropriate aliquot of the stock or primary dilution standard solution(s) to each of the four replicate laboratory reagent grade water or clean sand blanks. Purge and analyze each replicate according to the procedures described in Section 7.1.

8.3.1.2 Calculate the measured concentrations of each analyte in all replicates, the mean accuracy (as a percentage of true value) for each analyte, and the precision (as %RSD) of the measurements for each analyte.

8.3.1.3 For each analyte, the mean accuracy, expressed as a percentage of the true value, must be between 70% and 130%, and the %RSD must be less than or equal to 25%. Higher recoveries are permissible for n-nonane.

8.4 Ongoing Method QC Demonstrations

8.4.1 Each sample, blank, and Laboratory Control Sample must be spiked with the surrogate spiking solution. Required surrogate recovery is 70% to 130%.

Recoveries outside of this range must be noted and discussed in the data report form.

8.4.2 At a minimum, with every batch of 20 samples or less the laboratory must analyze the following:

8.4.2.1 **Calibration Check Standard** - A mid-range calibration standard, prepared from the same stock standard solution used to develop the calibration curve, must be analyzed prior to sample analysis to verify the calibration state of the instrument. For large analytical batches that contain more than 10 samples, the analysis of an additional mid-range calibration check standard is recommended after the analysis of the tenth sample. If the percent difference (%D) of any analyte within the calibration check standard varies from the predicted response by more than 25%, a new calibration curve must be prepared for that analyte.

8.4.2.2 **Laboratory Method Blank** - A water or soil Laboratory Method Blank is prepared by fortifying a 5 mL laboratory reagent grade water blank with 5 µL of the surrogate spiking solution, or by fortifying a 15 g sample of clean sand with 1 mL of the surrogate spiking solution. Peaks must not be detected above the Reporting Limit within the retention time window of any analyte of interest.

8.4.2.3 **Laboratory Control Sample and Duplicate**- The Laboratory Control Sample and Duplicate are prepared by fortifying a 5 mL laboratory reagent grade water blank with 10 µL of the matrix spiking solution, or by fortifying a 15 g sample of clean sand with 500 µL of the matrix spiking solution. The spike recovery must be between 70% and 130%. RPD is <25%.

8.4.2.4 **Sample duplicate** - Sample duplicates may be laboratory duplicates or field duplicates per the client's request. The %RPD of duplicate samples must not exceed 50%.

8.4.2.5 **System Solvent Blank** - If baseline correction will be employed, as specified in Section 7.7.4, a system solvent blank, air blank, and/or system run must be undertaken with every batch, and after the analysis of a sample that is suspected to be highly contaminated.

8.4.3 A Matrix Spike (MS) and Matrix Spike Duplicate (MSD is performed per the client's request.

8.4.3.1 **Matrix Spike (MS)/MS Duplicate (MSD)** –The water or soil MS/MSD spike is prepared by fortifying an actual 5 mL water sample with 10 µL of the matrix spiking solution, or by fortifying an actual 15g soil/sediment sample with 500 µL of the matrix spiking solution.

The purpose of the MS/MSD is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the MS/MSD corrected for background concentrations. The corrected concentrations of each analyte within the matrix spiking solution must be within 70 - 130% of the true value. Lower recoveries of naphthalene are permissible, but must be noted. The %RPD of the MS/MSD should be less than or equal to 25%.

8.4.4 If any of the performance standards specified in Section 8.4.1 and 8.4.2 are not met, the problem must be corrected before further samples are analyzed. Any samples run between the last QC samples that meet the criteria and those that are fallen out must be rerun. If this is not possible, that data must be reported as suspect.

8.5 NCR: Whenever data is not acceptable because of a failing LCS or surrogate recovery or other QC failure, a nonconformance report must be initiated as soon as possible.

9.0 METHOD PERFORMANCE

The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. The MDLs are determined annually per type of instrument and filed with the Organic Department Manager and with the QAO. Refer to the current revision of Katahdin SOP QA-806, "Method Detection Limit, Instrument Detection Limit and Reporting Limit Studies and Verifications," for procedures on determining the MDL.

Refer to the current revision Method MADEP VPH-04-1.1 for other method performance parameters and requirements.

10.0 APPLICABLE DOCUMENTS/REFERENCES

"Test Methods for Evaluating Solid Waste: Physical/Chemical Methods", USEPA SW846, third Edition, Final Updates I, II, IIA, IIB, III, IIIA, IIIB and IV, February 2007, Methods 8000B, 8015C, 5030B and the current edition of 8020.

TITLE: METHOD FOR THE DETERMINATION OF VOLATILE PETROLEUM HYDROCARBONS (MADEP - VPH)

Method for the Determination of Volatile Petroleum Hydrocarbons (VPH), MADEP, May 2004, Revision 1.1.

Katahdin SOP CA-101, "Equipment Maintenance and Troubleshooting," current revision.

Department of Defense Quality Systems Manual for Environmental Laboratories (DoD QSM), Version 4.1, 04/22/09.

The National Environmental Laboratory Accreditation Conference (NELAC) Standards, June 2003.

Katahdin SOP QA-806, "Method Detection Limit, Instrument Detection Limit and Reporting Limit Studies and Verifications," current revision.

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TABLE 1

SUMMARY OF CALIBRATION AND QC PROCEDURES FOR METHOD MADEP-VPH-04-1.1

QC check	Minimum Frequency	Acceptance Criteria	Corrective Action
Five-point external calibration of 15 VPH component standards, and a surrogate. Also, collective calibrations of C_9 through C_{10} aromatic hydrocarbons, C_5 through C_8 aliphatic hydrocarbons and C_9 through C_{12} aliphatic hydrocarbons.	Initial calibration prior to sample analysis	The %RSD must be ≤ 25%	Investigate and repeat initial calibration
Initial Calibration Verification (ICV)	Once after each calibration	All analytes ≤ 25 %D of the expected value.	Reanalyze sample Reprepare standard Reprepare standard from fresh stock.
CV	If initial calibration analyzed, daily and after 20 samples, and at end of sequence.	%D for all analytes within ±25%	Evaluate the samples: If the %D >±25% and sample results are < PQL, narrate. If %D >±25% and is likely a result of matrix interference, narrate. Otherwise, reanalyze all samples after last acceptable CV.
Method blank	One per prep batch	No analytes detected > PQL	(1) Investigate source of contamination (2) Evaluate the samples and associated QC: i.e. If the blank results are above the PQL, report samples results which are < PQL >10X the blank concentration. Otherwise, reprep a blank and the remaining samples.
Laboratory Control Sample/Laboratory Control Sample Duplicate (LCS/LCSD)	One LCS/LCSD per prep batch	Spike recovery must be between 70% and 130%	(1) Evaluate the samples and associated QC: i.e. If an MS/MSD was performed and acceptable, narrate. If an LCS/LCSD was performed and only one of the set was unacceptable, narrate. If the surrogate recoveries in the LCS are low but are acceptable in the blank and samples, narrate. If the LCS recovery is high but the sample results are < PQL, narrate. Otherwise, reprep a blank and the remaining samples.

TABLE 1 (cont.)

SUMMARY OF CALIBRATION AND QC PROCEDURES FOR METHOD MADEP-VPH-04-1.1

QC check	Minimum Frequency	Acceptance Criteria	Corrective Action
Surrogate	Every sample, blank, and QC sample	Recovery must be between 70% and 130%	Refer to section 7.8.2
Matrix Spike/Matrix Spike Duplicate	Per client request	Recovery must be between 70% and 130%.	(1) Evaluate the samples and associated QC: i.e. If the LCS results are acceptable, narrate. (2) If both the LCS and MS/MSD are unacceptable, reprep the samples and QC.
Sample duplicate if requested by the client	One per batch of 20 samples	%RPD of duplicate must be less than 50%.	(1)check calculations for errors (2) Evaluate QC
Demonstration of ability to generate acceptance accuracy and precision using four replicate analyses of a QC check sample	Once per analyst and yearly thereafter	For each analyte, the mean accuracy must be between 70% and 130% and the %RSD must be ≤ 25%	Investigate; reprep
MDL and/or LOD/LOQ Verification	Refer to KAS SOP QA-806, "Method Detection Limit, Instrument Detection Limit and Reporting Limit Studies and Verifications," current revision.		

TITLE: METHOD FOR THE DETERMINATION OF VOLATILE PETROLEUM HYDRO-CARBONS (MADEP - VPH)

TABLE 2

SUMMARY OF METHOD MODIFICATIONS

TOPIC	KATAHDIN SOP CA-312-07	METHOD MADEP-VPH-04-1.1
Apparatus/Materials		
Reagents		
Sample preservation/ handling		
Procedures		
Procedures	7.5.9 For non-target analytes and target analytes eluting in the aliphatic or aromatic fractions, the upper linear range of the system is based on the highest calibration standard. Refer to Table 3 for concentrations.	See Section 9.5.8
Procedures	7.5.4 Establish daily retention time windows for each analyte of interest using the absolute retention time for each analyte as the midpoint of the window for that day **if** after analyzing the midpoint it is determined that one or more analytes falls outside of the previously established absolute retention time window. The daily retention time window equals the midpoint ± three times the standard deviation determined in Section 7.3.	Section 9.5.4 Establish daily retention time windows for each analyte of interest. Use the absolute retention time for each analyte as the midpoint of the window for that day. The daily retention time window equals the midpoint ± three times the standard deviation determined in Section 9.3.
QC – Spikes		
QC – LCS		
QC - Accuracy/Precision		

TITLE: METHOD FOR THE DETERMINATION OF VOLATILE PETROLEUM HYDROCARBONS (MADEP - VPH)

TABLE 3

VPH CALIBRATION CONCENTRATIONS

Component	Level 1 µg/L	Level 2 µg/L	Level 3 µg/L	Level 4 µg/L	Level 5 µg/L	Level 6 µg/L
n-Pentane	5	10	50	100	200	300
2-Methylpentane	5	10	50	100	200	300
MTBE	5	10	50	100	200	300
2,2,4-Trimethylpentane	5	10	50	100	200	300
Benzene	5	10	50	100	200	300
Toluene	5	10	50	100	200	300
n-Nonane	5	10	50	100	200	300
n-Decane	5	10	50	100	200	300
n-Butylcyclohexane	5	10	50	100	200	300
Ethylbenzene	5	10	50	100	200	300
m,p-Xylene	5	10	50	100	200	300
o-Xylene	5	10	50	100	200	300
1,2,4-Trimethylbenzene	5	10	50	100	200	300
Naphthalene	5	10	50	100	200	300
2,5-Dibromotoluene	5	10	50	100	200	300
C_5-C_8	15	30	150	300	600	900
C_9-C_{12}	15	30	150	300	600	900
C_9-C_{10}	5	10	50	100	200	300

Amount of standard added to 5 mL volume:

Level 1 5 µL of 5 µg/mL standard
Level 2 10 µL of 5 µg/mL standard
Level 3 5 µL of 50 µg/mL standard
Level 4 10 µL of 50 µg/mL standard
Level 5 4 µL of 250 µg/mL standard
Level 6 6 µL of 250 µg/mL standard

TABLE 4

HOLDING TIMES AND PRESERVATIVES FOR VPH SAMPLES

Matrix	Container	Preservation	Holding time
Aqueous Samples	40 mL VOC vials w/ Teflon-lined septa screw caps.	Add 3 to 4 drops of 1:1 HCl; cool to 4 (±2) °C.	14 days
Soil/Sediment Samples	40 mL VOC vials w/ Teflon-lined septa screw caps: add 15 g soil	1 mL methanol for every g soil; add before or at time of sampling; cool to 4 (±2) °C	28 days

TITLE: METHOD FOR THE DETERMINATION OF VOLATILE PETROLEUM HYDROCARBONS (MADEP - VPH)

TABLE 5

PQLS FOR METHOD MADEP VPH

Parameter/ Method	Analytes	Practical Quantitation Level	
		PQL (µg/L)	PQL (mg/Kg)
VPH/MADEP-VPH-04-1.1	Methyl-tert-butylether	5	1.25
	Benzene	5	1.25
	Toluene	5	1.25
	Ethylbenzene	5	1.25
	m- & p-Xylene	10	2.5
	o-Xylene	5	1.25
	Naphthalene	5	1.25
	C_5 - C_8 Aliphatics(FID)	100	25
	C_9 - C_{12} Aliphatics(FID)	100	25
	C_9 - C_{10} Aromatics(PID)	100	25

TITLE: METHOD FOR THE DETERMINATION OF VOLATILE PETROLEUM HYDROCARBONS (MADEP - VPH)

FIGURE 1

EXAMPLE OF LOGBOOK PAGE

Katahdin Analytical Services, Inc. Instrument: GC09
GC Laboratory Instrument Runlog

Method (Circle): MADEP-VPH-98-1 MEDEP 4.2.17 SW846 8015(M)

Date	Init.	Sample Name	Amt. Purged	SP. #	Result File	Dil.	Y/N	Method	pH	Comments

	Std. Name	Conc.	Std. Code	Std. Code
1	VPH Cal mix	50 ug/ml	GCV	GCV
2	VPH Surr. mix	50 ug/ml	GCV	GCV
3	VPH LCS mix	50 ug/ml	AMP	AMP
4	GRO Cal mix	250 ug/mL Total	GCV	GCV
5	GRO Surr. Mix	50 ug/mL	GCV	GCV
6	GRO LCS mix	250 ug/mL Total	GCV	GCV
7				
8				

VPH CC = 5uL Std. 1
VPH LCS = 10uL Std. 3
VPH Samples = 5uL Std. 2

GRO CC = 2uL Std. 4
GRO LCS = 2uL Std. 5 and 6
GRO Samples = 2uL Std. 5

TITLE: METHOD FOR THE DETERMINATION OF VOLATILE PETROLEUM HYDRO-CARBONS (MADEP - VPH)

FIGURE 2

EXAMPLE OF DATA REVIEW CHECKLIST

PRIMARY REVIEW CHECKLIST

Verbal Due Date _____ (☐ **Verbals turned in**). **DueDate**_____

Client:		Primary	Secondary
Method:		Date:	Date:
SDG No:	Level:	Initials:	Initials:
KAS No:			Approved : ☐ Yes

DODQSM 3.0 ☐ **DODQSM 4.1** ☐ **WITH LAB. LIMITS** ☐
QUAPP ☐ **LAB** ☐ (*REPORT* ***ND's*** *to* ***MDL*** ☐)

List all curves that are scanned. _____ _____

_____ _____ _____ _____

Narrate which QC limits were used for (Surr., LCS,s MS/MSDs.) _____

All needed forms are present . _____

Correct Work Order Number or SDG name (all forms). _____

Correct project name and spelling (all forms). (Truncated ☐). _____

Correct file numbers (all forms). _____

Analysis Date Correct. _____

Extraction Method & Analysis Method Correct. _____

Product list compared to ROAs (compounds & PQLs). _____

Chromatogram reviewed for unlabeled peaks (check product list). _____

Flagging of all ROAs correct (Florida Flagging ☐). _____

All tunes included (level IV) . _____

All log book pages included (Soil weights,TCLP & SPLP). _____

Verify DOD QSM criteria. _____

Narrate any method deviations. (Blanks, LCS,s etc.) _____

Sign & Date Manual integration **(Narrate as needed).** _____

Sample I.D's Truncated (**NARRATED**). YES ☐ Please list KAS # below :

_____

TITLE: METHOD FOR THE ANALYSIS OF EXTRACTABLE PETROLEUM HYDROCARBONS (MADEP - EPH)

Prepared By: Peter Lemay Date: 6/98

Approved By:

Group Supervisor: Peter Lemay Date: 2/12/01

Operations Manager: John C. Burton Date: 2/13/01

QA Officer: Deborah J. Nadeau Date: 2·12·01

General Manager: Dennis P. Hughes Date: 2/13/01

Revision History:

SOP Revision	Changes	Approval Initials	Approval Date	Effective Date
01	Format changes, added pollution prevention, other updates to sections 7, 8 and QA Table.	DN	2·12·01	2/12/01
02	Changes to sections 2.2, 5.2.2, 7.3.1.3, 7.5.1.1, 7.6.3.4, and 8.0. Also changes to tables 2, 3, and 4	DN	5·2·02	5·2·02
03	Added definitions and information for new data processing system. Added or changed wording to clarify section 7 and Table 2. Added wording to sections 8 + 9 per recent NELAC + Navy audit responses. Minor changes throughout. New figures	MRC	11.15.04	11.15.04
04	Changed terminology for LCS's: MS's. Corrected Soil H.T. Added required LCSD and breakthrough check. Updated reference. Included KIMS forms, minor changes throughout.	LAD	051305	051305
05	Changed references from MADEP EPH-98-1 to MADEP EPH-04-1 Fixed typographical and grammatical errors	LAD	04/06	04/06

TITLE: METHOD FOR THE ANALYSIS OF EXTRACTABLE PETROLEUM HYDROCARBONS (MADEP - EPH)

SOP Revision	Changes	Approval Initials	Approval Date	Effective Date
06	Many changes made throughout, including but not limited to, adding linear regression calibration, spike concentrations, % RSD criteria, PQL's, standard solvent, freezing of soil samples. Refer to QAM/SOP change form filed w/ SOP in QA for more details.	LAD	09/07	09/07
07	Sect. 2.1: Changed solvent from hexane to methylene chloride and added solvent exchange step.	LAD	03/08	03/08
08	Changed surrogate from 1-chloro-octadecane to 5alpha androstane. Added HPLC fractionation references. Updated MDL/LOD/LOQ verification criteria. Updated references. Updated Logbook page and Data Review checklist.	LAD	04/10	04/10
	Added ICV criteria. Removed RSD. Added % Difference.			

TITLE: METHOD FOR THE ANALYSIS OF EXTRACTABLE PETROLEUM HYDROCARBONS MADEP - EPH METHOD

Please acknowledge receipt of this standard operating procedure by signing and dating both of the spaces provided. Return the bottom half of this sheet to the QA Department.

I acknowledge receipt of copy ____ of document **SOP CA-322-08**, titled **METHOD FOR THE ANALYSIS OF EXTRACTABLE PETROLEUM HYDROCARBONS MADEP - EPH METHOD.**

Recipient: _____Date:_____

KATAHDIN ANALYTICAL SERVICES, INC.
STANDARD OPERATING PROCEDURE

I acknowledge receipt of copy ____ of document **SOP CA-322-08**, titled **METHOD FOR THE ANALYSIS OF EXTRACTABLE PETROLEUM HYDROCARBONS MADEP - EPH METHOD.**

Recipient: _____Date:_____

TITLE: METHOD FOR THE ANALYSIS OF EXTRACTABLE PETROLEUM HYDROCARBONS MADEP - EPH METHOD

1.0 SCOPE AND APPLICATION

This method is designed to measure the collective concentrations of extractable aliphatic and aromatic petroleum hydrocarbons in water and soil. Extractable aliphatic hydrocarbons are collectively quantitated within two ranges: C_9 through C_{18}, and C_{19} through C_{36}. Extractable aromatic hydrocarbons are collectively quantitated within the C_{11} through C_{22} range. These aliphatic and aromatic hydrocarbon ranges correspond to a boiling point range between approximately 150 °C and 265 °C.

This method is based on a solvent extraction, HPLC or silica gel cartridge fractionation process, and gas chromatography (GC) analysis using a flame ionization detector (FID). This procedure should be used by, or under the supervision of, analysts experienced in extractable organics analysis. Analysts should be skilled in the interpretation of gas chromatograms and their use as a quantitative tool.

This method is also able to measure the individual concentrations of Target Polynuclear Aromatic Hydrocarbons (PAH) Analytes, including Diesel PAH Analytes, in water and soil.

The fractionation step described in this method may be eliminated to allow for the determination of a Total Petroleum Hydrocarbon (TPH) value, and/or obtain qualitative "fingerprinting" information. While TPH provides little information on the chemistry, toxicity, or environmental fate of petroleum mixtures, it may be a cost-effective screening tool in cases where a relatively low concentration of contamination is suspected.

Petroleum products suitable for evaluation by this method include kerosene, fuel oil #2, fuel oil #4, fuel oil #6, diesel fuel, jet fuel, and certain lubricating oils. This method, in and of itself, is not suitable for the evaluation of gasoline, mineral spirits, petroleum naphthas, or other petroleum products that contain a significant percentage of hydrocarbons lighter than C_9. This method, in and of itself, is also not suitable for the evaluation of petroleum products that contain a significant percentage of hydrocarbons heavier than C_{36}.

Like all GC procedures, this method is subject to a "false positive" bias in the reporting of Target PAH Analytes, in that non-targeted hydrocarbon compounds eluting or co-eluting within a specified retention time window may be falsely identified and/or quantitated as a Target or Diesel PAH Analyte. While cleanup procedures specified in this method to segregate aliphatic and aromatic fractions will serve to mitigate this concern, confirmatory analysis by dissimilar columns, gas chromatography/mass spectrometry (GC/MS) analysis, or other suitable technique is recommended in cases where a target PAH analyte reported by this method exceeds an applicable reporting or cleanup standard, and/or where coelution of a non-targeted hydrocarbon compound is suspected.

This is a performance-based method. Modifications to this method are permissible, provided that adequate documentation exists, or has been developed, to demonstrate an

equivalent or superior level of performance. MADEP encourages methodological innovations which (a) better achieve method and/or data quality objectives, (b) increase analytical precision and accuracy, (c) reduce analytical uncertainties and expenses, and/or (d) reduce the use of toxic solvents and generation of hazardous wastes. Laboratories that modify this method must achieve all required performance and acceptance standards, and must have on file a Standard Operating Procedure which thoroughly describes the revised or alternative method, and documentation which demonstrates an equivalent or superior level of performance. All significant modifications to the method must be disclosed and described on the data report form.

1.1 Definitions

Aliphatic Hydrocarbon Standard is defined as a 14 component mixture of the normal alkanes listed in Table 3. The compounds comprising the Aliphatic Hydrocarbon Standard are used to (a) define and establish windows for the two aliphatic hydrocarbons ranges, and (b) determine average chromatographic response factors that can in turn be used to calculate the collective concentration of aliphatic hydrocarbons in environmental samples within those hydrocarbon ranges.

Analytical Batch is defined as a group of field samples with similar matrices that are processed as a unit. For Quality Control purposes, if the number of samples in such a group is greater than 20, then each group of 20 samples or less are defined as separate analytical batches.

Aromatic Hydrocarbon Standard is defined as a 17 component mixture of the polynuclear aromatic hydrocarbons (PAHs) listed in Table 3. The compounds comprising the Aromatic Hydrocarbon Standard are used to (a) define the individual retention times and chromatographic response factors for each of the PAH analytes listed in Table 3, (b) define and establish the window for the C_{11} through C_{22} Aromatic Hydrocarbon range, and (c) determine an average chromatographic response factor that can in turn be used to calculate the collective concentration

C_9 through C_{18} Aliphatic Hydrocarbons are defined as all aliphatic hydrocarbon compounds eluting from n-nonane (n-C_9) to just before n-nonadecane (n-C_{19}).

C_{19} through C_{36} Aliphatic Hydrocarbons are defined as all aliphatic hydrocarbon compounds eluting from n-nonadecane (n-C_{19}) through n-hexatriacontane (n-C_{36}).

C_{11} through C_{22} Aromatic Hydrocarbons are defined as all aromatic hydrocarbon compounds eluting from naphthalene through Benzo(g,h,i)Perylene, excluding Target PAH Analytes.

Calibration Check Standard is defined as a calibration standard used to periodically check the calibration state of an instrument. The calibration check standard is prepared from the same stock standard solution as calibration standards, and is generally one of the mid-level range calibration standard dilutions.

Calibration Standards are defined as a series of standard solutions prepared from dilutions of a stock standard solution, containing known concentrations of each analyte and surrogate compound of interest.

Diesel PAH Analytes are defined as naphthalene, 2-methylnaphthalene, phenanthrene, and acenaphthene, and are a subset of Target PAH Analytes. For most sites contaminated by a release of (only) diesel or #2 fuel oil, Diesel PAH Analytes will be the only Target PAH Analytes of interest.

Extractable Petroleum Hydrocarbons (EPH) are defined as collective fractions of hydrocarbon compounds eluting from n-nonane to n-hexatriacontane, excluding Target PAH Analytes. EPH is comprised of C_9 through C_{18} Aliphatic Hydrocarbons, C_{19} through C_{36} Aliphatic Hydrocarbons, and C_{11} through C_{22} Aromatic Hydrocarbons.

Field Duplicates are defined as two separate samples collected at the same time and location under identical circumstances and managed the same throughout field and laboratory procedures. Analyses of field duplicates give a measure of the precision associated with sample collection, preservation and storage, as well as laboratory procedures.

Fractionation Surrogate Standards are compounds that are spiked into the sample extract immediately prior to fractionation, in order to determine if significant quantities of naphthalene or substituted naphthalenes are being stripped into the aliphatic extract and to evaluate fractionation efficiency.

Instrument Thermal Bleed is defined as a programmed run without the injection of any material. The purpose of the Instrument Blank is to determine the level of noise and baseline rise attributable solely to the GC system, in the absence of any other analytes or system contaminants.

Laboratory Control Sample (LCS) is defined as a laboratory reagent grade water blank or clean sand blank fortified with a matrix spiking solution. The LCS is prepared and analyzed in the same manner as the samples and its purpose is to determine the bias of the analytical method.

Laboratory Control Sample Duplicate (LCSD) is defined as a laboratory reagent grade water blank or clean sand blank fortified with a matrix spiking solution,

processed and analyzed in the same manner as the LCS. The analysis of the LCSD gives a measure of the precision associated with laboratory procedures, but not with sample collection, preservation or storage procedures.

Matrix Duplicates (DUP) are defined as duplicate samples prepared and analyzed separately with identical procedures. For soils samples DUPs are taken from the same sampling container; for aqueous samples, a second sample container is used. The analysis of laboratory duplicates give a measure of the precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

Matrix Spike Sample (MS) is defined as an environmental sample that has been spiked with a matrix spiking solution containing known concentrations of method analytes. The MS sample is treated and analyzed exactly as other samples, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentration of analytes in the sample matrix must be determined through the separate analyses of an unspiked sample aliquot. The measured values in the MS sample must be corrected for background concentrations when calculating recoveries of spiked analytes.

Laboratory Method Blank is defined as an aliquot of laboratory reagent grade water or clean sand spiked with a surrogate standard. The laboratory method blank is treated exactly as a sample, exposed to all glassware, solvents, reagents, and equipment. A laboratory method blank is analyzed with every batch of samples, to determine if method analytes or other interferences are present in the laboratory environment, reagents, or equipment.

Matrix Spiking Solution is defined as a solution prepared independently from the calibration standards, containing known concentrations of method analytes.

Surrogate Standards are compounds spiked into all samples, blanks, and matrix spikes to monitor the efficacy of sample extraction, chromatographic, and calibration systems.

Target PAH Analytes are defined as the 17 polynuclear aromatic hydrocarbon (PAH) compounds listed in Table 3.

Total Petroleum Hydrocarbons (TPH) are defined as the collective concentration of all hydrocarbon compounds eluting from n-nonane to n-hexatriacontane, excluding Target PAH Analytes. TPH is equivalent to the summation of C_9 through C_{18} Aliphatic Hydrocarbons, C_{19} through C_{36} Aliphatic Hydrocarbons, and C_{11} through C_{22} Aromatic Hydrocarbons.

Unadjusted C_{11} through C_{22} Aromatic Hydrocarbons are defined as all aromatic hydrocarbon compounds eluting from naphthalene through benzo(g,h,i)Perylene.

Unadjusted TPH is defined as the collective concentration of all hydrocarbon compounds eluting from n-nonane to n-hexatriacontane, including the target PAH analytes.

KATAHDIN INFORMATION MANAGEMENT SYSTEM (KIMS): A complete multi-user system with the capabilities of integrating laboratory instrumentation, generating laboratory worksheets, providing complete Lab Order status and generating reports. KIMS utilizes these features through a database.

PE NELSON TURBOCHROM: A data acquisition system that is used to collect, chromatographic data. The system can also be used to archive raw data files.

TARGET: A software system that combines full processing, reporting and comprehensive review capabilities, regardless of chromatographic vendor and data type.

TARGET DB: An oracle database used to store and organize all Target data files.

QUICKFORMS: A laboratory reporting software for Target and Target DB. The QuickForms report module for Target is preconfigured with generalized forms and US EPA CLP report forms and disk deliverables, which can be customized.

1.2 Responsibilities

This method is restricted to use by, or under the supervision of analysts experienced in the analysis of EPH by MADEP EPH-04-1. Analysts should be skilled in the interpretation of gas chromatograms and their use as a quantitative tool. Each analyst must demonstrate and document their ability to generate acceptable results with this method. Refer to Katahdin SOP QA-805, current revision, "Personnel Training & Documentation of Capability".

It is the responsibility of all Katahdin technical personnel involved in analysis of EPH by MADEP EPH-04-1 to read and understand this SOP, to adhere to the procedures outlined, and to properly document their data in the appropriate lab notebook. Any deviations from the test or irregularities with the samples should also be recorded in the lab notebook and reported to the Department Manager or designated qualified data reviewer responsible for this data.

It is the responsibility of the Department Manager to oversee that members of their group follow this SOP, to ensure that their work is properly documented and to initiate periodic review of the associated logbooks.

1.3 Safety

Users of this procedure must be cognizant of inherent laboratory hazards, proper disposal procedures for contaminated materials and appropriate segregation of hazardous wastes. The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical should be treated as a potential health hazard. A reference file of material safety data sheets is available to all personnel involved in the chemical analysis. Everyone involved with the procedure must be familiar with the MSDS (material safety data sheet) for all the materials used in this procedure.

Each qualified analyst or technician must be familiar with Katahdin Analytical safety procedures and the Katahdin Hazardous Waste Management Plan and must follow appropriate procedures. These include the use of appropriate personal protective equipment (PPE) such as safety glasses, gloves and lab coats when working with chemicals or near an instrument and not taking food or drink into the laboratory. Each analyst should know the location of all safety equipment. Each analyst shall receive a safety orientation from their Department Manager, or designee, appropriate for the job functions they will perform.

1.4 Pollution Prevention/Waste Disposal

Whenever possible, laboratory personnel should use pollution prevention techniques to address their waste generation. Refer to the current revision of the Katahdin Hazardous Waste Management Plan for further details on pollution prevention techniques.

Wastes generated during the preparation of samples must be disposed of in accordance with the Katahdin Hazardous Waste Management Plan and Safety Manual and SOP SD-903, "Sample Disposal," current revision. Expired standards are lab packed, placed in the Katahdin hazardous waste storage area, and disposed of in accordance with this SOP.

Any methylene chloride solvent waste generated during the preparation of standards etc. should be disposed of in the "D" waste stream satellite accumulation area nearest the point of generation. Acetone and hexane are considered flammable waste, and should be disposed of in the "O" waste stream satellite accumulation area nearest the point of generation. EPH sample vials are considered "P" waste and should be disposed of in the corresponding satellite waste accumulation area nearest the point of generation. Please refer to the

current revision of SOP CA-107 for the location of satellite waste accumulation areas.

2.0 SUMMARY OF METHOD

2.1 A sample submitted for EPH analysis is extracted with hexane, dried over sodium sulfate, and concentrated in a Kuderna-Danish apparatus. Sample separation into aliphatic and aromatic fractions is conducted using HPLC fractionation. The two extracts produced are then re-concentrated to final volumes of 1mL each (i.e., an aliphatic extract and an aromatic extract). The extracts are then separately analyzed by a capillary column gas chromatograph equipped with a flame ionization detector. The resultant chromatogram of aliphatic compounds is collectively integrated within the C_9 through C_{18} and C_{19} through C_{36} ranges. The resultant chromatogram of aromatic compounds is collectively integrated within the C_{11} through C_{22} range, and is (optionally) used to identify and quantitate individual concentrations of Target PAH Analytes.

2.2 Average calibration factors, determined using an aliphatic hydrocarbon standard mixture, are used to calculate the collective concentrations of C_9 through C_{18} and C_{19} through C_{36} aliphatic hydrocarbons. An average calibration factor determined using a PAH standard mixture is used to calculate a collective C_{11} through C_{22} aromatic hydrocarbon concentration. Calibration factors determined for individual components of the PAH standard mixture are also used to calculate individual concentrations of Target PAH Analytes.

2.3 This method is suitable for the analysis of waters, soils, and sediments.

2.4 This method is based on (1) USEPA Methods 8000, 8100, and 3630, SW-846, "Test Methods for Evaluating Solid Wastes: Physical/Chemical Methods." SW-846, 2nd edition, 1982 (revised 1984), 3rd edition, 1986, and Updates I, II, IIA, III, IIIA, and IIIB 1996, 1998 & 2004,; (2) Draft "Method for Determination of Diesel Range Organics", EPA UST Workgroup, November, 1990; (3) "Method for Determining Diesel Range Organics", Wisconsin Department of Natural Resources, PUBL-SW-141, 1992; and (4) Method for the Determination of Extractable Petroleum Hydrocarbons (EPH), Massachusetts DEP, May 2004, revision 1.1.

3.0 INTERFERENCES

3.1 Method interferences are reduced by washing all glassware with hot soapy water and then rinsing with warm tap water, acetone, and methylene chloride.

3.2 High purity reagents must be used to minimize interference problems.

3.3 Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. Whenever an unusually concentrated sample is analyzed, it must be followed by the analysis of a system solvent blank to check for cross-contamination.

3.4 Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interference will vary considerably from one source to another depending upon the nature and diversity of the site being sampled.

3.5 Certain organic compounds not associated with releases of petroleum products, including chlorinated hydrocarbons, phenols, and phthalate esters, will be quantitated as Extractable and Total Petroleum Hydrocarbons.

3.6 Because of their weakly polar nature, naphthalene and substituted naphthalenes are readily fractionated into the aliphatic extract. By using HPLC fractionation this contamination is eliminated. Because these compounds constitute a significant percentage of the water-soluble fraction of fuel oils, this occurrence is especially problematic in the analysis of water samples. For this reason, the method requires the evaluation of the aliphatic fraction for the presence of naphthalene and 2-methylnaphthalene in the LCS/LCSD pair on a batch basis. The fractionation surrogate, 2-Bromonaphthalene, is used to monitor sample-specific fractionation efficiency.

4.0 APPARATUS AND MATERIALS

4.1 The following glassware is used for this method:

4.1.1 auto sampler: 2mL glass vials with Teflon-lined rubber crimp caps

4.1.2 10mL vials with Teflon-lined caps

4.1.3 Class “A” volumetric flasks: 10, 25, 50 and 100mL

4.1.4 Class “A” volumetric pipettes: 1, 5 or 10mL

4.2 Analytical balance: An analytical balance capable of accurately weighing 0.0001g must be used for weighing standards. A top-loading balance capable of weighing to the nearest 0.1g must be used for weighing soil samples.

4.3 Gas Chromatograph

4.3.1 Gas Chromatograph: An analytical system complete with temperature programmable gas chromatograph for use with capillary columns is required. The data station must be capable of storing and reintegrating chromatographic data and must be capable of determining peak areas using a forced baseline projection. The current system is a Hewlett Packard 5890 GC connected to the Turbochrom data acquisition system, which is connected to the Target data processing system.

4.3.2 Current columns are: Primary aromatic analysis – ZB-5 30M x 0.53mm id x 1. 5µm film thickness. Secondary aromatic or aliphatic analysis – ZB-1 30M x 0.53mm id x 1. 0µm film thickness

4.3.3 Detector: A Flame Ionization Detector (FID) is required.

4.3.4 Auto sampler: An auto sampler capable of making 1 to 4 µL injections is recommended.

4.4 Microsyringes: 10-µL, 100-µL, 250-µL, 500-µL, 1000-µL

5.0 REAGENTS

5.1 Reagents- Solvents: hexane, methylene chloride, and acetone; pesticide grade or better. Store reagents away from other solvents.

5.2 Stock Standard Solutions

Stock standard solutions at approximately 1000ng/µL are purchased as certified solutions.

5.2.1 Aromatic Hydrocarbon Standard: The Aromatic Hydrocarbon Standard consists of the 17 PAH compounds listed in Table 3, a surrogate compound, and fractionation surrogate compounds in methylene chloride.

5.2.2 Aliphatic Hydrocarbon Standard: The Aliphatic Hydrocarbon Standard consists of the 14 normal alkanes listed in Table 3 and a surrogate compound in methylene chloride.

5.2.3 Petroleum Reference Standard: The Petroleum Reference Standard consists of an API or commercial diesel fuel. Prepare stock standard solutions by accurately weighing approximately 0.0100g of neat product.

Dissolve neat product in hexane and dilute to volume in a 10mL volumetric flask.

5.3 Surrogate Standards

5.3.1 Surrogate standards are used to monitor the efficacy of sample extraction, chromatographic, and calibration systems.

5.3.2 The recommended surrogate standards are 5-alpha androstane and ortho-terphenyl (OTP) which are available from Restek or similar supplier.

5.3.3 The surrogate standard 5-alpha androstane is purchased as a certified solution in hexane. This solution is added to the Aliphatic Hydrocarbon standard.

5.3.4 The surrogate standard OTP is purchased as a certified solution in methylene chloride. This solution is added to the Aromatic Hydrocarbon standard.

5.3.5 Surrogate Spiking Solution: The recommended surrogate spiking solution is comprised of a mixture of the COD and 5-alpha androstane surrogate standards. Prepare a surrogate spiking solution that contains the surrogate standards at a concentration of 90ng/µL in acetone. Each sample, blank, and matrix spike is fortified with 1.0mL of the surrogate spiking solution.

5.4 Fractionation Surrogate Standards

5.4.1 The fractionation surrogate standards are added to the sample (hexane) extract just prior to fractionation. The purpose of the fractionation surrogate standards is to monitor the efficacy of the fractionation process, and ensure that unacceptable quantities of naphthalene and substituted naphthalenes are not being stripped into the aliphatic extract.

5.4.2 The recommended fractionation surrogate standards are 2-Fluorobiphenyl and 2-Bromonaphthalene. Alternative fractionation surrogate compounds are permissible, provided that a demonstration is made that such compounds exhibit polarities/fractionation properties similar to naphthalene.

5.4.3 The fractionation surrogate standards are purchased as certified in Methylene Chloride. This solution is added to the Aromatic Hydrocarbon standard.

5.4.4 Fractionation Surrogate Spiking Solution: The recommended fractionation surrogate spiking solution is comprised of 2-Fluorobiphenyl and 2-Bromonaphthalene prepared in hexane at concentrations of 90ng/µL. An aliquot of 1mL of the fractionation surrogate spiking solution is added to the 1mL EPH sample extract prior to silica gel fractionation.

5.5 Matrix Spike Standard

5.5.1 Analytes from each hydrocarbon group (i.e., aromatic and aliphatic hydrocarbons) are used in a matrix spiking solution, which is prepared independently from the calibration standards.

5.5.2 The recommended spiking solution, consisting of all 14 normal alkanes and 17 PAHs as listed in Table 3, is prepared in acetone at concentrations of 90ng/µL each. Each selected matrix spike as well as laboratory control/laboratory control duplicate sample is fortified with 1.0mL of the matrix spike standard.

5.6 Fractionation Check Solution

5.6.1 The Fractionation Check Solution is used to monitor the fractionation efficiency of the silica gel cartridge, and establish the optimum volume of hexane needed to sufficiently elute aliphatic hydrocarbons, but not strip aromatic hydrocarbons.

5.6.2 Prepare a Fractionation Check Solution in hexane containing 200ng/µL of the Aliphatic Hydrocarbon standard (C_9-C_{36} alkanes), Aromatic Hydrocarbon standard (targeted PAH analytes), and extraction surrogates o-terphenyl and 5-alpha androstane. The final solution will contain 14 alkanes, 17 PAHs, and extraction surrogates at concentrations of 200ng/µL each. Alternative concentrations are permissible.

6.0 SAMPLE COLLECTION, PRESERVATION AND HANDLING

6.1 Aqueous samples are collected in 1 liter amber glass bottles with Teflon-lined screw caps.

6.2 Soil and sediment samples are collected in wide-mouth glass jars with Teflon-lined screw caps.

6.3 Aqueous samples must be preserved at the time of sampling by the addition of a suitable acid to reduce the pH of the sample to less than 2.0. This may be

accomplished by the addition of 5mL of 1:1HCl to a 1 liter sample. The use of alternative acids is permissible. Following collection and addition of acid, the sample must be cooled to 4°C (±2°C).

6.4 Soil and sediment samples must be cooled to 4°C (±2°C) immediately after collection.

6.5 A chain of custody form must accompany all aqueous, soil and sediment samples, documenting the time and date of sampling and any preservative additions.

6.6 Aqueous samples must be extracted within 14 days of collection, and analyzed within 40 days of extraction.

6.7 Soil and sediment samples must be extracted within 14 days of collection, and analyzed within 40 days of extraction.

A summary of sample collection, preservation, and holding times is provided in Table 1.

Refer to Katahdin SOP CA-511, Extraction of Petroleum Hydrocarbons from Samples for Analysis by MADEP - EPH Methods, current revision.

7.0 PROCEDURES

7.1 GC Conditions

Refer to instrument logbook for the current column and conditions.

Typical conditions are:

- Oven Program:
  - Set oven temperature to 70°C
  - then 10°C/min to 190°C
  - then 6°C/min to 238°C
  - then 2.5°C/min to 310°C and hold for 10 minutes.
  - Total run time is 58.80 minutes.
  - Sample injection is 1µL.
- The carrier gas is helium.
- The carrier gas Flow: 6mL/min.
- Air: 400mL/min.
- Make up gas flow: 30mL/min.
- FID temperature, 310°C
- Injection port temperature, 300°C
- GC operated in split/splitless mode

7.1.2 GC Maintenance

7.1.2.1 Capillary columns: Clean and deactivate the glass injection port insert or replace with a cleaned and deactivated insert.

7.1.2.2 Break off the first few inches, up to one foot, of the injection port side of the column.

7.1.2.3 Remove the column and solvent backflush according to the manufacturer's instructions.

7.1.2.4 Bake out the column at 300°C. If these procedures fail to eliminate a column degradation problem, it may be necessary to replace the column.

7.2 Retention Time Windows

7.2.1 Before establishing windows, make sure the GC system is within optimum operating conditions. Make three injections of the Aromatic Hydrocarbon and Aliphatic Hydrocarbon standard mixtures throughout the course of a 72-hr period. Serial injections over less than a 72-hr period may result in retention time windows that are too tight.

7.2.2 Calculate the standard deviation of the three absolute retention times for each individual component in the Aromatic Hydrocarbon standard, the Aliphatic Hydrocarbon standard, and all surrogate, fractionation surrogates.

7.2.3 Plus or minus three times the standard deviation of the absolute retention times for each standard should be used to define the retention time window. However, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

7.2.4 In those cases where the standard deviation for a particular standard is zero, the laboratory should substitute the standard deviation of a closely eluting structurally similar compound to develop a valid retention time window or use 0.1 minutes as a default value.

7.2.5 The laboratory must calculate retention time windows for each standard on each GC column and whenever a new GC column is installed. This data must be retained by the laboratory.

7.2.6 EPH retention time (RT) windows are defined as beginning 0.1 minutes before the RT of the beginning marker compound and ending 0.1 minutes

after the RT of the ending marker compound, except for n-C_{19}, which is both a beginning and ending marker compound for two different ranges.

The C_9 - C_{18} Aliphatic Hydrocarbon range ends immediately (0.1 min) before the elution of the n-C_{19} peak. The C_{19} - C_{36} Aliphatic Hydrocarbon range begins 0.1 before the elution of the n-C_{19} peak; therefore there is no overlap of the two ranges and the n-C_{19} peak is only included in the C_{19} - C_{36} Aliphatic Hydrocarbon range.

EPH marker compounds and windows are summarized in the table below.

Table - EPH Marker Compounds

Range/ Hydrocarbon Standard	Beginning Marker Cpd.	Ending Marker Compound
C_9-C_{18} Aliphatic Hydrocarbons	n-Nonane	Just Before n-Nonadecane
C_{19}-C_{36} Aliphatic Hydrocarbons	n-Nonadecane	n-Hexatriacontane
C_{11}-C_{22} Aromatic Hydrocarbons	Naphthalene	Benzo (g,h,i) Perylene

7.2.7 If a TPH analysis is done without fractionation, TPH retention time (RT) windows are defined as beginning 0.1 minutes before the RT of n-Nonane and ending 0.1 minutes after the RT of n-Hexatriacontane.

7.3 Calibration

Linear regression is used to calculate the slope and y-intercept that best describes the linear relationship between EPH target analyte and range concentrations and instrument response.

7.3.1 Linear regression calibration procedure

7.3.1.1 Prepare Aromatic and Aliphatic Hydrocarbon calibration standards at a minimum of five concentration levels by adding volumes of one or more stock standard solutions to volumetric flasks and diluting to volume with methylene chloride. The surrogate OTP and the fractionation surrogate standards are added to the Aromatic Hydrocarbon Standard; the surrogate 5-alpha androstane is added to the Aliphatic Hydrocarbon Standard. One of the calibration standards must be at the concentration of the Reporting Limit. The other concentrations must correspond to the expected range of concentrations found in real samples or should define the working range of the detector. The following calibration levels are recommended: 1, 10, 50, 100, and 200ng/µL for the individual components. The individual and collective concentrations of standard

analytes within each hydrocarbon range for these recommended calibration levels are provided in the table below.

Table - Recommended Calibration Standard Concentrations and masses (1µL Injection)

Component	Conc. of std. analytes (µg/ml)				
	1	10	50	100	200
Total Mass C_9 - C_{18} Aliphatic Hydrocarbons, ng (6 components)	6	60	300	600	1200
Total Mass C_{19} - C_{36} Aliphatic Hydrocarbons, ng (8 components)	8	80	400	800	1600
Total Mass C_{11}-C_{22} Aromatic Hydrocarbons/PAHs, ng (17components)	17	170	850	1700	3400

Each calibration standard is injected using the technique that is used to introduce the actual samples into the GC. The Target system will calculate a peak area for each compound.

A calibration curve is prepared using area responses versus concentration. A linear calibration applying a first order equation is used to prepare the curve. In order to be used for quantitative purposes, the correlation coefficient (r) must be greater than or equal to 0.990. The equation is:

$y = mx + b$

where: y = Instrument response
m = Slope of the line
x = Concentration of the calibration standard or range
b = The intercept

7.3.1.2 Calculate a linear regression (LR) for the individual PAH compounds that comprise the Aromatic Hydrocarbon standard. This is not necessary if the Target or Diesel PAH Analytes will not be individually identified and quantitated using the EPH method.

7.3.1.3 Calculate a LR for the extraction and fractionation surrogates.

7.3.1.4 A collective calibration curve must also be established for each hydrocarbon range of interest using the FID chromatogram of the appropriate fraction: C_9-C_{18} Aliphatic Hydrocarbons, C_{19}-C_{36} Aliphatic Hydrocarbons, and C_{11}-C_{22} Aromatic Hydrocarbons. Tabulate the summation of the peak areas of all components in that fraction against the total concentration injected. A listing of the collective

concentrations of standards within each hydrocarbon range is provided in the table in section 7.3.1.1.

Note: The area for the surrogates must be subtracted from the area summation of the range in which they elute (e.g., 5-alpha androstane is subtracted from the C_{19} - C_{36} Aliphatic Hydrocarbon range). Do not include the area of naphthalene or 2-methylnaphthalene in the linear regression analysis of the C_9-C_{18} Aliphatic Hydrocarbon range.

7.3.1.5 For TPH analyses, without fractionation, calculate a collective calibration curve. Tabulate the summation of the peak areas of all component standards in the aliphatic fraction (i.e., 14 components) against the total mass injected. Do not include any surrogates.

7.3.2 At a minimum, the working calibration curve must be verified on each working day, after every 20 samples or 24 hours (whichever is more frequent), and at the end of the sequence, by the injection of a mid-level calibration standard to verify instrument performance and linearity. If the percent difference (%D) for any analyte varies from the predicted response by more than ± 25% (± 30% for n-nonane), as calculated using the equation below, instrument maintenance must be performed (such as changing the liner) and/or a new calibration curve must be determined for that analyte or range.

Percent Difference (%D)

$$\%D = (R_1 / R_2) \times 100$$

Where: R1 = Calculated concentration from curve.
R2 = Expected concentration.

For the closing continuing calibration standard, four compounds may exhibit percent differences or percent drifts greater than 25 % but less than 40 %.

7.4 GC Analysis

7.4.1 Samples are analyzed in a set referred to as an analysis sequence. The sequence begins with instrument calibration (or calibration verification) followed by sample extracts interspersed with blanks and QC samples, and closes with a mid-range continuing calibration verification. The sequence ends when the set of sample extracts has been injected or when qualitative and/or quantitative QC criteria are exceeded.

7.4.2 Aliphatic and aromatic extracts are introduced into the gas chromatograph by direct injection of 1µl of sample.

7.4.3 Establish daily retention time windows for each analyte of interest using the absolute retention time for each analyte as the midpoint of the window for that day. The daily retention time window equals the midpoint ± three times the standard deviation determined in Section 7.2. Alternately, the default value of 0.1 minutes may be used for the daily retention time window.

7.4.3.1 Tentative identification of an aromatic analyte occurs when a peak from a sample extract falls within the daily retention time window. Confirmation is performed by reanalysis on a dissimilar GC column.

7.4.3.2 Validation of GC system qualitative performance must be accomplished by the analysis of midlevel standards within the analysis sequence. If any of the standards fall outside their daily retention time window, the system is out of control. In such cases, the cause of the problem must be determined and corrected.

7.4.4 Aliphatic and aromatic ranges of interest are determined by the collective integration of all peak eluted between specified range "marker" compounds. Due to the variability in software approaches and applications to collective peak area integration, it is recommended that a manual check be initially performed, to document proper integration functions.

7.4.5 When quantifying on a peak area basis by internal or external calibration, collective peak area integration for the fractional ranges, or TPH, must be from baseline (i.e. must include the unresolved complex mixture "hump" areas). For the integration of individual Target Analytes, surrogate compounds, a valley-to-valley approach should typically be used, though this approach may be modified on a case-by-case basis by an experienced analyst.

7.4.6 Baseline correction using an instrument thermal bleed is permissible, if conducted in accordance with the procedures and requirements specified in Section 7.6.5.

7.4.7 If the concentration of a Target or Diesel PAH Analyte, the aliphatic range C_9 through C_{18}, aliphatic range C_{19} through C_{36}, or aromatic range C_{11} through C_{22} exceed(s) the calibration range of the curve, dilute the extract and reanalyze. It is recommended that extracts be diluted so that all peaks are on scale, and bracketed by upper and lower calibration standards. Overlapping peaks are not always evident when peaks are off scale.

7.4.8 For non-target peaks eluting in the aliphatic, aromatic or TPH fractions, the upper linear range of the system should be defined by peak height measurement, based upon the maximum peak height documented for an aliphatic or aromatic standard within the fraction that is shown to be within the linear range for the detector. If any non-target peak eluting within any aliphatic or aromatic range exceeds twice the peak height documented for the highest range-specific calibration standard, dilute the extract and reanalyze.

7.5 Calculations

7.5.1 Linear Regression Analysis

The concentration of each analyte and/or hydrocarbon range in a sample may be determined by calculating the amount of analyte or hydrocarbon range injected, from the peak response, using linear regression analysis.

7.5.2 The concentration of an analyte is calculated by using the calibrated curve that is prepared in Target. When an analyte is identified, Target displays a concentration when the file is processed through the appropriate calibration method.

$$Amt = (y - b) / m$$

Where:
- Amt = Concentration calculated by Target in ug/mL.
- y = Instrument response
- m = Slope of the line
- b = The intercept

7.5.3 The concentrations from the reports are then incorporated with the extraction data to arrive at a final concentration.

Water: $\text{Concentration (ug/L)} = Amt \times DF\ [(Vt / Vo) \times 1000]$

Soil: $\text{Concentration (mg/Kgdrywt)} = Amt \times DF\ [(Vt / Vo) \times (100/(100-M))]$

Where:
- DF = Dilution factor.
- Vt = Final extract volume in L.
- Vo = Sample volume in L or kg.
- M = % Moisture.

7.6 Sample Analysis

7.6.1 Aliphatic Fraction

7.6.1.1 Determine the total area count for all peaks eluting 0.1 minutes before the retention time (Rt) for n-C_9 and 0.1 minutes before the Rt for n-C_{19}. It is not necessary to identify or quantitate individual aliphatic compounds within this range.

7.6.1.2 Determine the total area count for all peaks eluting 0.1 minutes before the Rt for n-C_{19} and 0.1 minutes after the Rt for n-C_{36}. It is not necessary to identify or quantitate individual aliphatic compounds within this range.

7.6.1.3 Determine the peak area count for the sample surrogate standard (5-alpha androstane) and any internal standard used. Subtract these values from the collective area count value within the appropriate hydrocarbon range(s).

7.6.1.4 Using linear regression in Target, calculate the collective concentrations of C_9 through C_{18} Aliphatic Hydrocarbons, C_{19} through C_{36} Aliphatic Hydrocarbons, and individual concentrations of any sample surrogate.

7.6.2 Aromatic Fraction

7.6.2.1 Determine the total area count for all peaks eluting 0.1 minutes before the retention time (Rt) for naphthalene and 0.1 minutes after the Rt for benzo(g,h,i)perylene.

7.6.2.2 Determine the peak area count for the sample surrogate (OTP), the fractionation surrogates, and any internal standard used. Subtract these values from the collective area count.

7.6.2.3 Optionally, determine the peak area count for the Target or Diesel PAH Analytes.

7.6.2.4 Using linear regression in Target, calculate the concentrations of Unadjusted C_{11} through C_{22} Aromatic Hydrocarbons, the sample surrogate standard (OTP), the fractionation surrogates, and, optionally, the Target or Diesel PAH Analytes.

7.6.2.5 If the concentrations of the Target or Diesel PAH Analytes were determined, either by this method or another method, subtract the concentration of the Target or Diesel PAH Analytes from the concentration of Unadjusted C_{11} - C_{22} Aromatic Hydrocarbons. If the concentration of Target or Diesel PAH Analytes were not determined, report a value for unadjusted C_{11} - C_{22} Aromatics, and indicate "Not Determined" for C_{11} - C_{22} Aromatics.

7.6.3 Total Petroleum Hydrocarbons

7.6.3.1 Determine the total area count for all peaks eluting 0.1 minutes before the retention time (RT) for n-C_9 and 0.1 minutes after the RT for n-C_{36}. It is not necessary to identify or quantitate individual aliphatic compounds within this range.

7.6.3.2 Determine the peak area count for any surrogate. Subtract these values from the collective area count value.

7.6.3.3 Optionally, determine the peak area count for the Target or Diesel PAH Analytes.

7.6.3.4 Using linear regression in Target, calculate the concentration of Unadjusted TPH, and, optionally, the Target or Diesel PAH Analytes.

7.6.3.5 If the concentrations of the Target or Diesel PAH Analytes were determined, either by this method or another method, subtract the concentration of the Target or Diesel PAH Analytes from the concentration of unadjusted TPH. If the concentration of Target or Diesel PAH Analytes were not determined, report a value for Unadjusted TPH, and indicate "Not Determined" for TPH.

7.6.4 Data Manipulations

7.6.4.1 By definition, the collective concentration of the aromatic fraction (and/or TPH) **excludes** the individual concentrations of the Target PAH Analytes. Accordingly, a data manipulation step is performed in KIMS that subtracts the individual PAH analyte concentrations.

7.6.4.2 Subtract the individual concentrations of the Target or Diesel PAH Analytes from the collective concentration of Unadjusted C_{11} through C_{22} Aromatic Hydrocarbons and/or Unadjusted TPH. If the individual concentrations of Target Analytes have not been quantitated, report a value for Unadjusted C_{11} through C_{22} Aromatic Hydrocarbons

and/or Unadjusted TPH, and indicate "Not Determined" for C_{11} through C_{22} Aromatic Hydrocarbons and/or TPH.

7.6.5 Baseline Correction for Instrument Noise Level

7.6.5.1 Range integration areas are corrected by the automatic subtraction of the baseline established by activation of an instrument thermal bleed.

7.6.5.2 If baseline correction is used, instrument baseline must be established for every batch of samples, and after the analysis of samples that are suspected to be highly contaminated.

7.7 Data Review

7.7.1 Initial Data Review

The initial data review is accomplished by the analyst who ran the samples. This review is of sufficient quality and detail to provide a list of samples that need to be reanalyzed or diluted and reanalyzed. The initial data review is performed in Target Review. This data review examines criteria that directly impact whether or not the sample needs to be reanalyzed and/or extracted. These criteria include:

- QC criteria for method blank, LCS/LCSD, MS/MSD, and calibration – refer to section 8.0.
- Surrogate recovery
- Chromatography: manual integration.
- Target compound detection: quantitation, false positives.

The requirement of the GC laboratory is that this initial data review be completed no later than the end of the next work day. After the analyst has completed his or her initial data review, the information is then ready to be processed for reporting. Refer to section 7.8.

7.7.2 Surrogate recovery

All recoveries must meet the method acceptance limits of 40-140%.
The sample is evaluated for recoveries of the surrogates. For the aliphatic extract, if the recovery of 5-alpha androstane is high and the sample results are less than the PQL, narrate. If the recovery is low and may be attributable to matrix interference, reanalyze to confirm a matrix effect and

narrate. If the recovery is low and there is no apparent matrix effect, the sample should be reanalyzed. If the reanalysis is still low, re-extract.

For the aromatic fraction, if the recovery of OTP is low and the fractionation surrogates are low, refractionate. If the fractionation surrogates are acceptable and the OTP is low and may be attributable to matrix interference, reanalyze to confirm a matrix effect and narrate. If the OTP is low and is not attributable to matrix interference, the sample results are less than the PQL, and the fractionation surrogates are acceptable, re-extract.

7.7.3 Chromatography

Manual integrations are to be performed when chromatographic conditions preclude the computer algorithm from correctly integrating the peak of concern. In no instance shall a manual integration be performed solely to bring a peak within criteria.

Each peak of concern is examined by the primary analyst to ensure that the peak was integrated properly by the computer algorithm. Any manual integrations that are necessary (for instance, if the sample contains a concentration of TPH/DRO which was integrated "valley to valley" instead of a "baseline to baseline"), are performed in Target Review. An "m" qualifier will automatically be printed on the quantitation report summary. The analyst must also date and initial in the space next to each of these qualifiers. For specific procedures on how to manually integrate, refer to Katahdin SOP QA-811, Manual Integration, current revision.

7.7.4 Target Compound Detection

The aromatic analysis chromatogram from channel A is evaluated with that from channel B. If a target analyte is present on both channels and the concentration is within the calibration range, and the quantitation from both chromatograms agrees within ±50%, the concentration from channel A is reported.

In order to avoid reporting false positives, identified peaks on a chromatogram may need to be undetected electronically in Target. The possible scenarios are: If an analyte is present on one column but its concentration is below the RL (Reporting Limit – based on the lowest calibration standard), if an analyte is present on one column but does not confirm on the other channel, if an analyte is present on both columns but the concentrations differ drastically, or if an analyte is present but it's retention time is outside of the retention time window for that analyte.

7.8 Reporting

7.8.1 After the chromatograms have been reviewed and any target analytes have been quantitated using Target, the necessary files are brought into QuickForms. Depending on the QC level requested by the client, reports, such as chronology or calibration forms, are generated. Reports of Analysis (ROA), LCS/LCSD, MS/MSD and surrogate forms are generated in KIMS. The package is assembled to include the necessary forms and raw data. The data package is reviewed by the primary analyst and then forwarded to the secondary reviewer. The secondary reviewer validates the data and checks the package for any errors. When completed, the package is sent to the Department Manager for final review. A completed review checklist is provided with each package. The final data package from the Organics department is then processed by the Data Management department.

7.8.2 The EPH reporting form contains an attestation, which indicates whether significant modifications were made to the EPH method, a clear affirmation on whether the QA/QC procedures and standards specified in the method were followed and achieved.

Significant modifications may include a different fractionation procedure than the one specified in the method, a change in the extraction procedure, the use of different surrogates. Any modifications, which were made along with any QA/QC deviations, are mentioned in the case narrative.

8.0 QUALITY CONTROL AND ACCEPTANCE CRITERIA

See below or refer to Table 4 for a summary of QC requirements, acceptance criteria, and corrective actions. These criteria are intended to be guidelines for analysts. The table does not cover all possible situations. If any of the QC requirements are outside the recovery ranges listed in Table 4, all associated samples must be evaluated against all of the QC. In some cases data may be reported, but may be reanalyzed in other cases. Making new reagents and standards may be necessary if the standardization is suspect. The corrective actions listed in Table 4 may rely on analyst experience to make sound scientific judgments. These decisions are based on holding time considerations, client and project specific Data Quality Objectives and on review of chromatograms. The Department Manager, Operations Manager and/or Quality Assurance Officer may be consulted to evaluate data. Samples may not be able to be reanalyzed within hold time. In these cases "qualified" data with narration may be advisable after consultation with the client.

In some cases the standard QC requirements listed in this section and in Table 4 may not be sufficient to meet the Data Quality Objectives of the specific project. Much of the work

performed at the lab is analyzed in accordance with specific QC requirements spelled out in a project specific Quality Assurance Project Plan (QAPP) or in a program specific Quality Systems Manual (QSM). The reporting limits, acceptance criteria and/or corrective actions may be different than those specified in this SOP. In these cases the appropriate information will be communicated to the Department Manager and/or senior chemists before initiation of the analyses so that specific product codes can be produced for the project. In addition, the work order notes for each project will describe the specific QAPP or QSM to be followed.

8.1 General Requirements and Recommendations

8.1.1 Each laboratory that uses this method is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and an ongoing analysis of spiked samples to evaluate and document data quality. The laboratory must maintain records to document the quality of the data generated.

8.1.2 A system solvent blank must be run after a sample suspected of being highly contaminated to determine if sample carryover has occurred.

8.1.3 At a minimum, for each analytical batch (up to 20 samples), a beginning and ending Calibration Check Standard, Method Blank, Laboratory Control Sample (LCS), and Laboratory Control Sample Duplicate (LCSD) must be run, and a Matrix Sample (MS) and/or MS duplicate or sample duplicate (DUP) should be analyzed, at the discretion of the analyst, based upon the nature of the sample. For analytical batches with more than 10 samples, the analysis of an additional mid-range calibration check standard should also be considered. The blank and spiked samples should be carried through all stages of the sample preparation and measurement process.

8.1.4 The recommended sequence of analysis is as follows:

- Calibration Standards (initial) or mid-range Calibration Check Standard (daily check of initial calibration) [REQUIRED]
- Method Blank [REQUIRED]
- Laboratory Control Sample and Laboratory Control Sample Duplicate [REQUIRED]
- Samples [up to 20]
- Matrix Sample/duplicate [As appropriate/Client Requested]
- Mid-range Calibration Check Standard [consider after 10 samples, as appropriate] [REQUIRED after 20 samples or at end of analytical sequence]

8.1.5 At a minimum, when the surrogate recovery from a sample, blank, or QC sample is less than 40% or more than 140%, check calculations to locate possible errors, the fortifying solution for degradation, and changes in instrument performance. If the cause cannot be determined, reanalyze the sample.

8.1.6 Each sample and QC sample must be evaluated for potential breakthrough on a sample-specific basis by evaluating the % recovery of the fractionation surrogate (2-bromonaphthalene) and on a batch basis by quantifying naphthalene and 2-methylnaphthalene in both the aliphatic and aromatic fractions of the LCS and LCSD. If the concentration of either naphthalene or 2-methylnaphthalene in the aliphatic fraction exceeds 5% of the total concentration (sum of analyte in aromatic and aliphatic fraction) for naphthalene and 2-methylnaphthalene in the LCS or LCSD, fractionation must be repeated on all archived batch extracts. If the fractionation surrogate recovery is outside the 40-140% limits, then fractionation must be repeated on the archived extract of the affected samples.

8.2 Minimum Instrument QC

8.2.1 The instrument must be able to achieve adequate separation and resolution of peaks and analytes of interest.

8.2.1.1 The n-nonane (n-C_9) peak must be adequately resolved from the solvent front of the chromatographic run.

8.2.1.2 The surrogates COD and 5-alpha androstane, fractionation surrogate standards must be adequately resolved from any individual components in the Aliphatic Hydrocarbon and Aromatic Hydrocarbon standards.

8.2.1.3 All peaks of interest from the Aliphatic Hydrocarbon standard must be adequately resolved to baseline. In the Aromatic Hydrocarbon standard, baseline separation is expected for Phenanthrene and Anthracene. Benzo(a)Anthracene, Chrysene, Benzo(b)Fluoranthene, Benzo(k)flouranthene, Dibenzo(a,h)Anthracene, and Indeno(1,2,3-cd)Pyrene are not expected to be chromatographically separated to baseline; however, sufficient separation should be obtained to 50% baseline.

8.2.2 Retention time windows must be established for each analyte of interest each time a new GC column is installed, and must be verified and/or adjusted on a daily basis.

8.2.3 Calibration curves must be developed based upon the analysis of calibration standards prepared at a minimum of 5 concentration levels and the correlation coefficient (r) must be at least 0.990.

8.2.4 The calibration ranges of the aliphatic and aromatic hydrocarbon fractions, and/or TPH fraction, are based on the respective high concentration standard.

8.2.5 In order to demonstrate the absence of mass discrimination, the response ratio of C_{28} to C_{20} must be at least 0.85. If <0.85, this nonconformance must be noted in the laboratory case narrative. The chromatograms of Continuing Calibration Standards for aromatics must also be reviewed to ensure that there are no obvious signs of mass discrimination.

8.2.6 Due care must be exercised to assure that the peaks for naphthalene and n-dodecane in the aliphatic hydrocarbon fraction are resolved to allow for an accurate determination of the naphthalene concentration in the LCS/LCSD pair.

8.3 Initial and Periodic Method QC Demonstrations

The procedures specified in Section 8.3.1 through 8.3.3 must be conducted as an initial demonstration of laboratory capability, prior to the analysis of any samples. Subsequent to this initial demonstration, additional evaluations of this nature should be conducted on a periodic basis, in response to changes in instrumentation or operations, and/or in response to confirmed or suspected systems, method, or operational problems.

8.3.1 Accuracy and Precision

To demonstrate initial laboratory capability, analyze a minimum of four replicate laboratory reagent grade water and/or clean sand blanks spiked with each analyte of interest at approximately 50µg/L and/or 5mg/kg, respectively.

8.3.1.1 Extract each replicate according to the procedures described in the current revision of Katahdin SOP CA-511. Analyze according to the procedures described in section 7.0.

8.3.1.2 Calculate the measured concentrations of each analyte in all replicates, the mean accuracy (as a percentage of true value) for each analyte, and the precision (as %RSD) of the measurements for each analyte.

8.3.1.3 For each analyte, excluding n-C_{36}, the mean accuracy, expressed as a percentage of the true value, must be between 40% and 140%. Poorer recoveries may be experienced for the n-C_{36} standard. For each analyte, the %RSD must be less than or equal to 25% (30% for n-nonane).

8.3.2 Fractionation

8.3.2.1 To demonstrate the capability of properly fractionating aliphatic and aromatic hydrocarbons in a sample, the analyst must first prepare and analyze the Fractionation Check Solution specified in Section 5.6, using the HPLC fractionation procedure.

8.3.2.2 For each analyte within the Fractionation Check Solution, excluding n-C_{36}, the mean accuracy, expressed as a percentage of the true value, must be between 40% and 140%.

8.4 Ongoing Method QC Demonstrations

8.4.1 Each sample, blank, and LCS/LCSD must be spiked with the surrogate spiking solution. Required surrogate recovery is 40% to 140%. Recoveries outside this range must be noted and discussed on the data report form.

8.4.2 Each sample extract must be spiked with a fractionation surrogate spiking solution prior to fractionation. Required recovery is 40% to 140%. Recoveries outside this range must be noted and discussed on the data report form.

8.4.3 At a minimum, with every batch of 20 samples or less the lab must analyze the following:

8.4.3.1 Independent Calibration Verification (ICV) Standard - A mid-range calibration standard, prepared from a source independent from the stock standard solution used to develop the calibration curve. This standard must be analyzed prior to sample analysis to verify the calibration. If the percent difference (%D) of any analyte, within a calibration check standard, varies from the predicted response by more than 25% (30% for n-nonane), corrective action must be performed (such as changing the reprepping the standard) and/or a new calibration curve must be prepared

8.4.3.2 Calibration Check Standard - A mid-range calibration standard, prepared from the same stock standard solution used to develop the calibration curve, must be analyzed prior to and after sample

analysis to verify the calibration state of the instrument. For large analytical batches that contain more than 10 samples, the analysis of an additional mid-range calibration check standard should also be considered after the analysis of the tenth sample. If the percent difference (%D) of any analyte, within a calibration check standard, varies from the predicted response by more than 25% (30% for n-nonane), instrument maintenance must be performed (such as changing the liner) and/or a new calibration curve must be prepared for that analyte.

8.4.3.3 Method Blank - A water or soil Method Blank is prepared by fortifying a laboratory reagent grade water or clean sand blank with 1.0mL of the surrogate spiking solution. Peaks detected within the retention time window of any analyte or range of interest above a Reporting Limit must be noted on the data report form.

8.4.3.4 Laboratory Control Sample - A Laboratory Control Sample is prepared by fortifying a laboratory reagent grade water or clean sand blank with 1.0mL of the matrix spiking solution. The spike recovery should be between 40% and 140%, excluding n-C_{36}.

8.4.3.5 Laboratory Control Sample Duplicate - A Laboratory Control Sample duplicate is prepared by fortifying a laboratory reagent grade water or clean sand blank with 1.0mL of the matrix spiking solution. The spike recovery should be between 40% and 140%, excluding n-C_{36}. The RPD between the laboratory control sample and laboratory control sample duplicate should be less than 25%.

8.4.3.6 Instrument Thermal Bleed - If baseline correction will be employed, a instrument thermal bleed must be undertaken with every batch, and after the analysis of a sample that is suspected to be highly contaminated.

8.4.4 At the discretion of the analyst, and in consideration of sample matrices and data quality objectives, it is recommended that with every batch of 20 samples or less the lab consider analysis of the following:

8.4.4.1 Matrix Sample (MS)/Duplicate (MSD) - The water or soil MS is prepared by fortifying an actual water or soil sample with 1.0mL of the matrix spiking solution. The purpose of the MS spike is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the MS corrected for background concentrations.

The corrected concentrations of each analyte within the MS spike sample should be within 40 to 140% of the true value, excluding n-C_{36}. The %RPD of MS Duplicates should be less than 50%.

8.4.5 If any of the performance standards specified in Section 8.4.1 through 8.4.3 are not met, the problem must be corrected before further samples are analyzed. Any samples run between the last QC samples that meet the criteria and those that are fallen out must be rerun. If this is not possible, that data must be reported as suspect.

8.4.6 The analyte and hydrocarbon range reporting limits should be verified/re-established at least once per year, or upon a major change in system equipment or operations.

9.0 METHOD PERFORMANCE

The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. The MDLs are determined annually per type of instrument and filed with the Inorganic Department Manager and with the QAO. Refer to the current revision of Katahdin SOP QA-806, "Method Detection Limit, Instrument Detection Limit and Reporting Limit Studies and Verifications", for procedures on determining the MDL.

The Practical Quantitation Limit (PQL) concentrations for all the target analytes are listed in Table 5.

Refer to the current revision Method MADEP EPH-04-1 for other method performance parameters and requirements.

10.0 APPLICABLE DOCUMENTS/REFERENCES

Method for the Determination of Extractable Petroleum Hydrocarbons (EPH), Massachusetts DEP, May 2004 revision 1.1

Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, USEPA SW846, 3rd Edition, Final Updates I, II, IIA, IIB, III, IIIA, IIIB and IV, February 2007.

Department of Defense Quality Systems Manual for Environmental Laboratories (DOD QSM), Version 4.1, 04/22/09.

The National Environmental Laboratory Accreditation Conference (NELAC) Standards, June 2003.

Katahdin SOP CA-101, "Equipment Maintenance and Troubleshooting", current revision.

Katahdin SOP QA-806, "Method Detection Limit, Instrument Detection Limit and Reporting Limit Studies and Verifications", current revision.

Katahdin Analytical Services, Inc. SOP CA-511, "Extraction of Petroleum Hydrocarbons from Samples for Analysis by MADEP - EPH Methods", current revision

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TABLE 1

SUMMARY OF CALIBRATION AND QC PROCEDURES FOR METHOD MADEP EPH

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action
Five-point external calibration of 17 targeted PAH standards, and collective calibrations of C_{11} through C_{22} aromatic hydrocarbons, C_9 through C_{18} aliphatic hydrocarbons and C_{19} through C_{36} aliphatic hydrocarbons.	Initial calibration prior to sample analysis	The correlation coefficient (r) must be greater than or equal to 0.99.	Investigate and repeat initial calibration
Initial Calibration Verification (ICV)	Once after each calibration	All analytes ≤ 25 %D of the expected value.	Reanalyze sample Reprepare standard Reprepare standard from fresh stock.
CV	If initial calibration analyzed, daily and after 10 to 20 samples, and at end of sequence.	%RPD within 30% for n-nonane and for all other analytes within 25% The closing CCV may have up to 4 compounds > 25% but less than 40% D.	Evaluate the samples: If the %RPD >25% (30% for n-nonane) and sample results are < PQL, narrate. If %RPD >25% (30% for n-nonane) and is likely a result of matrix interference, narrate. Otherwise, reanalyze all samples after last acceptable CV.
Method blank	One per prep batch	No analytes detected > PQL	(1) Investigate source of contamination (2) Evaluate the samples and associated QC: i.e. if the blank results are above the PQL, report samples results which are < PQL >10X the blank concentration. Otherwise, reprep a blank and the remaining samples.
LCS/LCSD	One LCS/LCSD pair per prep batch	Spike recovery must be between 40% and 140% and RPD less than 25%	(1) Evaluate the samples and associated QC: i.e. If an MS/MSD was performed and acceptable, narrate. If an LCS/LCSD was performed and only one of the set was unacceptable, narrate. If the surrogate recoveries in the LCS are low but are acceptable in the blank and samples, narrate. If the LCS recovery is high but the sample results are < PQL, narrate. Otherwise, reprep a blank and the remaining samples.
LCS/LCSD	One LCS/LCSD pair per prep batch	Concentration of naphthalene and 2-methylnaphthalene in the aliphatic fraction must be less than 5% of total concentration	Refractionate all archived extracts from the extraction batch
Surrogate	Every sample, blank, and QC	Recovery must be between 40% and 140%	Refer to section 7.7.2

	sample		

TABLE 1, cont'd

SUMMARY OF CALIBRATION AND QC PROCEDURES FOR METHOD MADEP EPH

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action
Matrix Spike/Matrix Spike Duplicate	One MS/MSD per batch of 20 samples (optional), as requested by clients.	Recovery must be between 40% and 140% and RPD less than 50%	(1) Evaluate the samples and associated QC: i.e. If the LCS is acceptable, narrate. (2) If both the LCS and MS/MSD are unacceptable, reprep the samples and QC.
Sample duplicate if requested by the client	One per batch of 20 samples	%RPD of duplicate must be less than 50%.	(1)check calculations for errors (2) Evaluate QC
Fractionation Check Solution	Prepare for each new lot of silica gel cartridge lot or every 3 months, whichever is sooner	Mean accuracy must be between 40 and 140%.	Investigate and refractionate.
Demonstration of capability - four replicate analyses of a QC check sample	One time per analyst initially and annually thereafter	For each analyte, the mean accuracy must be 40 to 140 %R and the %RSD must be $\leq$ 25%	Investigate; reprep
MDL and/or LOD/LOQ Verification	Refer to the current revision of Katahdin SOP QA-806, "Method Detection Limit, Instrument Detection Limit and Reporting Limit Studies and Verifications", for procedures on determining the MDL.		

TITLE: METHOD FOR THE ANALYSIS OF EXTRACTABLE PETROLEUM HYDROCARBONS MADEP - EPH METHOD

TABLE 2

SUMMARY OF METHOD MODIFICATIONS

TOPIC	KATAHDIN SOP CA-322-08	METHOD MADEP - EPH
Apparatus/ Materials		
Reagents/ Standards	1) Aliphatic hydrocarbon standards prepared in methylene chloride.	1) Aliphatic hydrocarbon standards prepared in hexane.
Sample preservation/ handling	1) Soil samples collected in clear jars	1) Soil samples collected in amber jars
Procedures	1) Baseline correction made by the automatic subtraction of the baseline established by activation of a instrument thermal bleed 2) Prepare petroleum reference spiking solution by weighing 0.0100g of neat product	1) Baseline correction made by the subtraction of the baseline established by the injection of a system solvent blank 2) Prepare petroleum reference spiking solution by weighing 0.0250g of neat product
QC - Standards	1) Surrogate, spike and fractionation surrogate all prepared at 90 ug/mL for use in a 2 mL or prefractionated volume. 2) Fractionation check solution: aliphatics, aromatics, 5-alpha androstane, and o-terphenyl at 200ug/mL each	1) Surrogate at 40 ug/mL, matrix spike at 50-150 ug/mL, fractionation surrogate at 40 ug/mL. 2) Fractionation check solution: aliphatics and aromatics at 200ug/mL each
QC - LCS		
QC - Accuracy/ Precision		
QC - MDL		

TABLE 3

HOLDING TIMES AND PRESERVATIVES FOR EPH SAMPLES

MATRIX	CONTAINER	PRESERVATION	HOLDING TIME
Aqueous Samples	1 Liter amber glass bottle with Teflon- lined screw cap	Add 5mL of 1:1HCl; cool to 4°C	Samples must be extracted within14 days and extracts analyzed within40 days of extraction
Soil/Sediment Samples	4-oz. (120mL) Wide-mouth glass jar with Teflon-lined screw cap	Cool to 4°C	Samples must be extracted within14 days and extracts analyzed within40 days of extraction
Soil/Sediment Samples	4-oz. (120 mL) wide-mouth glass jar with Teflon-lined screw cap. Jar should be filled to only 2/3 capacitiy to avoid breakage if expansion occurs during freezing.	Freeze at -10 °C in the field or in the laboratory*	Samples must be extracted within 14 days of the date thawed and extracts analyzed within 40 days of extraction*

*Samples processed in the laboratory must be preserved at 4 (±2) °C and frozen within 48 hours of the time of collection. Frozen samples may be held for up to one year prior to analysis and must be extracted within 24 hours of thawing.

TITLE: METHOD FOR THE ANALYSIS OF EXTRACTABLE PETROLEUM HYDROCARBONS MADEP - EPH METHOD

TABLE 4

RECOMMENDED STOCK, FRACTIONATION CHECK SOLUTION, MATRIX SPIKE AND CALIBRATION STANDARD CONCENTRATIONS - MADEP - EPH

ANALYTE	Stock * Standards (ng/µL)	Fractionation ** Check Solution (ng/µL)	Matrix Spike Standard *** (ng/µL)	Calibration Standard Concentrations (in $MeCl_2$) (ng/µL) level 1	(ng/µL) level 2	(ng/µL) level 3	(ng/µL) level 4	(ng/µL) level 5
Naphthalene	1,000	200	90	1	10	50	100	200
2-Methylnaphthalene	1,000	200	90	1	10	50	100	200
Acenaphthylene	1,000	200	90	1	10	50	100	200
Acenaphthene	1,000	200	90	1	10	50	100	200
Fluorene	1,000	200	90	1	10	50	100	200
Phenanthrene	1,000	200	90	1	10	50	100	200
Anthracene	1,000	200	90	1	10	50	100	200
Fluoranthene	1,000	200	90	1	10	50	100	200
Pyrene	1,000	200	90	1	10	50	100	200
Benzo(a)Anthracene	1,000	200	90	1	10	50	100	200
Chrysene	1,000	200	90	1	10	50	100	200
Benzo(b)Fluoranthene	1,000	200	90	1	10	50	100	200
Benzo(k)Fluoranthene	1,000	200	90	1	10	50	100	200
Benzo(a)Pyrene	1,000	200	90	1	10	50	100	200
Indeno(1,2,3-cd)Pyrene	1,000	200	90	1	10	50	100	200
Dibenzo(a,h)Anthracene	1,000	200	90	1	10	50	100	200
Benzo(g,h,i)Perylene	1,000	200	90	1	10	50	100	200
Ortho-Terphenyl (surr)	1,000	200	----	1	10	50	100	200
Nonane	1,000	200	90	1	10	50	100	200
Decane	1,000	200	90	1	10	50	100	200
Dodecane	1,000	200	90	1	10	50	100	200
Tetradecane	1,000	200	90	1	10	50	100	200
Hexadecane	1,000	200	90	1	10	50	100	200
Octadecane	1,000	200	90	1	10	50	100	200
Nonadecane	1,000	200	90	1	10	50	100	200
Eicosane	1,000	200	90	1	10	50	100	200
Docosane	1,000	200	90	1	10	50	100	200
Tetracosane	1,000	200	90	1	10	50	100	200
Hexacosane	1,000	200	90	1	10	50	100	200
Octacosane	1,000	200	90	1	10	50	100	200
Triacontane	1,000	200	90	1	10	50	100	200
Hexatriacontane	1,000	200	90	1	10	50	100	200
5-alpha androstane(surrogate)	1,000	200	------	1	10	50	100	200

TABLE 4, cont'd

RECOMMENDED STOCK, FRACTIONATION CHECK SOLUTION, MATRIX SPIKE AND CALIBRATION STANDARD CONCENTRATIONS - MADEP - EPH

* The Aromatic Hydrocarbon Standards (17 PAH compounds and ortho-Terphenyl) should be prepared in methylene chloride. The Aliphatic Hydrocarbon Standards (consisting of 14 normal alkanes and 1-chloro-octadecane) should be prepared in Methylene chloride.

** The Fractionation Check Standard should be prepared in hexane.

*** The Matrix Spike Solution should be prepared in acetone.

TITLE: METHOD FOR THE ANALYSIS OF EXTRACTABLE PETROLEUM HYDROCARBONS MADEP - EPH METHOD

TABLE 5

PQLs FOR METHOD MADEP EPH

PARAMETER/ METHOD	ANALYTE	PRACTICAL QUANTITATION LEVEL (PQL)	
		Aqueous (µg/L)	Soil (mg/kg)
Extractable Petroleum Hydrocarbons	Naphthalene	2	0.2
	2-Methylnaphthalene	2	0.2
	Acenaphthylene	2	0.2
	Acenaphthene	2	0.2
	Fluorene	2	0.2
	Phenanthrene	2	0.2
	Anthracene	2	0.2
	Fluoranthene	2	0.2
	Pyrene	2	0.2
	Benzo(a)Anthracene	2	0.2
	Chrysene	2	0.2
	Benzo(b)Fluoranthene	2	0.2
	Benzo(k)Fluoranthene	2	0.2
	Benzo(a)Pyrene	2	0.2
	Indeno(1,2,3-cd)Pyrene	2	0.2
	Dibenzo(a,h)Anthracene	2	0.2
	Benzo(g,h,i)Perylene	2	0.2
		2	0.2
	C_9 - C_{18} Aliphatics	100	20
	C_{19} - C_{36} Aliphatics	100	20
	C_{11} - C_{22} Aromatics	100	20

TITLE: METHOD FOR THE ANALYSIS OF EXTRACTABLE PETROLEUM HYDROCARBONS MADEP - EPH METHOD

FIGURE 1

EXAMPLE OF MADEP-EPH ANALYTICAL LOGBOOK PAGE

Katahdin Analytical Services, Inc.
Instrument: GC12 (FID)
Amount Injected 1ul

GC Laboratory Instrument Runlog

Method (circle) EPH(MADEP) / FL PRO / TNRCC 1005

Reviewed by/ Date:

DRO/TPH - 8015Mod. / MDEP 4.1.25 / 8100Mod.

Date	Init.	Result File	Sample ID	Y/N	Method	Column	Comments
4-2-10	JLP	CDD1037	GC07361	Y	AROA029A	334	SSLCS JLP 4/05/10
4-3-10		38	SD14255 3510				OTP↓
		39	-6				All SS↓
		40	-7				OTP↓
		41	-8				
		42	-9				
		43	-10				OTP↓
		44	SD1390-10				PF
		45	MeCl2	N			
		46	TB	Y			
		47	ARO 50ug/mL	Y			↑ H1923
		48	TB	N			
		49					
		50					
4-5-10	JLP	51	TB	N			
		52	TB	Y			
		53	ARO 50ug/mL	Y			H1923
		54	WG75480-1 3510	Y			
		55	-2	Y			
		56	-3				
		57	SD14472-62 JLP 04/06/10				
		58	-3				
		59	-4				
		60	-5				
		61	-6				
		62	TB	Y			
		63	ARO 50ug/mL	Y			H1923
		64	TB	N			
		65		N			
4-6-10	JLP	66	TB				

TITLE: METHOD FOR THE ANALYSIS OF EXTRACTABLE PETROLEUM HYDROCARBONS MADEP - EPH METHOD

FIGURE 2

EXAMPLE OF DATA REVIEW CHECKLIST

PRIMARY REVIEW CHECKLIST

Verbal Due Date _____ (☐ **Verbals turned in**). **DueDate**_____

Client:		Primary	Secondary
Method:		Date:	Date:
SDG No:	Level:	Initials:	Initials:
KAS No:			Approved : ☐ Yes

DODQSM 3.0 ☐ **DODQSM 4.1** ☐ **WITH LAB. LIMITS** ☐
QUAPP ☐ **LAB** ☐ (*REPORT* ***ND's*** *to* ***MDL*** ☐)

List all curves that are scanned. _____ _____

_____ _____ _____ _____

Narrate which QC limits were used for (Surr., LCS,s MS/MSDs.) _____

All needed forms are present . _____

Correct Work Order Number or SDG name (all forms). _____

Correct project name and spelling (all forms). (Truncated ☐). _____

Correct file numbers (all forms). _____

Analysis Date Correct. _____

Extraction Method & Analysis Method Correct. _____

Product list compared to ROAs (compounds & PQLs). _____

Chromatogram reviewed for unlabeled peaks (check product list). _____

Flagging of all ROAs correct (Florida Flagging ☐). _____

All tunes included (level IV) . _____

All log book pages included (Soil weights,TCLP & SPLP). _____

Verify DOD QSM criteria. _____

Narrate any method deviations. (Blanks, LCS,s etc.) _____

Sign & Date Manual integration **(Narrate as needed).** _____

Sample I.D's Truncated (**NARRATED**). YES ☐ Please list KAS # below :

_____

QA-044 - Revision 1 - 04/05/2010

TITLE: ANALYSIS OF PCBs AS TOTAL AROCLORS BY GAS CHROMATOGRAPHY/ ELECTRON CAPTURE DETECTOR (GC/ECD): SW-846 METHOD 8082

Prepared By: Peter Lemay Date: 4/98

Approved By:

Group Supervisor: [signature] Date: 1/15/01

Operations Manager: John C. Burton Date: 1/15/01

QA Officer: Deborah J. Nadeau Date: 1.22.01

General Manager: [signature] Date: 1/16/01

Revision History:

SOP Revision	Changes	Approval Initials	Approval Date	Effective Date
01 8082	Format changes, added pollution prevention, minor changes to sections 7, 8 and Table 1	DN	1.22.01	1/22/01
02 8082	Revised sections 7.3.1, 7.4.5 and 7.6.1 to be compliant with South Carolina requirements.	DN	5.23.01	5.23.01
03 8082	Changed to practice of reporting higher value. Other minor changes to sections 7.5.2, 7.7.3 + to Table 2.	DN	5.21.02	5.21.02
04 8082	Revised SOP to indicate Turbochrom is being used as instrument control + data collection software. Included Target-related definitions. Changes to sections 7.7.3, 7.7.4 and 7.8.	MRC	08.20.04	08.20.04
05 8082	Changed 7.5.2 to reflect alternating CV Changed Table 2 Sect. 7.3.1 New Checklist added wording to sect. 8	LAD	020305	020305

TITLE: ANALYSIS OF PCBs AS TOTAL AROCLORS BY GAS CHROMATOGRAPHY/ ELECTRON CAPTURE DETECTOR (GC/ECD): SW-846 METHOD 8082

SOP Revision	Changes	Approval Initials	Approval Date	Effective Date
06 8082	Changed PCB 1260 to Aroclor 1260. Removed references to 3541. Updated table 2. Added instructions to shake extract before vialing	LAD	04/06	04/06
07	Added waste streams to sect. 1.0. Added ICV to definitions, sect. 5, sect. 7 and Table 1. Added wording regarding 2nd column confirmation criteria and flagging rules to sect. 7.7.4. Added CCV criteria to sect. 7.5.3 and Table 1. Added wording regarding MI to sect. 7.7.3	LAD	08/07	08/07
08	Added tissue, wipe and oil matrices. Added extraction method 3535. Added DDT analog interference, Std. information and analysis frequency criteria. Added HTs are a recommendation. Added note that 2 detectors must be used for dual column. Updated method references. Removed calibration and surrogate method mod. from Table 2. Added more info @ linear calib. Added extraction references.	LAD	02/09	02/09
09	Added Chemstation to definitions. Clarified that Surrogates are added to only the aroclor 1660 standards, not ALL standards.	LAD	05/09	05/09
10	Revised sections 7, 8, and 10 to reflect compliance with the DoD QSM version 4.1	LAD	08/09	08/09
11	Added Table 2 with DoD QSM Ver. 4.1 QC criteria. Minor changes to Table 1.	LAD	04/10	04/10

TITLE: ANALYSIS OF PCBs AS TOTAL AROCLORS BY GAS CHROMATOGRAPHY/ ELECTRON CAPTURE DETECTOR (GC/ECD): SW-846 METHOD 8082

Please acknowledge receipt of this standard operating procedure by signing and dating both of the spaces provided. Return the bottom half of this sheet to the QA Department.

I acknowledge receipt of copy ___ of document **SOP CA-329-11**, titled **ANALYSIS OF AS TOTAL AROCLORS BY GAS CHROMATOGRAPHY/ELECTRON CAPTURE DETECTOR (GC/ECD): SW-846 METHOD 8082**.

Recipient: _____ Date: _____

KATAHDIN ANALYTICAL SERVICES, INC.
STANDARD OPERATING PROCEDURE

I acknowledge receipt of copy ___ of document **SOP CA-329-11**, titled **ANALYSIS OF PCBs AS TOTAL AROCLORS BY GAS CHROMATOGRAPHY/ELECTRON CAPTURE DETECTOR (GC/ECD): SW-846 METHOD 8082**.

Recipient: _____ Date: _____

TITLE: ANALYSIS OF PCBs AS TOTAL AROCLORS BY GAS CHROMATOGRAPHY/ ELECTRON CAPTURE DETECTOR (GC/ECD): SW-846 METHOD 8082

1.0 SCOPE AND APPLICATION

This SOP describes all aspects of the analysis of extracts of aqueous, solid, tissue, wipe and oil samples for PCBs by EPA Method 8082A as performed by Katahdin Analytical Services, Inc. including sample analysis, data review, standard preparation and instrument calibration.

It is applicable to the following compounds: Aroclor-1242, Aroclor-1254, Aroclor-1221, Aroclor-1232, Aroclor-1248, Aroclor-1260 and Aroclor-1016. Extracts are analyzed by Gas Chromatography-Electron Capture Detector (GC-ECD)

1.1 Definitions

ANALYTICAL BATCH: 20 or fewer samples which are analyzed together with the same method sequence and the same lots of reagents and with the manipulations common to each sample within the same time period or in continuous sequential time periods.

METHOD BLANK (laboratory reagent blank): An artificial sample designed to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus. For aqueous samples, laboratory reagent grade water is used as a blank matrix; for soil samples, muffled sand is used as a blank matrix. The blank is taken through the appropriate steps of the process.

CALIBRATION CHECK: Verification of the ratio of instrument response to analyte amount, a calibration check is done by analyzing for analyte standards in an appropriate solvent. Calibration check solutions are made from a stock solution that is different from the stock used to prepare standards.

CALIBRATION STANDARD (WORKING STANDARD): A solution prepared from the stock standard solution that is used to calibrate the instrument response with respect to analyte concentration.

INDEPENDENT CALIBRATION VERIFICATION STANDARD (ICV): A solution prepared from a stock standard solution independent of the calibration mix that is used to verify the calibration.

LABORATORY CONTROL SAMPLE (LCS): A blank that has been spiked with the analyte(s) from an independent source and is analyzed exactly like a sample. Its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements. The matrix used should be phase matched with the samples and well characterized.

MATRIX SPIKE/MATRIX SPIKE DUPLICATE (MS/MSD): Predetermined quantities of stock solutions of certain analytes are added to a sample matrix prior to sample

extraction and analysis. Samples are split into duplicates, spiked and analyzed. Percent recoveries are calculated for each of the analytes detected. The relative percent difference between the samples is calculated and used to assess analytical precision.

STANDARD CURVE (CALIBRATION CURVE): A curve that plots concentration of known analyte standard versus the instrument response to the analyte.

STOCK STANDARD SOLUTION: A concentrated solution containing a single certified standard that is a method analyte, or a concentrated solution of a single analyte prepared in the laboratory with an assay reference compound. Stock standard solutions are used to prepare calibration standards.

SURROGATES: Organic compounds which are similar to analytes of interest in chemical composition, extraction and chromatography, but which are not normally found in environmental samples. These compounds are spiked into all blanks, Aroclor 1660 standard, samples and spiked samples prior to analysis. Percent recoveries are calculated for each surrogate.

KATAHDIN INFORMATION MANAGEMENT SYSTEM (KIMS): A complete multi-user system with the capabilities of integrating laboratory instrumentation, generating laboratory worksheets, providing complete Lab Order status and generating reports. KIMS utilizes these features through a database.

PE NELSON TURBOCHROM OR HP CHEMSTATION: data acquisition systems that are used to collect chromatographic data. The systems can also be used to archive raw data files.

TARGET: A software system that combines full processing, reporting and comprehensive review capabilities, regardless of chromatographic vendor and data type.

TARGET DB: An oracle database used to store and organize all Target data files.

QUICKFORMS: A laboratory reporting software for Target and Target DB. The QuickForms report module for Target is preconfigured with generalized forms and US EPA CLP report forms and disk deliverables, which can be customized.

1.2 Responsibilities

1.2.1 This method is restricted to use by, or under the supervision of analysts experienced in the analysis of PCBs by method 8082. Each analyst must demonstrate and document their ability to generate acceptable results with this

method. Refer to Katahdin SOP QA-805, "Personnel Training & Documentation of Capability," current revision.

1.2.2 It is the responsibility of all Katahdin technical personnel involved in analysis by method 8082 to read and understand this SOP, adhere to the procedures outlined, and to properly document their data in the appropriate lab notebook. Any deviations from the test or irregularities with the samples should also be recorded in the lab notebook and reported to the Department Manager or designated qualified data reviewer responsible for this data.

1.2.3 It is the responsibility of the Department Manager to oversee that members of their group follow this SOP, to ensure that their work is properly documented and to initiate periodic review of the associated logbooks.

1.3 Health and Safety

1.3.1 Users of this procedure must be cognizant of inherent laboratory hazards, proper disposal procedures for contaminated materials and appropriate segregation of hazardous wastes. The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical should be treated as a potential health hazard. A reference file of material safety data sheets is available to all personnel involved in the chemical analysis. Everyone involved with the procedure must be familiar with the MSDSs (material safety data sheets) for all the materials used in this procedure.

1.3.2 Each qualified analyst or technician must be familiar with Katahdin Analytical Environmental Health and Safety Manual including the Katahdin Hazardous Waste Plan and must follow appropriate procedures. These include the use of appropriate personal protective equipment (PPE) such as safety glasses, gloves and lab coats when working with chemicals or near an instrument and not taking food or drink into the laboratory. Each analyst should know the location of all safety equipment. Each analyst shall receive a safety orientation from their Department Manager, or designee, appropriate for the job functions they will perform.

1.4 Pollution Prevention/Waste Disposal

1.4.1 Whenever possible, laboratory personnel should use pollution prevention techniques to address their waste generation. Refer to the current revision of the Katahdin Hazardous Management Program for further details on pollution prevention techniques.

1.4.2 Wastes generated during the preparation of samples must be disposed of in accordance with the Katahdin Analytical Environmental Health and Safety Manual and SOP SD-903, "Sample Disposal," current revision. Expired standards are lab packed, placed in the Katahdin hazardous waste storage area, and disposed of in accordance with this SOP.

1.4.3 Wastes generated during standards preparation are disposed of in the Mixed Flammable Waste (O). After the extracts have been analyzed, the autosampler vials and any expired standard vials or ampules are disposed of in the PCB Vial Waste (H).

2.0 SUMMARY OF METHOD

2.1 Method 8082 provides gas chromatographic conditions for the detection of PPB concentrations of certain PCBs. Prior to the use of this method, appropriate sample extraction techniques must be used. Both neat and diluted organic liquids (Method 3580, waste dilution) may be analyzed by direct injection. A 2 to 5 ul aliquot of sample is injected into a gas chromatograph (GC) using the direct injection technique, and compounds in the GC effluent are detected by an electron capture detector (ECD).

2.2 The sensitivity of Method 8082 usually depends on the concentration of interferences rather than on instrumental limitations. If interferences prevent detection of the analytes, Method 8082 may also be performed on samples that have undergone the following cleanups: Method 3660 - Sulfur Cleanup and Method 3665 - Sulfuric Acid Cleanup.

3.0 INTERFERENCES

Interferences by phthalate esters can pose a problem in PCB determinations when using the electron capture detector. Common flexible plastics contain various amounts of phthalates. Care has to be taken to avoid using any plastic materials during the extraction process. Exhaustive cleanup of reagents and glassware may be required to eliminate background phthalate contamination.

Compounds from the sample matrix to which the detector will respond, such as single-component chlorinated pesticides including the DDT series.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph

4.1.1 GC Hewlett Packard 5890 series I or II connected to the Turbochrom or HP Chemstation data system, or equivalent.

4.1.2 Columns - Instruments are configured with a pre-column originating from the injection port, which is connected to a deactivated glass Y splitter that connects two different columns to two detectors. The most commonly used columns are: RTX-35 30M x 0.53 mm ID, RTX-5 30M x 0.53 MM ID, or RTX-1701 30M x 0.53 mm ID. Equivalent columns can be used.

4.1.3 Detectors: Electron capture detectors (ECD). Note: Two detectors must be employed when using dual columns.

4.2 Volumetric flasks, class A: sizes as appropriate with the ground-glass stoppers.

4.3 Syringes: various sizes for preparing standards and injecting samples on the instrument.

4.4 Vials: various sizes and types including crimp tops.

4.5 Balances: Analytical, 0.0001 g

4.6 Refrigerator for storage of extracts and standards.

5.0 REAGENTS

5.1 Solvents

5.1.1 Hexane: pesticide quality or equivalent for diluting samples and standards.

5.2 Standards

5.2.1 Stock standard solutions: Solutions purchased from suppliers like Restek or other acceptable retailers. Expiration dates are one year from date of opening vial or sooner if manufacturers date is less. Upon receipt, all standards are logged into the appropriate logbook with the date of receipt, expiration date, source, lot number, solvent and concentration of compounds. Standard solutions are stored at 4°C in polytetrafluoroethylene (PTFE)-sealed containers in the dark.

5.2.2 Calibration standards: Prepared through the dilution of the stock standards with hexane. Expiration date is 6 months or sooner. Information is documented in standards prep logbook. The concentrations of the working PCB calibration

standards are 0.05 ug/ml, 0.10 ug/ml, 0.25 ug/ml, 1.0 ug/ml, 2.5 ug/ml, and 10.0 ug/ml. The Aroclor 1660 standard also contain the surrogates Tetrachloro-m-xylene (TCX) and Decachlorobiphenyl (DCB) at the respective concentrations: 0.001 ug/ml, 0.002 ug/ml, 0.005 ug/ml, 0.020 ug/ml, 0.050 ug/ml, and 0.20 ug/ml.

5.2.3 Independent Calibration Verification standard (ICV): Prepared through the dilution of the stock standards with hexane. Expiration date is 6 months or sooner. Information is documented in standards prep logbook. The concentration of the ICV PCB standard is 1.0 ug/ml.

5.2.4 DDT Analog Standard: Standard containing the DDT series in hexane at 0.05 ug/ml.

6.0 SAMPLE COLLECTION, PRESERVATION AND HANDLING

Extracts must be stored under refrigeration and analyzed within 40 days of extraction.

Note: The holding time above is a recommendation. PCBs are very stable in a variety of matrices, and holding times under the conditions listed above may be as long as a year.

7.0 PROCEDURES

7.1 Extraction

Refer to the appropriate SOPs for the correct extraction procedure. In general, water samples are extracted using methods 3510, 3520 or 3535 while solid samples use methods 3540, 3545, or 3550. Tissue samples are extracted using method 3545. Wipes and oils are generally extracted using method 3580.

7.2 Instrument conditions

Refer to the instrument logbook for the current column and conditions.

Typical conditions are:

Makeup flow: 60 ml/min Ar/Methane or Nitrogen
Column flow: 6 ml/min
Injector Temp: 200
Detector Temp: 300
Oven Ramp: 160(0) - 5/min - 260(10)

Run time: 30 min
Injection size: 2 ul

7.3 Calibration

7.3.1 The GC system is calibrated using the external standard calibration procedure. Six-point calibration standards of Aroclor 1660 (Aroclor 1016 and Aroclor 1260), Aroclor 1242, Aroclor 1248 and Aroclor 1254 are prepared along with mid-point calibration standards of Aroclor 1221 and Aroclor 1232. If Aroclor 1221 or Aroclor 1232 are suspected, then a six-point curve of the respective Aroclor will be analyzed prior to the analysis and quantitation of the sample.

Each calibration standard is injected using the technique that is used to introduce the actual samples into the GC. Three to five characteristic peaks from each Aroclor are used to calibrate a curve. The Target system will calculate a peak height for all three to five peaks in each Aroclor. A separate calibration curve for each of the three to five peaks can be prepared in Target using the peak height against the concentration of the standard. A non-linear calibration applying a second order polynomial (quadratic fit) equation is used to prepare the curve. In order to be used for quantitative purposes, the Coefficient of Determination (r^2) must be greater than or equal to 0.990. The quadratic equation is:

$$y = ax^2 + bx + c$$

where: y = Instrument response
b = Slope of the line
x = Concentration of the calibration standard
c = the intercept

7.3.2 A non-linear calibration model may not be allowable for certain states, federal programs, or clients. South Carolina does not allow non-linear calibration work originating in their state. In these cases, a linear calibration model must be used. Each calibration standard is injected using the technique that is used to introduce the actual samples into the GC. Three to five characteristic peaks from each Aroclor are used to calibrate a curve. The Target system will calculate a peak height for all three to five peaks in each Aroclor. A separate calibration curve for each of the three to five peaks can be prepared in Target using the peak height against the concentration of the standard.

7.3.2.1 Linear calibration using the average calibration factor

The calibration factor (CF) is calculated using the following formula:

$$CF = A_s / C_s$$

Where: A_s = Peak area (or height) of the analyte or surrogate.
C_s = Concentration of the analyte or surrogate, in µg/L.

To evaluate the linearity of the initial calibration, calculate the mean CF, the standard deviation (SD), and the RSD.

If the RSD of the calibration factor is less than or equal to 20% over the calibration range, then linearity through the origin may be assumed, and the average calibration or response factor may be used to determine sample concentrations.

7.3.2.2 Linear calibration using a least squares regression

$$y = bx + c$$

where: y = Instrument response
b = Slope of the line
x = Concentration of the calibration standard
c = the intercept

The analyst should not force the line through the origin, but have the intercept calculated from the five data points. In addition, do not include the origin (0,0) as a sixth calibration point. The regression calculation will generate a correlation coefficient (r) that is a measure of the "goodness of fit" of the regression line to the data. A value of 1.00 indicates a perfect fit. In order to be used for quantitative purposes, r must be greater than or equal to 0.995. The ICAL must be successful before any samples or other QC check samples can be analyzed.

7.3.3 The AR1660 calibration curve must be checked initially by analyzing a standard containing the same analytes as the curve but prepared from another source. If the response of the analytes from the independent source varies by more than ± 20%, a new independent source standard must be analyzed or a new calibration curve must be prepared and/or analyzed.

7.3.4 The working calibration curve must be verified prior to sample analysis and every 10 samples thereafter by injecting the mid-point calibration standard. If the response for any analyte varies from the expected response by more than ± 15%, a new calibration curve must be prepared for that analyte. The average result for 5 peak heights of the Aroclors is used for quantitation.

For clients or projects requiring DoD QSM 4.1, the response for any analyte must not vary from the expected response by more than ± 20%, or a new calibration curve must be prepared for that analyte. If the CCV fails the above criteria, reanalyze all samples since the last successful calibration verification. If reanalysis cannot be performed, data must be qualified and explained in the narrative. Additionally, apply a Q-flag to all results for the specific analyte(s) in all samples since the last acceptable calibration verification.

7.4 Retention time windows

7.4.1 Three injections are made of all the PCBs throughout the course of a 72 hour period.

7.4.2 A major peak from the envelope is chosen and a standard deviation is calculated using the three retention times for that peak.

7.4.3 Plus or minus three times the standard deviation of the retention times for each standard is used to define the retention time window; however, the experience of the analyst should weight heavily in the interpretation of chromatograms. The analyst should use the retention time window, but should primarily rely on pattern recognition.

7.4.4 Retention time windows are calculated for each standard on each GC column at method setup and after major maintenance, including whenever a new GC column is installed. The data is kept on file in the laboratory.

7.4.5 If the calculated retention time window results in a value of 0.03 minutes or less, the laboratory will apply nominal windows. This is done in order to avoid any false negative hits because of the window being to narrow. The windows are: ± 0.07 for all target analytes. By utilizing these windows, a false positive hit may be initially indicated, but an experienced analyst could determine a false positive from scrutinizing the chromatograms. Please note that the use of nominal retention time windows may not be allowable for certain states, federal programs, or clients. South Carolina does not allow the use of nominal limits for compliance work originating in their state. In these cases, a window of ± 0.03 minutes must be used if the established retention time window is less than 0.03 minutes.

7.5 DDT Analog standard; This standard should be analyzed to determine if the commonly found DDT analogs (DDT, DDE, DDD) elute at the same retention times of any of the target PCBs. This standard should be analyzed in conjunction with the retention time window determination.

7.6 Gas chromatographic analysis

7.6.1 Shake samples and let them sit for one minute before vialing for analysis.

7.6.2 All instrument injections are performed using the direct injection technique with an autosampler set for 2-5 ul injection volumes.

7.6.3 Samples are analyzed in a set referred to as an analysis sequence. The sequence begins with instrument calibration as listed in section 7.3 followed by sample extracts interspersed with mid-concentration calibration standards. Before any samples are analyzed the instrument must be calibrated by analyzing a six-point calibration or a 1.0ppm concentration standard (CV-calibration verification standard) for Aroclor 1660, Aroclor 1242, Aroclor 1248 and Aroclor 1254. If a CV is run, the calculated concentration must not exceed a difference of ± 15%. For clients or projects requiring DoD QSM 4.1, the response for any analyte must not vary from the expected response by more than ± 20%, or a new calibration curve must be prepared for that analyte. If the CCV fails the above criteria, reanalyze all samples since the last successful calibration verification. If reanalysis cannot be performed, data must be qualified and explained in the narrative. Additionally, apply a Q-flag to all results for the specific analyte(s) in all samples since the last acceptable calibration verification. Each sample analysis must be bracketed with an acceptable initial calibration or an opening CV and an ending CV for each 12-hour shift. The closing CV for Aroclor 1660 is a 0.25ppm concentration standard. All other Aroclors at the closing of the run remain at 1.0ppm concentration. If a second window of samples is run immediately after the closing CVs, the concentration of Aroclor 1660 at the completion of this window would be 1.0ppm. The calibration standard must also be injected at intervals of not less than once every ten samples and at the end of the analysis sequence. If the CV fails, the instrument is checked for any obvious problems and maintenance is performed if deemed necessary. Another CV is analyzed or the instrument is recalibrated and then samples are injected. All samples that were injected after the standard exceeding the criterion must be reinjected to avoid errors in quantitation, if the initial analysis indicated the presence of the specific target analyte that exceeded the criterion.

7.6.3.1 However, if the standard analyzed <u>after</u> a group of samples exhibits a response for an analyte that is <u>above</u> the acceptance limit, i.e. >15%, and the analyte was not detected in the specific samples analyzed during the analytical shift, then the extracts for those samples do not need to be reanalyzed, as the CV standard has demonstrated that the analyte would have been detected were it present. In contrast, if an analyte above the QC limits <u>was</u> detected in a sample extract, then re-

injection is necessary to ensure accurate quantitation. If an analyte was not detected in the sample and the standard response is more than 15% below the initial calibration response, then re-injection is necessary to ensure that the detector response has not deteriorated to the point that the analyte would not have been detected even though it was present.

7.6.4 The center of the retention time window for each analyte and surrogate is established by using the absolute retention time for each analyte and surrogate from the daily opening calibration verification or initial calibration.

7.6.5 The identification of PCBs is based on agreement between the retention times of peaks in the sample chromatogram with the retention time windows established through the analysis of standards of the target analytes. An analyte is tentatively identified when a peak from a sample falls within the daily retention time window. Each tentative identification must be confirmed using a second GC column of dissimilar stationary phase or using another technique such as GC/MS. If the retention times of the peaks on both columns fall within the retention time windows on the respective columns, then the target analyte identification has been confirmed.

7.6.5.1 An additional criterion is applied for the identification and quantitation of PCBs. Identification is based on the characteristic fingerprint retention time and shape of the major peaks. Major peaks are defined as those peaks in the Aroclor standard that are at least 25% of the height of the largest Aroclor peak. The sample chromatogram is compared to the individual Aroclor standard chromatograms. Once the Aroclor pattern has been identified, a concentration is then calculated in Target.

7.6.5.2 Three to five Aroclor concentrations are calculated using the peak heights of the three to five characteristic peaks of the Aroclor. These three to five concentrations are then averaged to determine the concentration of that Aroclor.

7.6.6 When samples are analyzed from a source known to contain specific Aroclors, the results from a single-column analysis may be confirmed on the basis of a clearly recognizable Aroclor pattern.

7.6.7 If the response for an analyte exceeds the calibration range of the system, the sample must be diluted and reanalyzed.

7.6.8 If peak detection and identification are prevented due to interferences, the hexane extract may need to undergo a cleanup. The extract may be subjected to a sulfur cleanup (method 3660) and/or a sulfuric acid cleanup (method 3665).

Note: Samples routinely receive a sulfuric acid clean up. However, for samples from a known site with a clean matrix, a sulfuric acid clean up may not be performed. Whenever a sample receives a cleanup, the associated QC must also be subjected to the same cleanup(s) and reanalyzed.

7.6.9 When a GC system is determined to be out of control because either a CV cannot pass or a six point calibration does not meet the correlation coefficient criteria, instrument maintenance is likely necessary. Routine instrument maintenance may involve changing the septum, replacing the liner, clipping the pre-column, or replacing the column. This information is recorded in the instrument run log (Figure 1). When an instrument requires more severe maintenance like replacing the ECD or an electronic board, this information is written in the instrument maintenance logbook.

7.7 Calculations

7.7.1 The concentration of an analyte is calculated by using the calibrated curve that is prepared in Target. When an analyte is identified, Target displays a concentration after the file is processed through the appropriate calibration method. Aroclor quantitation is accomplished by the method described in section 7.5.4.1.1. However, if a sample contains more than one Aroclor, a peak common to both analytes must not be used to quantitate either compound.

7.7.2 The concentrations from the reports are then incorporated with the extraction data to arrive at a final concentration.

Water: Concentration (ug/L) = (C) (Vt)/ (Vs)

Soil/Sediment: Concentration (mg/kg) = (C) (Vt)/ (Ws) (D)

where,
C = concentration calculated by Target in ug/ml
Vt = Volume of total extract including any instrument dilutions
Vs = Volume of sample extracted
Ws = Weight of sample extracted
D = Decimal total solids

7.8 Data Review

7.8.1 Initial Data Review

The initial data review is accomplished by the analyst who ran the samples. This review is of sufficient quality and detail to provide a list of samples that need to be reanalyzed or diluted and reanalyzed. The initial data review is performed on the detailed quantitation reports of the analyzed samples. This data review examines criteria that directly impact whether or not the sample needs to be reanalyzed and/or extracted. These criteria include:

- QC criteria for method blank, LCS, MS/MSD, and calibration – refer to section 8.0.
- Surrogate recovery
- Chromatography: cleanups, manual integration.
- Target compound detection: quantitation, confirmation, false positives.

The requirement of the GC laboratory is that this initial data review be completed no later than the end of the next workday. After the analyst has completed his or her initial data review, the information is then ready to be processed for reporting. Refer to section 7.8.

7.8.2 Surrogate recovery

All recoveries must meet the most recently laboratory established acceptance limits, which are listed on the GC Laboratory Surrogate Acceptance Limit sheet.

The sample is evaluated for recoveries of the two surrogates. If the recovery of one surrogate is within the acceptance limit, and the second is out, the data is narrated. If the surrogate recoveries are high for both and the sample contains less than the PQL for all target analytes, the data is narrated. If the surrogate recoveries are low and may be attributable to matrix interference or a matrix effect, the data is narrated. If the surrogate recoveries are low and the sample concentration is less than the PQL for all target analytes and there is no apparent matrix effect, reextract the sample.

For method blanks, if the recoveries of both surrogates are low or high, and the blank does not contain any target analytes above the PQL, and the recoveries of both surrogates in the sample(s) are acceptable, the data is narrated. If the recoveries in the blank are low and it does not contain any target analytes above the PQL, and the recoveries in the samples are acceptable but the

sample contains one or more target analytes above the PQL, the sample may be reextracted.

For laboratory control samples (LCS), if the only discrepancy in the extraction batch is with the LCS, and the analyte spike recoveries are acceptable, the data is narrated. If the recoveries of both the surrogates and the analyte spikes are low, the samples may need to be reextracted.
For DoD QSM 4.1, use QC acceptance criteria specified by DoD, if available. Otherwise, use in-house control limits. When the surrogate recoveries fall outside of the acceptance criteria, apply Q-flag to all associated analytes.

7.8.3 Chromatography

The chromatography should be examined for the presence of any non-target peaks, which can be used as an indication of whether or not matrix interference might be influencing surrogate recoveries. If the chromatogram indicates interferences, then a cleanup may be needed. See section 7.5.7.

Manual integrations are to be performed when chromatographic conditions preclude the computer algorithm from correctly integrating the peak of concern. In no instance shall a manual integration be performed solely to bring a peak within criteria.
Each peak of concern is examined by the primary analyst to ensure that the peak was integrated properly by the computer algorithm. Should a manual integration be necessary (for instance, due to a split peak, peak tailing, or incomplete resolution of isomeric pairs), an "m" qualifier will automatically be printed on the quantitation report summary. The analyst will date and initial the "m" on the quanitation report summary and assign a code that indicates the reason for the manual integration. Refer to Katahdin SOP QA-812 "Manual Integration on GC/MS, GC, HPLC and IC Datasystems" for more information.

7.8.4 Target Compound Detection

GC analysis relies heavily on the experience of the analyst. Sample chromatograms must be evaluated focusing on scientific judgment, knowledge of the column behavior and matrix effects. The chromatogram from channel A is evaluated with that from channel B. If a target analyte is present on both channels and the concentration is within the calibration range, and the quantitation from both chromatograms agrees within ±40%, the analyte is considered present in the sample. In cases where the RPD is greater than 40% and the analyte is reported, the analyte must be J-flagged and narrated. The higher of the two concentrations is reported unless matrix

interference is causing erroneously high results. In this case report the lower result and narrate. In some cases a non-confirming analyte may be reported. In these cases the analyte must be Q-flagged and narrated...

In order to avoid reporting false positives, identified peaks on a chromatogram may need to be undetected electronically in Target. The possible scenarios are: If an analyte is present on one column but its concentration is below the PQL, if an analyte is present on one column but does not confirm on the other channel, if an analyte is present on both columns but the concentrations differ by more than 40%, or if an analyte is present but its retention time is ±0.04 minutes or more than the retention time of the analyte in the preceding CV. The GC Analyst must rely on technical experience in reviewing chromatograms in determining if a hit is an actual analyte or a false positive.

If reporting data that has an RPD that is >40%, the data must be flagged with a "J" indicating that the result is an estimated value. Sometimes interference on one column (i.e. sulfur) will prevent a target analyte from detection and it is present on the conformational column. In this scenario, the result would be reported from one column and need to be "Q" flagged to indicate that it was not confirmed on a second column.

7.8.5 Reporting

After the chromatograms have been reviewed and any target analytes have been quantitated using Target, the necessary files are brought into QuickForms. Depending on the QC level requested by the client, a Report of Analysis (ROA) and additional reports, such as LCS forms and chronology forms, are generated. The package is assembled to include the necessary forms and raw data. The data package is reviewed by the primary analyst and then forwarded to the secondary reviewer. The secondary reviewer validates the data and checks the package for any errors. When completed, the package is sent to the Department Manager for final review. A completed review checklist is provided with each package. The final data package from the Organics department is then processed by the Data Management department.

8.0 QUALITY CONTROL AND ACCEPTANCE CRITERIA

Refer to Table 1 and to details in this section for a summary of QC requirements, acceptance criteria, and corrective actions. These criteria are intended to be guidelines for analysts. The criteria does not cover all possible situations. If any of the QC requirements are outside the recovery ranges listed in this section or in Table 1, all associated samples must be evaluated against all the QC. In some cases data may be reported, but may be reanalyzed

in other cases. Making new reagents and standards may be necessary if the standardization is suspect. The corrective actions listed in this section and in Table 1 may rely on analyst experience to make sound scientific judgments. These decisions are based on holding time considerations, client and project specific Data Quality Objectives and on review of chromatograms. The supervisor, Operations Manager, and/or Quality Assurance Officer may be consulted to evaluate data. Some samples may not be able to be reanalyzed within hold time. In these cases "qualified" data with narration may be advisable after consultation with the client.

In some cases the standard QC requirements listed in this section and in Table 1 may not be sufficient to meet the Data Quality Objectives of the specific project. Much of the work performed at the lab is analyzed in accordance with specific QC requirements spelled out in a project specific Quality Assurance Project Plan (QAPP) or in a program specific Quality Systems Manual (QSM). The reporting limits, acceptance criteria and/or corrective actions may be different than those specified in this SOP. In these cases the appropriate information will be communicated to the Department Manager and/or senior chemists before initiation of the analyses so that specific product codes can be produced for the project. In addition, the work order notes for each project will describe the specific QAPP or QSM to be followed.

8.1 For each analytical batch (up to 20 samples), a method blank, laboratory control sample (LCS), matrix spike and matrix spike duplicate are analyzed. They are carried through all stages of the sample preparation and analysis steps.

8.2 Spike concentrations: The LCS and the MS/MSD are spiked at the same concentration with Aroclor 1660. The spike concentrations are:

Compound	WATER ug/L	SOILS mg/kg
Aroclor 1660	5.0	0.17

The surrogate spike concentrations in the final extract are:

Compound	WATER ug/ml	SOILS ug/ml
Tetrachloro-m-xylene(TCX)	0.10	0.10
DCB	0.10	0.10

8.3 LCS and MS/MSD acceptance criteria and Corrective Action: All QC samples are calculated for percent recovery of the spiked analyte. The recoveries are compared to laboratory established acceptance limits. The LCS acceptance limits for PCBs are established for both water and soil matrices. The MS/MSD acceptance limits for PCBs use the respective matrix LCS acceptance limits. Separate limits for MS/MSD pairs are not calculated because of the varying matrices involved. In addition many of the MS/MSD data points cannot be used (i.e. recoveries not calculable due to a matrix effect).

If any spike compound in the laboratory control sample falls outside of the established recovery acceptance limit window, the QC sample is considered to be out of control and any sample that is associated should be evaluated with other QC elements to determine the corrective action. If the recovery is high and the associated samples do not contain the specific compound(s), the data can possibly be accepted with narration. In other cases, the associated samples must be extracted.
If a spike compound is outside of the acceptance limits in the matrix spike sample but is acceptable in the LCS, the data is considered acceptable. The cause of the failure is possibly attributable to matrix interference. However, if the compound fails in both the LCS and the MS/MSD, the result for that analyte is suspect and may not be reported for regulatory compliance purposes.

For DoD QSM 4.1, use QC acceptance criteria specified by DoD, if available. Otherwise use in-house control limits. In-house control limits must not be greater than $\pm$ 3 times the standard deviation of the mean LCS recovery. If the LCS fails the acceptance criteria, 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 narrative. Apply Q-flag to specific analyte(s) in all samples in the associated preparatory batch.

For MS, when applying DoD QSM 4.1, apply J-flag to specific analyte(s) also in parent sample, if acceptance criteria not met. RPD must be $\leq$ 30% between MS and MSD.

8.4 Surrogate acceptance criteria and Corrective Action: Surrogate recoveries are calculated on all samples, blanks and spikes. The recoveries are compared to laboratory established acceptance limits.

When a sample has a surrogate that falls outside of the laboratory established acceptance limit window, the problem should be investigated. If the recovery looks like it is affected by the sample matrix, the sample may be reinjected to confirm matrix interference. When a sample has no detectable surrogate recovery, the sample should be reextracted.

For DoD QSM 4.1, use QC acceptance criteria specified by DoD, if available. Otherwise, use in-house control limits. When the surrogate recoveries fall outside of the acceptance criteria, apply Q-flag to all associated analytes.

8.5 CAR: Whenever data is not acceptable because of a failing LCS or surrogate recovery, a corrective action report (CAR) must be initiated as soon as possible to document resolution.

TITLE: ANALYSIS OF PCBs AS TOTAL AROCLORS BY GAS CHROMATOGRAPHY/ ELECTRON CAPTURE DETECTOR (GC/ECD): SW-846 METHOD 8082

9.0 METHOD PERFORMANCE

The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. The MDLs are determined prior to sample analysis per type of instrument and filed with the Organic Department Manager and with the QAO. Refer to the current revision of Katahdin SOP QA-806, Method Detection Limit, Instrument Detection Limit and Reporting Limit Studies and Verifications, for procedures on determining the MDL.

Refer to the current revision of Method 8082 for other method performance parameters and requirements.

10.0 APPLICABLE DOCUMENTS/REFERENCES

Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition. Final Update IV, dated February, 2007, Method 8082A.

Department of Defense Quality Systems Manual for Environmental Laboratories (DoD QSM), Version 4.1, 04/22/09.

The National Environmental Laboratory Accreditation Conference (NELAC) Standards, June 2003.

Katahdin Analytical Services, Inc., SOP CA-101, Equipment Maintenance and Troubleshooting, current revision.

Katahdin Analytical Services, Inc., SOP CA-106, Standard Preparation, Documentation and Traceability, current revision.

Katahdin Analytical Services, Inc., SOP CA-500, Preparation of Soil/Sediment Samples by Sonication Using Method 3550 for Subsequent Pesticides/PCBs Analysis, current revision.

Katahdin Analytical Services, Inc., SOP CA-515, Preparation of Aqueous Samples for Pesticides/PCBs Analysis-Methods 3510 and 3520, current revision.

Katahdin Analytical Services, Inc., SOP CA-524, Preparation of Soil/Sediment Samples by Soxhlet Extraction Using Method 3540 for Subsequent Pesticides/PCBs Analysis, current revision.

Katahdin Analytical Services, Inc., SOP QA-806, Method Detection Limit, Instrument Detection Limit and Reporting Limit Studies and Verifications, current revision.

TITLE: ANALYSIS OF PCBs AS TOTAL AROCLORS BY GAS CHROMATOGRAPHY/ ELECTRON CAPTURE DETECTOR (GC/ECD): SW-846 METHOD 8082

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Table 2 DoD QSM Version 4.1 QC Requirements
Table 2 Summary of Method Modifications
Figure 1 Instrument Run Log
Figure 2 Review Checklist
Figure 3 PQLs

TITLE: ANALYSIS OF PCBs AS TOTAL AROCLORS BY GAS CHROMATOGRAPHY/ ELECTRON CAPTURE DETECTOR (GC/ECD): SW-846 METHOD 8082

TABLE 1

QC REQUIREMENTS

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action
6pt calibration of Aroclor 1660, 1242, 1248, 1254 and mid-point cal of other Aroclors	Initial cal prior to sample analysis	6 pt calibration – Coefficient of Determination (r^2) ≥ 0.990	(1) Repeat Initial calibration (2) If single pt cal Aroclor is identified in analysis of sample, 6-pt calibration run of identified compound with reanalysis of sample.
5pt calibration of Aroclor 1660, 1242, 1248, 1254 and mid-point cal of other Aroclors	Initial cal prior to sample analysis	5 pt calibration – (r) ≥ 0.990	(1) Repeat Initial calibration (2) If single pt cal Aroclor is identified in analysis of sample, 6-pt calibration run of identified compound with reanalysis of sample.
Independent Calibration Verification	Immediately following calibration	± 20 % D	(1) Reanalyze standard (2) Reprep standard (3) Reprep standard from fresh stock.
CCV	After every 10 samples; If calibration curve previously analyzed, analyze daily before samples.	± 20 % D	(1) Evaluate the samples: If the %D >+15% and sample results are <PQL, narrate. (2) If %D >±15% only on one channel, narrate. If %D >±15% for closing CV, and is likely a result of matrix interference, narrate. (3) Otherwise, reanalyze all samples back to last acceptable CV.
Method blank	One per prep batch	No analyte detected >PQL	(1) Investigate source of contamination (2) Evaluate the samples and associated QC: i.e. If the blank results are above the PQL, report sample results which are <PQL or > 10X the blank concentration. (3) Otherwise, reprep a blank and the remaining samples.
LCS	One per prep batch of twenty or fewer samples	± 15% D	(1) Evaluate the samples and associated QC: i.e. If an MS/MSD was performed and acceptable, narrate. (2) If an LCS/LCSD was performed and only one of the set was unacceptable, narrate. (3) If the surrogate recoveries in the LCS are also low but are acceptable in the blank and samples, narrate. (4) If the LCS recovery is high but the sample results are <PQL, narrate. (5) Otherwise, reprep a blank, QC and the remaining samples.
Matrix Spike\ Matrix Spike Duplicate	One for every set of 20 samples	Same as for LCS	(1) Evaluate the samples and associated QC: i.e. If the LCS results are acceptable, narrate. (2) If both the LCS and MS/MSD are unacceptable reprep samples and QC.

TITLE: ANALYSIS OF PCBs AS TOTAL AROCLORS BY GAS CHROMATOGRAPHY/ ELECTRON CAPTURE DETECTOR (GC/ECD): SW-846 METHOD 8082

TABLE 1 (cont.)

QC REQUIREMENTS

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action
Sample Duplicate	One sample duplicate per ten samples if requested	RPD $\leq$20	(1) If lab QC in criteria and matrix interference suspected, flag data or narrate (2) Otherwise, reanalyze
Demonstration of analyst proficiency – 4 replicates	Once per analyst initially and annually thereafter	P&A meet method criteria	(1) Repeat P&A study
MDL study	Refer to KAS SOP QA-806, "Method Detection Limit, Instrument Detection Limit and Reporting Limit Studies and Verifications", current revision.		

TITLE: ANALYSIS OF PCBs AS TOTAL AROCLORS BY GAS CHROMATOGRAPHY/ ELECTRON CAPTURE DETECTOR (GC/ECD): SW-846 METHOD 8082

TABLE 2

DOD QSM VERSION 4.1 QC REQUIREMENTS

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 significant 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.	Not Applicable (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.
LOD determination and verification	Refer to current revision of SOP QA-806				
LOQ establishment and verification	Refer to current revision of SOP QA-806				
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.	6 point calibration of Aroclors 1660, 1242, 1248, and 1254 - One of the options below: Option 1: RSD for each analyte ≤ 20%; 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). Mid point calibration of Aroclors 1221 and 1232; if targets are detected, 6-point calibration is performed.	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 Aroclors 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. On days when ICAL is not performed, the initial CCV is used.	NA.	NA.	

TITLE: ANALYSIS OF PCBs AS TOTAL AROCLORS BY GAS CHROMATOGRAPHY/ ELECTRON CAPTURE DETECTOR (GC/ECD): SW-846 METHOD 8082

TABLE 2 (cont)

DOD QSM VERSION 4.1 QC REQUIREMENTS

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
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.
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 methods: 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 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. Retention time windows are updated per the method.
Method blank	One per preparatory batch.	No analytes detected > ½ RL (> RL for common lab contaminants) 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 the problem. Report sample results that are <LOD or >10x the blank concentration. Reprepare and reanalyze the method blank and all associated samples with results > LOD and < 10x the contaminated blank result. Contact Client if samples cannot be reprepped within hold time.	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.
Laboratory control sample (LCS) containing all analytes to be reported, including surrogates	One per preparatory batch.	The laboratory shall use laboratory control limits (CLs) or use DoD-generated LCS-CLs, if available depending on project requirements. In-house CLs may not be greater than ± 3 times the standard deviation of the mean LCS recovery. A number of analytes may fall outside the CL but within marginal exceedance limit depending on the total number of analytes in the LCS.	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. Refer to Table G-1 for number of marginal exceedences allowed. Contact Client if samples cannot be reprepped within hold time.	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.

TITLE: ANALYSIS OF PCBs AS TOTAL AROCLORS BY GAS CHROMATOGRAPHY/ ELECTRON CAPTURE DETECTOR (GC/ECD): SW-846 METHOD 8082

TABLE 2 (cont.)

DOD QSM VERSION 4.1 QC REQUIREMENTS

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Matrix spike (MS)	One per preparatory batch per matrix if sufficient sample is available.	For matrix evaluation, use LCS acceptance criteria.	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 there is a matrix effect or analytical error.
Matrix Spike duplicate (MSD)	One per preparatory batch per matrix if sufficient sample is available.	MSD: For matrix evaluation, use LCS acceptance criteria. MS/MSD: RPD ≤ 30%.	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.	The laboratory shall use laboratory control limits (CLs) or use DoD-generated LCS-CLs, if available depending on project requirements.	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. Contact Client if samples cannot be reprepped within hold time.	Apply Q-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 (with the exception of Method 8015).	Calibration and QC criteria same as for initial or primary column analysis. Results between primary and second column RPD ≤ 40%.	NA.	Apply J-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 (see Box D-16).
Results reported between DL and LOQ	NA.	NA.	NA.	Apply J-flag to all results between DL and LOQ.	

TITLE: ANALYSIS OF PCBs AS TOTAL AROCLORS BY GAS CHROMATOGRAPHY/ ELECTRON CAPTURE DETECTOR (GC/ECD): SW-846 METHOD 8082

TABLE 3

SUMMARY OF METHOD MODIFICATIONS

TOPIC	KATAHDIN SOP CA-329-11	METHOD 8082, current revision
Procedures	7.4.5 If the calculated retention time window results in a value of 0.03 minutes or less, the laboratory will apply nominal windows. This is done in order to avoid any false negative hits because of the window being to narrow. The windows are: ± 0.07 for all target analytes. By utilizing these windows, a false positive hit may be initially indicated, but an experienced analyst could determine a false positive from scrutinizing the chromatograms. Please note that the use of nominal retention time windows may not be allowable for certain states, federal programs, or clients. South Carolina does not allow the use of nominal limits for compliance work originating in their state. In these cases, a window of ± 0.03 minutes must be used if the established retention time window is less than 0.03 minutes.	9.3 refers to method 8000B section 7.6.3: If the standard deviation of the retention times for a target compound is 0.000 (i.e., no difference between the absolute retention times), then the laboratory may either collect data from additional injections of standards or use a default standard deviation of 0.01 minutes. (Recording retention times to three decimal places rather than only two should minimize the instances in which the standard deviation is calculated as 0.000).
Apparatus/Materials		
Reagents		
Sample Preservation and handling		
QC – Spikes		
QC – LCS		
QC – Accuracy/ Precision		
QC - MDL	PQL Practical Quantitation Level – three to ten times the MDL.	EQL Estimated Quantitation Level – five to ten times the MDL

TITLE: ANALYSIS OF PCBs AS TOTAL AROCLORS BY GAS CHROMATOGRAPHY/ ELECTRON CAPTURE DETECTOR (GC/ECD): SW-846 METHOD 8082

FIGURE 1

EXAMPLE OF INSTRUMENT RUN LOG

Katahdin Analytical Services, Inc.
GC Laboratory Instrument Runlog
Instrument: GC06
Amount Injected 2 µl

Method: SW846 8082 or EPA 608
Reviewed by/ Date:

Date	Init.	Result File	Sample ID	Y/N	Method	Column	Comments
7.31.07	SJC	6AG3141152	WG41666-3 3510	Y	PCBA1B074A	298/299	
		153	Hexane	N			
		154	AR1660 0.25	Y			↑DCB ↑1260 both P4274
		155	AR1242 1.0	Y			P4274
		156	AR1248				P4275
		157	AR1254				P4276
		158	SA3963-1 3540				
		159	SA3987-1				
		160	-2				
		161	-3				
		162	-4				
		163	SA3978-1				
		164	-2				
		165	-3				
8.1.07		166	-4				
		167	-5	N			needs SC.
		168	Hexane				
		169	AR1660 1.0	Y			P4273
		170	AR1242				P4274
		171	AR1248				P4275
		172	AR1254				P4276
		173	SA3978-6 3540	N			needs SC
		174	SA3958-4 3510	Y			
		175	-6				
		176	WG41667-1				
		177	-2				
		178	-3				
		179	-4				
		180	~~SA3958-5~~				
		181	SA3958-1				
		182	-2				
		183	Hexane	N			

TITLE: ANALYSIS OF PCBs AS TOTAL AROCLORS BY GAS CHROMATOGRAPHY/ ELECTRON CAPTURE DETECTOR (GC/ECD): SW-846 METHOD 8082

FIGURE 2

DATA REVIEW CHECKLIST

PRIMARY REVIEW CHECKLIST

Verbal Due Date _____ (☐ **Verbals turned in**). **DueDate**_____

Client:		Primary	Secondary
Method:		Date:	Date:
SDG No:	Level:	Initials:	Initials:
KAS No:			Approved : ☐ Yes

DODQSM 3.0 ☐ **DODQSM 4.1** ☐ **WITH LAB. LIMITS** ☐
QUAPP ☐ **LAB** ☐ (*REPORT* ***ND's*** *to* ***MDL*** ☐)

List all curves that are scanned. _____ _____

_____ _____ _____ _____

Narrate which QC limits were used for (Surr., LCS,s MS/MSDs.) _____

All needed forms are present . _____

Correct Work Order Number or SDG name (all forms). _____

Correct project name and spelling (all forms). (Truncated ☐). _____

Correct file numbers (all forms). _____

Analysis Date Correct. _____

Extraction Method & Analysis Method Correct. _____

Product list compared to ROAs (compounds & PQLs). _____

Chromatogram reviewed for unlabeled peaks (check product list). _____

Flagging of all ROAs correct (Florida Flagging ☐). _____

All tunes included (level IV) . _____

All log book pages included (Soil weights,TCLP & SPLP). _____

Verify DOD QSM criteria. _____

Narrate any method deviations. (Blanks, LCS,s etc.) _____

Sign & Date Manual integration (**Narrate as needed**). _____

Sample I.D's Truncated (**NARRATED**). YES ☐ Please list KAS # below :

_____

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TITLE: ANALYSIS OF PCBs AS TOTAL AROCLORS BY GAS CHROMATOGRAPHY/ ELECTRON CAPTURE DETECTOR (GC/ECD): SW-846 METHOD 8082

FIGURE 3

PQLs FOR METHOD 8082

ANALYTE	Practical Quantitation Level (PQL) (ug/L)	Practical Quantitation Level (PQL) (ug/kg)
PCB-1016	0.50	17
PCB-1221	0.50	17
PCB-1232	0.50	17
PCB-1242	0.50	17
PCB-1248	0.50	17
PCB-1254	0.50	17
PCB-1260	0.50	17

KATAHDIN ANALYTICAL SERVICES, INC.
STANDARD OPERATING PROCEDURE

SOP Number: CA-500
Revision History
Cover Page
Page 1

TITLE: PREPARATION OF SEDIMENT/SOIL SAMPLES BY SONICATION USING METHOD 3550 FOR SUBSEQUENT PESTICIDES/PCBs ANALYSIS

Prepared By: Mike Thomas Date: 7/96

Approved By:

Group Supervisor: Michael F. Thomas Date: 11/15/00

Operations Manager: [illegible] Date: 10/25/00

QA Officer: Deborah J. Nadeau Date: 10·23·00

General Manager: Duncan F. Hughes Date: 11/16/00

Revision History:

SOP Revision	Changes	Approval Initials	Approval Date	Effective Date
01	Minor changes throughout. Clarifications to procedure section.	DN	10·23·00	10/23/00
02	removed references to medium level extraction. New logbook figures minor changes through out	LAD	020305 ~~DT~~ LAD 020305	020305
03	updated compound list changes in wording to clarify updated logbook	LAD	04/06	04/06
04	Added definitions, added waste information, added LCSD, updated solvent exchange, updated Table 1, replaced fig. 2, added PCB cleanup to Sect. 2	LAD	09/07	09/07
05	Updated LB example. Added temp. of nitrogen water bath, lot numbers of filter paper, lot #'s of acids need to be recorded in LB. Change "N-Lo" waste to "K" waste.	LAD	07/08	07/08

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SOP Revision	Changes	Approval Initials	Approval Date	Effective Date
06	Added requirement to add spike before Na_2SO_4. Changed N_2 waterbath temperature from < 37°C to < 30°C. Removed respirator references. Added KAEHS Manual, Added CA-108 reference for subsampling	LAD	02/09	02/09
07	Removed targeting sample weights. Minor changes to section 7. Updated logbook example.	LAD	08/10	08/10

TITLE: **PREPARATION OF SEDIMENT/SOIL SAMPLES BY SONICATION USING METHOD 3550 FOR SUBSEQUENT PESTICIDES/PCBs ANALYSIS**

Please acknowledge receipt of this standard operating procedure by signing and dating both of the spaces provided. Return the bottom half of this sheet to the QA Department.

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TITLE: **PREPARATION OF SEDIMENT/SOIL SAMPLES BY SONICATION USING METHOD 3550 FOR SUBSEQUENT PESTICIDES/PCBs ANALYSIS**

1.0 SCOPE AND APPLICATION

The purpose of this SOP is to describe the procedures and requirements for the preparation of solid samples for pesticides/PCBs analysis in accordance with SW-846 Method 3550, current revision..

1.1 Definitions

METHOD BLANK (laboratory reagent blank): An artificial sample designed to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus. For aqueous samples, reagent water is used as a blank matrix; for soil samples, baked organic-free sand is used as a blank matrix. The blank is taken through the appropriate steps of the process.

LABORATORY CONTROL SAMPLE (LCS): A blank that has been spiked with the analyte(s) from an independent source, and is analyzed exactly like a sample. Its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements. The matrix used should be phase matched with the samples and well characterized.

MATRIX SPIKE/MATRIX SPIKE DUPLICATE (MS/MSD): Predetermined quantities of stock solutions of certain analytes are added to a sample matrix prior to sample extraction and analysis. Samples are split into duplicates, spiked and analyzed. Percent recoveries are calculated for each of the analytes detected. The relative percent difference between the samples is calculated and used to assess analytical precision.

SURROGATES: Organic compounds which are similar to analytes of interest in chemical composition, extraction and chromatography, but which are not normally found in environmental samples. These compounds are spiked into all blanks, standards, samples and spiked samples prior to analysis. Percent recoveries are calculated for each surrogate.

1.2 Responsibilities

This method is restricted to use by, or under the supervision of, analysts experienced in the extraction of sediment/soil samples for pesticides/PCBs analysis. Each analyst must demonstrate the ability to generate acceptable results with this method.

It is the responsibility of all Katahdin personnel involved in the preparation of solid samples for pesticides/PCBs analysis to read and understand this SOP, adhere to the procedures outlined, and to properly document their data in the appropriate lab notebook. Any deviations from the test or irregularities with the samples should also

be recorded in the lab notebook and reported to the Department Manager or designated qualified data reviewer responsible for the data.

It is the responsibility of the Department Manager to oversee that the members of his/her group follow this SOP, that their work is properly documented, and to indicate periodic review of the associated logbooks.

Users of this procedure must be cognizant of inherent laboratory hazards, proper disposal procedures for contaminated materials, and appropriate segregation of hazardous wastes. Everyone involved with the procedure must be familiar with the material safety data sheets for all the materials used in this procedure. Each qualified analyst or technician must be familiar with Katahdin Analytical safety procedures.

1.3 Safety

Users of this procedure must be cognizant of inherent laboratory hazards, proper disposal procedures for contaminated materials and appropriate segregation of hazardous wastes. The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical should be treated as a potential health hazard. A reference file of material safety data sheets is available to all personnel involved in the chemical analysis. Everyone involved with the procedure must be familiar with the MSDSs for all the materials used in this procedure.

Each qualified analyst or technician must be familiar with Katahdin Analytical Environmental Health and Safety Manual including the Katahdin Hazardous Waste Plan and must follow appropriate procedures. These include the use of appropriate personal protective equipment (PPE) such as safety glasses, gloves and lab coats when working with chemicals or near an instrument and not taking food or drink into the laboratory. Each analyst should know the location of all safety equipment. Each analyst shall receive a safety orientation from their Department Manager, or designee, appropriate for the job functions they will perform.

1.4 Waste Disposal

Wastes generated during the preparation of samples must be disposed of in accordance with the procedures described in the current revision of the Katahdin Analytical Environmental Health and Safety Manual and SOP SD-903, “Sample Disposal,” current revision. Expired standards are lab packed, placed in the Katahdin hazardous waste storage area, and disposed of in accordance with this SOP.

Any methylene chloride solvent waste generated during the rinsing of glassware etc. should be disposed of in the “D” waste stream satellite accumulation area nearest

the point of generation. Acetone and hexane are considered flammable waste, and should be disposed of in the "O" waste stream satellite accumulation area nearest the point of generation. Post-extraction soil samples, used glass wool, and sodium sulfate waste should be disposed of in the soil with organics "I" waste stream satellite accumulation area nearest the point of generation. Acid waste generated during the cleanup of PCB samples should be disposed of in the "K" satellite accumulation area nearest the point of generation. Please refer to the current revision of SOP CA-107 for the location of satellite waste accumulation areas.

2.0 SUMMARY OF METHOD

Pesticides/PCBs are extracted from solid samples by sonication with a methylene chloride/acetone solution (1:1 by volume) following EPA Method 3550, current revision. The resulting extract is dried, concentrated, and solvent exchanged to hexane for analysis by GC. Sulfuric acid cleanup is performed on extracts for 8082 PCB analysis.

This SOP applies to low level extraction of pesticide/PCB pollutants from solid sample matrices.

3.0 INTERFERENCES

Solvents, reagents, glassware, and other sample preparation apparatus may yield interferences to GC analysis due to the presence of contaminants. These contaminants can lead to discrete artifacts or elevated baselines in chromatograms. Routinely, all of these materials must be demonstrated to be free from interferences under the conditions of the analysis by running reagent blanks. Interferences caused by phthalate esters can pose a major problem in pesticide analysis. Common flexible plastics contain varying amounts of phthalates that are easily extracted during laboratory operations, so cross-contamination of glassware frequently occurs when plastics are handled. Interferences from phthalates can best be minimized by avoiding the use of such plastics in the laboratory. At no time may gloves that have not been tested for phthalates or gloves known to contain phthalates be used or stored in the organic extraction lab. Whenever possible, plastic items in this lab, must be replaced with metal, teflon or other non-phthalate plastic substitute.

Special care should be taken to ensure clean glassware and apparatus are used, pre-rinsed with the appropriate solvent prior to use. Solvents should be analyzed prior to use to demonstrate that each lot is free of contaminants that may interfere with the analysis.

Interferences coextracted from the samples will vary considerably from source to source. If analysis of an extracted sample is prevented due to inteferences, further cleanup of the sample extract may be needed to minimize interferences.

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4.0 APPARATUS AND MATERIALS

Prior to use, all glassware must be rinsed three times with methylene chloride.

4.1 Beakers - 400 mL

4.2 Kuderna-Danish (KD) apparatus - Concentrator tube - 10 mL
Evaporative flask - 500 mL
Snyder column - 3-ball macro

4.3 Powder funnels, 100 mm diameter, 35 mm stem

4.4 Vacuum filtration flask - 500 mL Erlenmeyer

4.5 Buchner funnel, porcelain, Coors® with 85 mm plate diameter (or equivalent)

4.6 Sonic disruptor – Misonix XL2015 (or equivalent), equipped with dual titanium horn extenders for extracting two samples at a time.

4.7 Spatula - stainless steel

4.8 Filter paper, 18.5 cm, Fisherbrand or Whatman 114V (or equivalent)

4.9 Boiling chips - 12 mesh, silicon carbide (or equivalent)

4.10 Water bath - eight position concentric ring bath or equivalent, equipped with a calibrated thermometer

4.11 Filter paper - 7.0 cm, Whatman, #4, or equivalent

4.12 Syringe - gas tight, 1.0 mL, solvent rinsed between each use

4.13 Balance – top-loading, capable of weighing to 0.01 g

4.14 Nitrogen evaporation apparatus

5.0 REAGENTS

5.1 Sodium sulfate - (ACS reagent grade) powdered, anhydrous, certified by the manufacturer/vendor as purified by heating to 400 °C prior to receipt by the laboratory. Solvent rinse immediately before use by rinsing three times with pesticide grade methylene chloride.

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5.2 Sodium sulfate - (ACS reagent grade) granular, anhydrous, purified as described in section 5.1.

5.3 Methylene chloride - (pesticide grade or equivalent) purchased by lot, evaluated prior to use by concentration of 300mLs to 1.0 mL followed by GC/MS analysis.

5.4 Acetone and hexane - pesticide grade or equivalent

5.5 Organic-free sand, purified by baking at 400 °C for four hours. Method blanks serve as checks on the baked sand.

5.6 Surrogate spiking solution - Prepare a solution of decachlorbiphenyl (DCB) and tetrachloro-meta-xylene (TCMX) at a concentration of 1 ug/mL each in acetone. Store the solution at –10 to -20 °C (±2 °C) in a Teflon sealed container. Solution must be verified by GC/ECD prior to use, and must be replaced every 6 months or sooner if degradation is evident.

5.7 Pesticide Matrix spike/Lab control sample spiking solution - Prepare a spiking solution in pesticide grade methanol that contains all target analytes listed below:

Analyte	ug/mL
4,4'-DDD	0.5
4,4'-DDE	0.5
4,4'-DDT	0.5
Aldrin	0.5
alpha-BHC	0.5
beta-BHC	0.5
delta-BHC	0.5
Dieldrin	0.5
Endosulfan I	0.5
Endosulfan II	0.5
Endosulfan Sulfate	0.5
Endrin	0.5
Endrin Aldehyde	0.5
Endrin Ketone	0.5
gamma-BHC (Lindane)	0.5
Heptachlor	0.5
Heptachlor Epoxide	0.5
Methoxychlor	0.5
alpha-Chlordane	0.5
gamma-Chlordane	0.5

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Store the solution at –10 to -20 °C (±2 °C) in a Teflon sealed container. Solution must be verified by GC/ECD prior to use, and must be replaced every 6 months or sooner if degradation is evident.

5.8 PCB Matrix Spike/Lab Control Sample Spiking Solution – Prepare spiking solution in pesticide grade acetone that contains PCB's Arochlor 1016 and Arochlor 1260 (1660), both at 5.0 ug/mL.

Store the solution at –10 to -20 °C (±2 °C) in a Teflon sealed container. Solution must be verified by GC/ECD prior to use, and must be replaced every 6 months or sooner if degradation is evident.

6.0 SAMPLE COLLECTION, PRESERVATION AND HANDLING

Soil samples are collected in glass soil jars and stored at 4°C (±2°C) until time of extraction.

Holding time for extraction of sediment/soil samples for Method 3550 is 14 days from date of sample collection, although the analyst should be aware that actual holding times employed may be project/program specific.

Store all extracts at 4°C (±2°C) in the dark in labeled Teflon-sealed containers. See SOP SD-902, "Sample Receipt and Internal Control," current revision, for storage areas and temperature maintenance procedures.

7.0 PROCEDURES

The following information must be recorded in the extraction logbook.

- Extraction method
- Surrogate and spike IDs
- Lot numbers of all solvents, acids and bases, sodium sulfate, filter paper
- Nitrogen evaporation water bath temperature
- Sample pH (if applicable)
- Extraction and Concentration dates
- Extraction and Concentration analyst
- Sample ID or QC sample ID
- Initial and final volumes or weight
- Surrogate and spike amounts
- Any sample cleanup preformed
- Final extract tray location
- Any comments regarding the sample extraction (ie. Emulsion)

- Prep batch start time and end time
- CLLE or Soxhlett start time and end time (if applicable)
- Lot numbers of the vials the concentrated extracts are stored in.

LOW LEVEL EXTRACTION OF SOIL/SEDIMENT FOR PESTICIDES/PCBs

The low level extraction procedure is designed for the preparation of soil/sediment samples that may contain analytes at levels lower than 20,000 ug/kg. The procedure involves extraction of pesticides and PCBs from an initial sample weight of approximately 30.0 g using an ultrasonic cell disruptor.

Many solid samples may need to be cleaned up to reduce matrix interferences. The cleanup procedure employed will be dependent upon the nature of the interferences and the target compounds to be analyzed, and options may include acid wash, sulfur cleanup, florisil cleanup, or gel permeation chromatography (GPC). The Department Manager should be consulted to determine if a particular sample should be subjected to further cleanup procedures; the decision should consider sample history, sample appearance, and project/client needs. All extracts or extract splits for subsequent 8082 PCB analysis will, at a minimum, undergo acid cleanup. (Refer to SOP CA-525, current revision)

7.1 Do not decant any water on the sediment sample. Mix with a stainless steel spatula to ensure homogeneity of the sample. If the sample container is full to the extent that stirring the sample is impractical, try to remove the “best representative” aliquot from the jar based on color, particle size, moisture, etc. Remove any foreign objects such as sticks, leaves, or rocks, and note actions taken in the appropriate extraction logbook. **Please refer to the current revision of Katahdin Analytical Services SOP CA-108, “Basic Laboratory Technique“, for more detailed guidance on subsampling to ensure reproducibility.**

7.2 Weigh out approximately 30.0 g plus (> 30 g) portion of sample into a labeled 400 mL beaker. Record sample weight to nearest 0.01 g in appropriate extraction logbook. Refer to sections 7.6 and 7.7 for spike and surrogate addition instructions. Add between 30 g and 60 g of powdered sodium sulfate, as required, to produce a “free-flowing” mixture. The amount of sodium sulfate added will depend upon the moisture content of the sample (e.g., low moisture content will require less sodium sulfate). Mix well with a spatula. Keep the spatula in the sample beaker and <u>cover</u> the beaker with aluminum foil.

7.3 A method blank must be prepared with each extraction batch, not to exceed 20 client samples. To prepare method blank, weigh out approximately 30.0 g portion of purified sand in a labeled 400 mL beaker. Refer to sections 7.6 and 7.7 for spike and surrogate addition instructions. Add 60 g sodium sulfate and mix well. (Although a “free-flowing” mixture can be achieved with less than 60 g sodium

sulfate, the method blank must contain 60 g in order to evaluate the sodium sulfate as a potential source of contamination.)

7.4 A laboratory control sample (LCS) must be prepared with each extraction batch, not to exceed 20 client samples. To prepare LCS, weigh out approximately 30.0 g of purified sand into a labeled 400 mL beaker. Refer to sections 7.6 and 7.7 for spike and surrogate addition instructions. Add 30 g sodium sulfate and mix well. With extraction batches prepared for combined 8081/8082 Pesticide and PCB analysis, separate Pesticide and PCB LCS's must be prepared (refer to sections 5.7 and 5.8). If an MS/MSD pair is not extracted on a particular day, an LCS/LCSD pair may be required in order to meet client-specific or program-specific requirements. This information will be disseminated from the project manager or Department Manager.

7.5 A matrix spike/matrix spike duplicate (MS/MSD) set must be prepared for every 20 samples. To prepare MS/MSD, weigh out two approximately 30.0 g plus (>30 g) portions of the sample designated for MS/MSD into each of two labeled 400 mL beakers. Record sample weights to nearest 0.01 g in appropriate extraction logbook. Refer to sections 7.6 and 7.7 for spike and surrogate addition instructions. Add 30 - 60 g sodium sulfate to each to produce a free-flowing mixture, and mix well. With extraction batches prepared for combined 8081/8082 Pesticide and PCB analysis, separate Pesticide and PCB MS/MSD pairs must be prepared (refer to sections 5.7 and 5.8).

7.6 To all samples, method blank, LCS/LCSD, and MS/MSD add 1.0 mL pesticide/PCBs surrogate spiking solution using a 1.0 mL gas tight syringe. The surrogate spike should be added **prior** to the addition of the sodium sulfate. Record surrogate spike volume and identification code in extraction logbook. Thoroughly rinse syringe with solvent prior to each use.

7.7 To LCS/LCSD and MS/MSD pairs add 1.0 mL of pesticide or PCB matrix spike/LCS spiking solution using a 1.0 mL gas tight syringe. The LCS/MS spike should be added **prior** to the addition of the sodium sulfate. Record matrix spike/LCS spiking solution volume and identification code in extraction logbook. Thoroughly rinse syringe with solvent prior to spiking a different solution and when spiking is completed.

7.8 To assure optimum operation and maximum energy output, the sonicators <u>must</u> be tuned daily prior to extracting samples. The following tuning procedure must be performed with the sonicator probes vibrating in air.

7.8.1 Turn OUTPUT CONTROL knob counter-clockwise to zero, and turn Pulsar Duty Cycle to off (or continuous mode).

7.8.2 Press POWER SWITCH to ON (up) position. Engage the Timer Switch (W-375)

7.8.3 Press and hold down the TUNE switch.

7.8.4 Turn the Output Control Knob towards setting 10. Note the position of the needle on the % output power meter. **DO NOT exceed 70%. If you reach 70% - STOP!!** Rotate the Tuning Knob clockwise or counter-clockwise until a minimum (not maximum) reading (usually less than 20%) is obtained.

7.8.5 Turn the Output Control Knob towards setting 10. Again, note the position of the needle and do not exceed 70%. Rotate the Tuning Knob until you obtain a minimum reading of 20% or below.

7.8.6 Release the TUNE switch. **CAUTION: Do NOT touch probe. The probe is still active.**

7.8.7 Turn OUTPUT CONTROL KNOB counter-clockwise to zero (or disengage timer).

7.8.8 Confirm that the sonicators were tuned by recording the date and/or percent in the extractions logbook.

Note: If the unit will not be used immediately, please turn the power switch to off.

7.9 Prior to extracting any samples, ensure that the sonicator probes are decontaminated by rinsing with a methylene chloride wash bottle. Collect the waste in a waste beaker. It may sometimes be necessary to wipe the upper part of each probe with a methylene chloride dampened KimWipe. Repeat this decontamination step between each sample on each probe.

7.10 To the mixed and spiked blank and LCS, add 100 mL of the 1:1 methylene chloride/acetone solution and proceed with steps 7.11 through 7.14.

7.11 It may be necessary at this time to stir the sample/sodium sulfate mixture with the spatula to loosen up the mixture prior to extracting. Position beaker in the ultrasonic cell disruptor so that the bottom surface of the tip of the 3/4 inch disruptor horn is about halfway below the surface of the solvent and above the sediment layer.

7.12 Sonicate for 3 minutes with the output control knob set at 10, and mode switch on “pulsed” and % duty cycle knob set at 50%. While the mixture is sonicating, one should be able to see all, or most of the material, moving in the beaker under the influence of the energized probes. If not, stir the mixture again.

7.13 Prepare a filter flask fitted with a Buchner funnel. The Buchner funnel should contain a 7.0 cm Whatman #4 filter; prerinse flask, funnel and filter with methylene chloride and discard rinsings into solvent waste container. Decant extract into the filter flask through Buchner funnel. A vacuum pump may be used to facilitate filtration or the extract may be gravity filtered.

Note: The lot number of the filter paper must be recorded in the extraction logbook.

7.14 Repeat the extraction two additional times using 100 mL portions of 1:1 methylene chloride:acetone. Before each extraction, make certain that the sodium sulfate is free-flowing and not a consolidated mass. As required, break up large lumps with the clean spatula. Decant the extraction solvent into the Buchner funnel after each sonication. On the final sonication, pour the entire sample contents into the Buchner funnel and rinse thoroughly with methylene chloride to complete the quantitative transfer of the extract.

CONCENTRATION OF LOW LEVEL EXTRACTS

7.15 Rinse the K-D glassware (flask, concentration tube, and Snyder column, including the ground glass joints on the flask and columns) three times with methylene chloride before assembling. Add two boiling chips to the K-D. Insert 18.5 cm filter papers into short stem powder funnels and add ~ 2 inches of sodium sulfate crystals. Rinse the sodium sulfate in the assembled funnels with ~20-30 mLs of methylene chloride. Place the assembled K-D's under the funnels.

Note: The lot number of the filter paper must be recorded in the extraction logbook.

7.16 If samples are to be GPC'd, refer to the current revision of Katahdin SOP CA-513, Extract Cleanup Using Gel Permeation Chromatography, for appropriate concentrating procedures.

7.17 For a solvent exchange, add approximately 50 mL hexane to funnel and let drain through. Since methylene chloride has a lower boiling point than hexane, this will result in a final extract in hexane only.

Note: For Pesticide / PCB samples originating from South Carolina (see worknotes) do not add the hexane at this step. Solvent exchange will be during the nitrogen blow down procedure.

7.18 Transfer the extracts to the K-D concentrator setups through the sodium sulfate in the funnels. This is the drying step, which is required to remove residual water from the extracts. Any large water layers must be removed by other means, prior to pouring through the sodium sulfate. After pouring all of the extract volume through

the sodium sulfate, rinse the extract flask three times with ~ 2 – 3 mLs of methylene chloride. Add the rinsings through the sodium sulfate to complete a quantitative transfer. Rinse the sodium sulfate with ~ 15 mLs of methylene chloride and allow to drain.

7.19 If samples are not to be GPC'd follow Steps 7.19 through 7.23 to concentrate extracts to final volume of 10.0 mLs. Otherwise proceed to GPC cleanup procedure as described in the current revision of Katahdin SOP CA-513.

7.20 Transfer the labels from the extract flasks to the K-Ds. Remove the funnel and attach a 3-ball macro Snyder column. Pre-wet the Snyder column with 1 mL of methylene chloride.

7.21 Place the K-D in a hot water bath (75-85°C). Gently swirl K-D in the water until boiling begins. At the proper distillation rate, the Snyder balls should chatter but the chambers should not flood with condensed solvent. The K-D should be kept in a vertical orientation while on the bath. When the apparent volume in the concentrator tube reaches ≈ 6 mL, remove the K-D from the water bath. Allow the K-D to cool for 10 minutes. Rinse the Snyder column lower joint with ≈ 1 mL of methylene chloride. Remove the Snyder column. Wipe off any water from the neck above the lower joint of the flask. Separate the K-D flask from the concentrator tube, rinsing the ground glass joint with ≈ 1 mL methylene chloride.

7.22 Reduce the extract in the concentrator tube to approximately 10 mL using the nitrogen blow-down apparatus. The bath temperature must be no higher than 35° C. Turn the gas to 3 psi. Be careful not to splash the extract out of the tube. During concentration on the N-evap, the internal wall of the concentrator tube and the N-evap sparging pipet must be rinsed down at least once or twice with ≈1 mL of hexane (methylene chloride for samples not yet solvent exchanged). The solvent level in the concentrator tube must be positioned below the level of the water bath as much as possible to prevent water from condensing into the sample extract. As the extract volume is reduced, lower the N_2 sparging pipet closer to the surface of the extract to expedite the concentration. Note any problems or extract losses, if they occur, in the extractions logbook.

Note: The temperature of the water in the nitrogen evaporation water bath must be recorded in the logbook.

7.23 For samples that still need to be solvent exchanged, reduce the methylene chloride extract to ~ 1 mL. Add 10 mL of hexane to the concentrator tube and reduce to ~ 1 mL again on the N-evap. Adjust final extract to 10 mL by rinsing sides of tube with hexane and transferring rinsings to vial.

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7.24 Complete quantitative transfer of the extract to a vial by using hexane. Adjust the volume of the hexane extract to 10 mL in either a 12 or 16 mL vial using the appropriate "reference vial" for volume comparison.

7.25 Transfer the sample label from the concentrator tubes to the vials. Store extract vials at a temperature of 4 ± 2 °C until ready for analysis. Indicate in the extractions logbook the box number and "tray location" of the individual extract vials.

7.26 All sample extracts for 8082 PCB analysis must undergo a sulfuric acid wash (cleanup) prior to analysis. All sample extracts for 8081 pesticide analysis do not undergo further cleanup unless requested by the client. All sample extracts for combined 8081/8082 analyses must be split. One portion must be acid cleaned for 8082 analysis. The associated method blank must be split and acid-cleaned in the same fashion. Prior to splitting, contents of vial must be shaken well. PCB LCSs and matrix spikes are acid cleaned also. Pesticide LCSs and matrix spikes are not subjected to further cleanup. Please refer to Katahdin SOP CA-525 (current revision), Extract Cleanup Using Sulfuric Acid, for further instructions.

Note: The lot number of the acid used in PCB cleanup must be recorded in the extraction logbook.

8.0 QUALITY CONTROL AND ACCEPTANCE CRITERIA

Each extractions analyst must demonstrate proficiency in performing the extractions that prepare samples for analysis. Demonstration consists of preparation (extraction), by the analyst, of at least four aliquots which are then analyzed according to the analytical method in question. These QC samples must meet all quality control acceptance limits. Demonstration must be documented by use of a form which summarizes the results of the analysis of these aliquots, calculated percent recoveries, and standard deviation. Demonstration of proficiency must be done one time per analyst initially and then annually thereafter. Refer to SOPs QA-805 and QA-807, current revision.

If, upon analysis of the extracted samples, it is discovered that quality control acceptance criteria have not been met, all associated samples must be evaluated against all the QC. In some cases data may be reported, perhaps with narration, while in other cases, other corrective action may be taken. The corrective actions may include re-extraction of the samples associated with the quality control sample that did not meet acceptance criteria, or may include making new reagents and standards if the standardization is suspect. These decisions are based on holding time considerations, client and project specific Data Quality Objectives and on review of chromatograms. The supervisor, Operations Manager, and/or Quality Assurance Officer may be consulted to evaluate data. Some samples may not be able to be reanalyzed within hold time. In these cases "qualified" data with narration may be advisable after consultation with the client.

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Much of the work performed at the lab is analyzed in accordance with specific QC requirements spelled out in a project specific Quality Assurance Project Plan (QAPP) or in a program specific Quality Systems Manual (QSM). The reporting limits, acceptance criteria and/or corrective actions may be different than those specified in this SOP. In these cases the appropriate information will be communicated to the Department Manager and/or senior chemists before initiation of the analyses so that specific product codes can be produced for the project. In addition, the work order notes for each project will describe the specific QAPP or QSM to be followed.

8.1 A method blank must be extracted for each and every item listed below:

- Each extraction method
- Every extraction batch of twenty or fewer samples
- Each analysis (pesticides and/or PCBs)

8.2 A laboratory control sample (LCS) is required for each and every item listed below:

- Each extraction method
- Every extraction batch of twenty or fewer samples
- Each analysis (pesticides and/or PCBs)

Refer to the current revision of the applicable Katahdin SOP for analysis of Pesticides and PCBs for quality control acceptance criteria.

9.0 METHOD PERFORMANCE

Refer to the applicable analytical SOP.

10.0 APPLICABLE DOCUMENTS/REFERENCES

Test Methods for Evaluating Solid Waste - Physical/Chemical Methods, Method 3550C, USEPA SW-846, Third Edition, Final Update IV, February 2007.

Table 1 Summary of Method Modifications
Figure 1 Example of Pest./PCB Soil Sample Prep Logbook Page

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TABLE 1

SUMMARY OF METHOD MODIFICATIONS

TOPIC	KATAHDIN SOP CA-500-07	METHOD 3550, current revision
Apparatus/Materials	1. short stem funnels	1. drying columns
Reagents		
Sample preservation/ handling		
Procedures	1. extract dried using Na_2SO_4 in short stem funnels 2. place sonicator horns ½ way between the surface of the solvent and the sediment layer 3. no apparatus height specification for concentration on water bath 4. water bath at 75-85 deg C 5. sample removed from water bath when volume reaches ~6 mL 6. Solvent exchange to hexane is performed using K-D apparatus with addition of approximately 50 mL hexane at the start of concentration process	1. extract dried using Na_2SO_4 in drying columns 2. place sonicator horns ½ inch below the solvent surface but above sediment layer 3. partially immerse concentrator tube in water and lower apparatus to complete concentration in 10-15min 4. water bath at 80-90 deg C 5. sample removed from water bath when volume reaches 1-2 mL 6. Solvent exchange to hexane is performed using K-D apparatus with addition of approximately 50 mL hexane after concentrating methylene chloride extract to 1 mL
QC - Spikes	Refer to analytical SOP	
QC - LCS		
QC - Accuracy/Precision		

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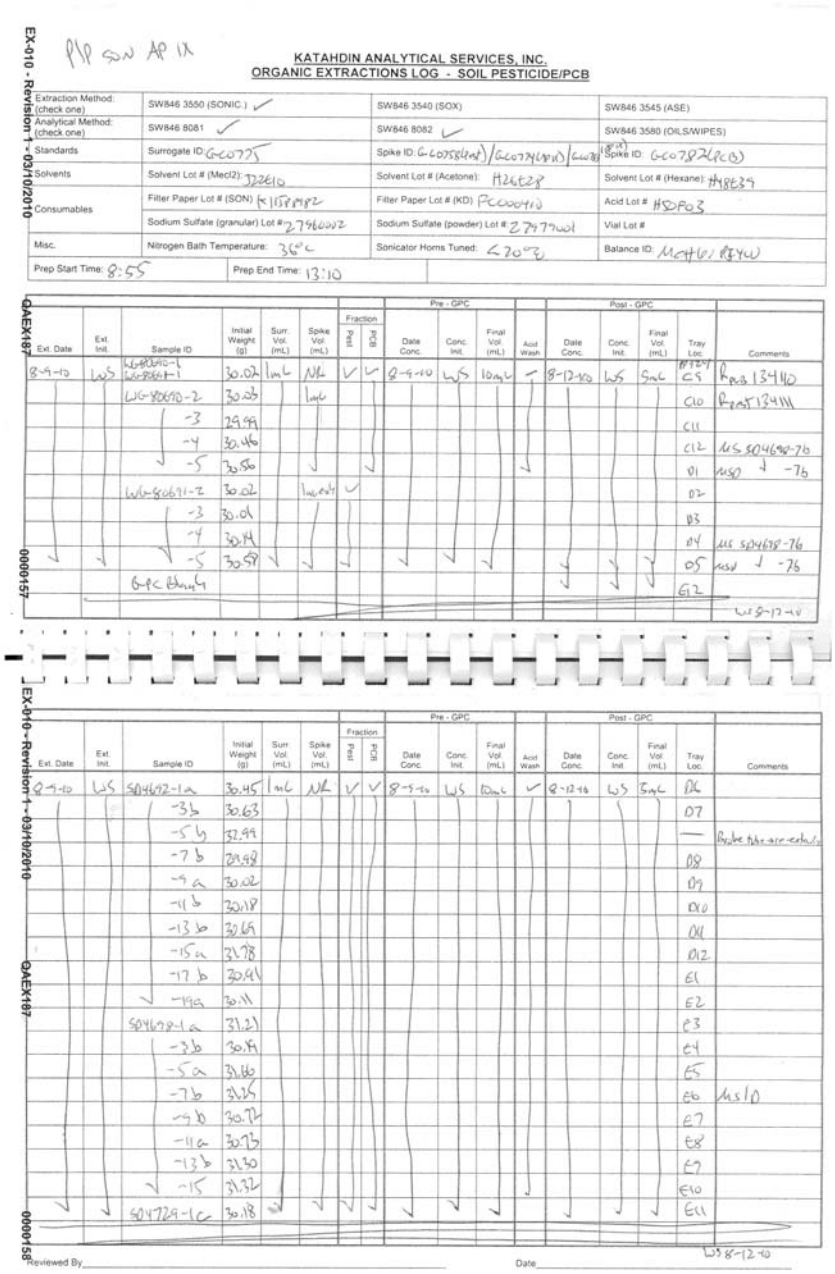
FIGURE 1

EXAMPLE OF LOGBOOK PAGE



EX-010 - Revision 1 - 03/10/2010

PIP SON AP IX

KATAHDIN ANALYTICAL SERVICES, INC.
ORGANIC EXTRACTIONS LOG - SOIL PESTICIDE/PCB

Extraction Method: (check one)	SW846 3550 (SONIC.) ✓	SW846 3540 (SOX)	SW846 3545 (ASE)
Analytical Method: (check one)	SW846 8081 ✓	SW846 8082 ✓	SW846 3580 (OILS/WIPES)
Standards	Surrogate ID: GC0775	Spike ID: GC0758(pest)/GC0761(pcb)/GC0787	(8081) Spike ID: GC0782(PCB)
Solvents	Solvent Lot # (MeCl2): J22610	Solvent Lot # (Acetone): H26E28	Solvent Lot # (Hexane): H48E39
Consumables	Filter Paper Lot # (SON) K1558982	Filter Paper Lot # (KD) PC000410	Acid Lot # H5P03
	Sodium Sulfate (granular) Lot # 27960002	Sodium Sulfate (powder) Lot # 27979001	Vial Lot #
Misc.	Nitrogen Bath Temperature: 36°C	Sonicator Horns Tuned: 6 20°C	Balance ID: MEHU/RFYU
Prep Start Time: 8:55	Prep End Time: 13:10		

QAEX187 — 00001157

Ext. Date	Ext. Init.	Sample ID	Initial Weight (g)	Surr. Vol. (mL)	Spike Vol. (mL)	Fraction Pest	Fraction PCB	Pre-GPC Date Conc.	Pre-GPC Conc. Init.	Pre-GPC Final Vol. (mL)	Acid Wash	Post-GPC Date Conc.	Post-GPC Conc. Init.	Post-GPC Final Vol. (mL)	Tray Loc.	Comments
8-9-10	WS	WG-80690-1 WG-80691-1	30.02	1mL	NA	✓	✓	8-9-10	WS	10mL	✓	8-12-10	WS	5mL	C9	Rest 13410
		WG-80690-2	30.03		1mL										C10	Rest 13411
		-3	29.99												C11	
		-4	30.46												C12	MS 504698-7b
		-5	30.50				✓				✓				D1	MSD ↓ -7b
		WG-80691-2	30.02		1mL ✓	✓									D2	
		-3	30.01												D3	
		-4	30.14												D4	MS 504698-7b
↓	↓	-5	30.59	✓	✓	✓		✓	✓	✓		↓	↓	↓	D5	MSD ↓ -7b
		GPC Blank													E12	

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QAEX187 — 00001158

Ext. Date	Ext. Init.	Sample ID	Initial Weight (g)	Surr. Vol. (mL)	Spike Vol. (mL)	Fraction Pest	Fraction PCB	Pre-GPC Date Conc.	Pre-GPC Conc. Init.	Pre-GPC Final Vol. (mL)	Acid Wash	Post-GPC Date Conc.	Post-GPC Conc. Init.	Post-GPC Final Vol. (mL)	Tray Loc.	Comments
8-9-10	WS	504692-1a	30.45	1mL	NA	✓	✓	8-9-10	WS	10mL	✓	8-12-10	WS	5mL	D6	
		-3b	30.63												D7	
		-5b	32.99												—	Probe tube are exhausted
		-7b	29.98												D8	
		-9a	30.02												D9	
		-11b	30.18												D10	
		-13b	30.69												D11	
		-15a	31.78												D12	
		-17b	30.94												E1	
		-19a	30.11												E2	
		504698-1a	31.21												E3	
		-3b	30.19												E4	
		-5a	31.66												E5	
		-7b	31.25												E6	MS 1D
		-9b	30.72												E7	
		-11a	30.73												E8	
		-13b	31.30												E9	
		-15	31.32												E10	
↓	↓	504729-1c	30.18	✓	✓	✓	✓	↓	↓	↓		↓	↓	↓	E11	

WS 8-12-10

Reviewed By_____ Date_____

TITLE: PREPARATION OF AQUEOUS SAMPLES FOR EXTRACTABLE SEMIVOLATILE ANALYSIS

Prepared By: Michael Thomas Date: 07-24-00

Approved By:

Department Manager: [signature] Date: 6-23-06

Operations Manager: Deborah J. Radeau Date: 6-23-06

QA Officer: Susie Dimond Date: 6-23-06

Revision History:

SOP Revision	Changes	Approval Initials	Approval Date	Effective Date
03	Changes to sect. 5.5 & Figures 3 & 4 to reflect current spike solutions and concentrations. Replaced cover page. Original cover page filed with SOP CA502-02	LAD	04/06	04/06
04	Added definitions, added waste information added LCSD, added SIM LCS/D, MS/D, updated Table 1, added use of narrow range pH paper. Minor changes throughout to reflect current practice.	LAD	09/07	09/07
05	Removed MS/MSD 14 day requirement. Changed CLLE extraction time to 18 → 24 hours. Added information on determining initial sample volume. Added extracted sample disposal. Removed all references to method 625.	LAD	09/08	09/08
06	Added to check pH after B/N CLLE extraction to ensure pH ≥11. If not add more NaOH and continue extracting. Added information for initial volume determination. Added reference to CA-108. Updated logbook example. Added if extract goes dry - re extract.	LAD	10/09	10/09

TITLE: PREPARATION OF AQUEOUS SAMPLES FOR EXTRACTABLE SEMIVOLATILE ANALYSIS

Revision History (cont.):

SOP Revision	Changes	Approval Initials	Approval Date	Effective Date

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TITLE: PREPARATION OF AQUEOUS SAMPLES FOR EXTRACTABLE SEMIVOLATILE ANALYSIS

Please acknowledge receipt of this standard operating procedure by signing and dating both of the spaces provided. Return the bottom half of this sheet to the QA Department.

I acknowledge receipt of copy ___ of document **SOP CA-502-06**, titled **PREPARATION OF AQUEOUS SAMPLES FOR EXTRACTABLE SEMIVOLATILE ANALYSIS**.

Recipient: _____Date:_____

KATAHDIN ANALYTICAL SERVICES, INC.
STANDARD OPERATING PROCEDURE

I acknowledge receipt of copy ___ of document **SOP CA-502-06**, titled **PREPARATION OF AQUEOUS SAMPLES FOR EXTRACTABLE SEMIVOLATILE ANALYSIS**.

Recipient: _____Date:_____

TITLE: PREPARATION OF AQUEOUS SAMPLES FOR EXTRACTABLE SEMIVOLATILE ANALYSIS

1.0 SCOPE AND APPLICATION

The purpose of this SOP is to describe procedures utilized by Katahdin Analytical personnel in the preparation of all non-CLP aqueous samples for analysis of extractable semivolatile organic compounds.

The goal of this procedure is to ensure uniformity involving the preparation of samples for subsequent SVOA analysis by GC/MS. This SOP is applicable to EPA Methods 3510 (modified separatory funnel extraction) and 3520 (continuous liquid-liquid extraction), current revisions.

1.1 Definitions

METHOD BLANK (laboratory reagent blank): An artificial sample designed to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus. For aqueous samples, reagent water is used as a blank matrix; for soil samples, baked organic-free sand is used as a blank matrix. The blank is taken through the appropriate steps of the process.

LABORATORY CONTROL SAMPLE (LCS): A blank that has been spiked with the analyte(s) from an independent source, and is analyzed exactly like a sample. Its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements. The matrix used should be phase matched with the samples and well characterized.

MATRIX SPIKE/MATRIX SPIKE DUPLICATE (MS/MSD): Predetermined quantities of stock solutions of certain analytes are added to a sample matrix prior to sample extraction and analysis. Samples are split into duplicates, spiked and analyzed. Percent recoveries are calculated for each of the analytes detected. The relative percent difference between the samples is calculated and used to assess analytical precision.

SURROGATES: Organic compounds which are similar to analytes of interest in chemical composition, extraction and chromatography, but which are not normally found in environmental samples. These compounds are spiked into all blanks, standards, samples and spiked samples prior to analysis. Percent recoveries are calculated for each surrogate.

1.2 Responsibilities

This method is restricted to use by, or under the supervision of analysts experienced in the extraction of samples for semivolatile analysis. Each analyst must demonstrate and document their ability to generate acceptable results with this method. Refer to

Katahdin SOP QA-805, current revision, "Personnel Training & Documentation of Capability".

It is the responsibility of all Katahdin technical personnel involved in the extraction of samples for semivolatile analysis to read and understand this SOP, to adhere to the procedures outlined, and to properly document their data in the appropriate lab notebook. Any deviations from the test or irregularities with the samples should also be recorded in the lab notebook and reported to the Department Manager or designated qualified data reviewer responsible for this data.

It is the responsibility of the Department Manager to oversee that members of their department follow this SOP, to ensure that their work is properly documented and to initiate periodic review of the associated logbooks.

1.3 Safety

Users of this procedure must be cognizant of inherent laboratory hazards, proper disposal procedures for contaminated materials and appropriate segregation of hazardous wastes. The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical should be treated as a potential health hazard. A reference file of material safety data sheets is available to all personnel involved in the chemical analysis. Everyone involved with the procedure must be familiar with the MSDS's for all the materials used in this procedure.

Each qualified analyst or technician must be familiar with Katahdin Analytical Health and Safety Manual including the Katahdin Hazardous Waste Management Plan and must follow appropriate procedures. These include the use of appropriate personal protective equipment (PPE) such as safety glasses, gloves and lab coats when working with chemicals or near an instrument and not taking food or drink into the laboratory. Each analyst should know the location of all safety equipment. Each analyst shall receive a safety orientation from their Department Manager, or designee, appropriate for the job functions they will perform.

1.4 Pollution Prevention/Waste Disposal

Whenever possible, laboratory personnel should use pollution prevention techniques to address their waste generation. Refer to the current revision of the Katahdin Hazardous Waste Management Plan for further details on pollution prevention techniques.

Wastes generated during the preparation of samples must be disposed of in accordance with the Katahdin Hazardous Waste Management Plan and Safety

Manual and SOP SD-903, "Sample Disposal," current revision. Expired standards are lab packed, placed in the Katahdin hazardous waste storage area, and disposed of in accordance with this SOP.

Any methylene chloride solvent waste generated during the rinsing of glassware, disassembly of CLLEs after extraction, etc. should be disposed of in the "D" waste stream satellite accumulation area nearest the point of generation. Acetone and methanol are considered flammable waste, and should be disposed of in the "O" waste stream satellite accumulation area nearest the point of generation. Post-extraction aqueous samples are considered either N-Hi or N-Low waste and should be disposed of in the corresponding satellite waste accumulation area nearest the point of generation. Sodium sulfate used for sample drying should be disposed of in the soil with organics "I" waste stream satellite accumulation area nearest the point of generation. Please refer to the current revision of SOP CA-107 for the location of satellite waste accumulation areas.

2.0 SUMMARY OF METHOD

For aqueous samples extracted by CLLE, a one liter aliquot of sample is adjusted to pH $\leq$ 2 and extracted with methylene chloride using a continuous liquid-liquid extractor. The pH is then adjusted to pH $\geq$ 11 and the sample is extracted again with methylene chloride. A modified separatory funnel extraction may also be used. If this procedure is used, the sample aliquot is first adjusted to pH $\geq$ 11 and then to pH $\leq$ 2. The methylene chloride extract is dried and concentrated to a volume of 1.0 mL.

3.0 INTERFERENCES

Solvents, reagents, glassware, and other sample preparation apparatus may yield interferences to GC/MS analysis due to the presence of contaminants. These contaminants can lead to discrete artifacts or elevated baselines in the total ion current profiles (TICPs). Routinely, all of these materials must be demonstrated to be free from interferences under the conditions of the analysis by running reagent blanks. Interferences caused by phthalate esters can pose a major problem in semivolatile analysis. Common flexible plastics contain varying amounts of phthalates that are easily extracted during laboratory operations, so cross-contamination of glassware frequently occurs when plastics are handled. Interferences from phthalates can best be minimized by avoiding the use of such plastics in the laboratory. At no time may gloves that have not been tested for phthalates or gloves known to contain phthalates be used or stored in the organic extraction lab. Additionally, whenever possible plastic items in this lab must be replaced with metal or teflon or other non-phthalate plastic substitute.

TITLE: PREPARATION OF AQUEOUS SAMPLES FOR EXTRACTABLE SEMIVOLATILE ANALYSIS

Special care should be taken to ensure that clean glassware and apparatus are used and pre-rinsed with the appropriate solvent prior to use. Solvents should be analyzed prior to use to demonstrate that each lot is free of contaminants that may interfere with the analysis.

Interferences coextracted from the samples will vary considerably from source to source. If analysis of an extracted sample is prevented due to inteferences, further cleanup of the sample extract may be needed to minimize interferences.

4.0 APPARATUS AND MATERIALS

Brand names and catalog numbers are included for illustration purposes only.

4.1 Continuous liquid-liquid extractors - including body, 500 mL round bottom flask and Alhin condensers and equipped with Teflon or glass connecting joints requiring no lubrication (Hershberg-Wolf Extractor, Ace Glass Company, Vineland, NJ, P/N 6841-10 or equivalent).

4.2 Glass powder funnels.

4.3 Fluted filter paper, 18.5cm diameter.

4.4 Concentrator tube - Kuderna-Danish, 10 mL, graduated (Kontes K-570050-1025 or equivalent). Calibration must be checked at the volumes employed in the test.

4.5 Evaporation flask - Kuderna-Danish, 500 mL (Kontes K-570001-0500 or equivalent). Attach to concentrator tube with neck clips.

4.6 Snyder column - Kuderna-Danish, three- or four-ball macro (Kontes K-503000-0121 or equivalent).

4.7 Syringe - gas tight, 1.0 mL, solvent rinsed between each use.

4.8 Vials - Glass, 1.8 mL capacity, with polytetrafluoroethylene (PTFE)-lined screw top and 12 mL with Teflon-lined caps.

4.9 2 L separatory funnel, equipped with Teflon stopper and stopcock; Nalgene Teflon FEP separatory funnels may also be used.

4.10 Organic Free Boiling Chips - approximately 10/40 mesh, Teflon or silicon carbide (or equivalent). Cleaned by Soxhlet for 18 hours.

4.11 Water bath - heated, with concentric ring cover, capable of temperature control (± 20°C). The bath should be used in a hood.

4.12 Nitrogen evaporation apparatus.

4.13 Wide range pH test strips, pH 0-14, Whatman CF Type.

4.14 Glass rods for stirring samples.

4.15 Amber bottles or other appropriate containers for collection of extracts from separatory funnel extraction.

4.16 5 ¾" Pasteur pipets.

4.17 Narrow range pH test strips, pH 0 to 2.5 pH, EMD ColorpHast or equivalent.

4.18 Narrow range pH test strips, pH 11 to 13 pH, EMD ColorpHast or equivalent.

5.0 REAGENTS

All reagent and solvent lots must be checked for possible contamination. Refer to the current version of Katahdin SOP CA-105, Reagent and Solvent Handling, for further details. The extraction staff is responsible for submitting samples to the GC or GC/MS sections for appropriate analysis. All information concerning preparation of the reagent/solvent lot sample will be recorded in the Organic Extraction Log (Figure 1) and acceptance or rejection of these lots must be recorded in the solvent/reagent lot check logbook (Figure 2). All reagents and solvents must be free (<PQL) of any target compounds.

5.1 Laboratory Reagent Grade Water - defined as water in which an interferent is not observed at or above the PQL of each parameter of interest. Deionized water filtered through activated charcoal.

5.2 Sodium sulfate - granular. Bake at 400°C for 4 hours (may be done by vendor). Purify by rinsing three times with pesticide grade methylene chloride. Allow residual methylene chloride to evaporate before each use. Cool in a desiccator and store in a glass bottle with a Teflon-lined cap.

5.3 Sulfuric acid solution (1:1 H_2SO_4 : H_2O) - slowly add 500 mL of H_2SO_4 (sp gr 1.84) to 500 mL reagent water.

5.4 Acetone, methanol, methylene chloride - pesticide residue analysis grade or equivalent.

5.5 Standard Preparation - For all standard preparations, see current revision of the following Katahdin Analytical SOPs:

- "Standards Preparation, Documentation and Traceability", (CA-106, current revision)
- "Balance Calibration," (CA-102, current revision)

5.5.1. Base/Neutral and Acid (SVOA) Surrogate Spiking Solution - Surrogate standards are added to all samples and calibration solutions. Prepare a surrogate standard spiking solution that contains the following compounds at the indicated concentrations in acetone.

Compound	Conc.
phenol-$_{d6}$	100 ug/mL
2,4,6-tribromophenol	100 ug/mL
2-fluorophenol	100 ug/mL
nitrobenzene-$_{d5}$	50 ug/mL
p-terphenyl-$_{d14}$	50 ug/mL
2-fluorobiphenyl	50 ug/mL

Store the spiking solution at -10°C to -20°C in Teflon-sealed containers. These solutions must be replaced after six months, or sooner if comparison with quality control check samples indicates a problem. If reanalysis of a method blank still indicates surrogates out of criteria, a new surrogate solution must be used.

5.5.2 SIM Surrogate Spiking Solution- Surrogate Standards are added to all samples and calibration solutions. Prepare a surrogate solution that contains the following compounds at a concentration of 2 ug/mL in acetone.

Compound	Conc. ug/mL
Fluorene-d10	2.0 ug/mL
2-Methylnaphthalene-d10	2.0 ug/mL
Pyrene-d10.	2.0 ug/mL
2,4-Dibromophenol	2.0 ug/mL

Store the spiking solution at -10°C to -20°C in Teflon-sealed containers. These solutions must be replaced after six months, or sooner if comparison with quality control check samples indicates a problem. If reanalysis of a method blank still indicates surrogates out of criteria, a new surrogate solution must be used.

5.5.3 SVOA Matrix Spike/Lab Control Samples Spiking Solution - the matrix spike/LCS solution consists of the compounds listed in Figure 3.

Prepare a spiking solution that contains each of the base/neutral compounds listed in Figure 3 at 50 ug/mL in methanol and the acid compounds at 100 ug/mL in methanol. Matrix spike/LCS standards are stored in the freezer (-10°C to -20°C) located in the storage area.

5.5.4 Base/Neutral (SIM) Matrix Spike/ Lab Control Sample Spike Solution for SIM-SVOA. Prepare a spiking solution in methanol that contains the compounds listed in Figure 3 at a concentration of 2 ug/mL for base/neutral. Take out 1.0 mL of Base/Neutral and Acid Matrix Spike/Lab Control Spiking Solution for SVOA and dilute it to 25.0 mL of methanol. Store the solution Spiking at -10°C to -20°C in Teflon-sealed containers. These solutions must be replaced after six months, or sooner if comparison with quality control check samples indicates a problem.

5.5.5 Base/Neutral and Acid (SVOA) Appendix IX Lab Control Sample / Matrix Spike Spiking Solution – Prepare a spiking solution in methanol that contains the compounds listed in Figure 4 at concentrations of 100 ug/ml. Store the spiking solution at -10°C to -20°C in Teflon-sealed containers. These solutions must be replaced after six months, or sooner if comparison with quality control check samples indicates a problem.

6.0 SAMPLE COLLECTION, PRESERVATION AND HANDLING

Continuous liquid-liquid (Method 3520) and/or separatory funnel (Method 3510) extractions for semivolatiles must be started within seven days of date of sample collection, although the analyst should be aware that actual holding times employed may be project/program specific. If sampling date is unknown, the hold time is counted from one day prior to date received.

7.0 PROCEDURES

The following information must be recorded in the extraction logbook.

- Extraction method
- Surrogate and spike IDs
- Lot numbers of all solvents, acids and bases, sodium sulfate, filter paper
- Nitrogen evaporation water bath temperature
- Sample pH if appicable
- Extraction and Concentration dates
- Extraction and Concentration analyst
- Sample ID or QC sample ID

- Initial and final volumes or weight
- Surrogate and spike amounts
- Any sample cleanup preformed
- Final extract tray location
- Any comments regarding the sample extraction (ie. Emulsion)
- Prep batch start time and end time
- CLLE start time and end time
- Lot number of the vials the concentrated extracts are stored in.

The internal chain-of-custody must be signed when removing and replacing samples in storage locations.

7.1 CONTINUOUS LIQUID-LIQUID EXTRACTION (Method 3520)

7.1.1 Set up the CLLE apparatus. All glassware should be pre-rinsed three times with methylene chloride in order to eliminate any contamination factors.

7.1.2 Add approximately 500 - 600 mL of methylene chloride to the CLLE body. Label each flask with the following: sample number (or QC identification number), analyte (SVOA), extraction method (CLLE), and extraction date.

7.1.3 A method blank and a laboratory control sample (LCS) must be prepared for each daily extraction batch of twenty samples or fewer (if a work order consists of more than twenty samples, a new batch must be started on a separate page with its own method blank and LCS). To prepare method blank and LCS, add 1 L reagent water to a CLLE body. Be sure that no water leaks into the round bottom flask. If combined SIM-SVOA analysis is requested, a separate LCS must be prepared for each analysis. This blank and LCS are carried through the entire extraction and analytical procedure.

7.1.4 Mark the sample level (meniscus) on the sample bottle with a wax crayon so that the volume can be measured (this may be done prior to removal from the walk-in cooler). Transfer the sample to a CLLE body, being sure that no water leaks into the round bottom flask.

7.1.5 If the batch requires a MS/MSD, transfer two 1 L portions of the sample selected/designated for MS/MSD to CLLE bodies for preparation of a matrix spike/matrix spike duplicate if required. If combined SIM-SVOA analysis is requested, a separate MS/MSD must be prepared for each analysis. If extra MS/MSD aliquots of sample are unavailable a laboratory control sample duplicate (LCSD) may be substituted.

7.1.6 Check the pH of each sample with wide range pH paper by removing a couple of sample drops with a clean disposable pipet or on the tip of a stirring rod. Adjust the pH of the samples (including method blank, LCS/LCSD, and MS/MSD) to $\leq$ pH 2 with 1:1 H_2SO_4 after addition of surrogates and spikes and prior to attaching Allihn condensers (Step 7.1.11). Stir with a glass stirring rod and check pH by tapping the glassrod onto wide range pH paper. The pH must be $\leq$ 2. If the pH test strip does not clearly indicate the pH is less than 2, narrow range pH paper must be used.

7.1.7 For each sample, rinse the original sample container with approximately 30 mL of methylene chloride. Add this rinse to the CLLE body.

7.1.8 Determine the initial volume of the samples by comparing the grease marking where the sample meniscus was to the reference bottle located in the lab. Record the volume and any notable characteristics (e.g. color, presence of sediment, or odor) in the extraction logbook.

7.1.9 To all samples, method blank, LCS/LCSD, and MS/MSD add 1.0 mL base/neutral and acid (SVOA) surrogate spiking solution using a 1.0 mL or 2.5 mL gas tight syringe. Record surrogate spike volume and identification code in extraction logbook. Thoroughly rinse syringe with acetone before and after each use.

7.1.9.1 If the request is for SVOA, use the SVOA Surrogate Solution (sect. 5.5.1).

7.1.9.2 If the request is for SIM, use the SIM surrogate solution (sect. 5.5.2).

7.1.9.3 If the request is for SIM-SVOA, use the SIM surrogate solution as well as SVOA surrogate solution. NOTE: Separate LCS/LCSD and/or MS/MSD are needed for each analysis and should be spiked with the appropriate surrogate.

7.1.10 To LCS/LCSD and MS/MSD add 1.0 mL base/neutral and acid (SVOA) matrix spike/LCS spiking solution using a 1.0 mL or 2.5 mL gas tight syringe. Record matrix spike/LCS spiking solution volume and identification code in extraction logbook. Thoroughly rinse syringe with methanol before and after each use.

7.1.10.1 If the request is for SVOA -
add 1.0 mL of SVOA Matrix Spike/Lab Control Samples Spiking Solution (sect 5.5.3).

7.1.10.2 If the request is for SIM -
add 1.0 mL of SVOA Matrix Spike/Lab Control Samples Spiking Solution (sect 5.5.3) and
add 1.0 mL of Base/Neutral (SIM) Matrix Spike/ Lab Control Sample Spike Solution (sect 5.5.4).

7.1.10.3 If the request is for SVOA Appendix IX, use the SVOA Appendix IX Spiking solution as well as the SVOA spiking solution -
add 1.0 mL of SVOA Matrix Spike/Lab Control Samples Spiking Solution (sect 5.5.3) and
add 1.0 mL of Base/Neutral and Acid (SVOA) Appendix IX Lab Control Sample / Matrix Spike Spiking Solution (sect 5.5.5).

7.1.11 Attach cooling water Allihn condensers, after first rinsing each 45/50 joint with methylene chloride. Turn on the heating mantles and allow the samples to extract for 18 to 24 hours. Turn off the mantles and let samples cool.

7.1.12 Detach condensers and verify that the pH is still $\leq$ 2 in the same manner mentioned in 7.1.6. If the pH has changed, more acid should be added to make the pH $\leq$ 2 and the sample extracted for several more hours.

7.1.13 Upon completion of acid extraction, allow the sample to cool. Detach condensers and add enough 10N NaOH to adjust the pH to $\geq$ 11 with stirring. Use glass stirring rods to stir and check the pH of each sample in the same manner mentioned in 7.1.6.

7.1.14 Re-attach Allihn condensers, turn on heating mantles, and allow samples to extract for 18 to 24 hours. Turn off mantles and allow samples to cool.

7.1.15 Detach condensers and verify that the pH is still $\geq$ 11 in the same manner mentioned in 7.1.6. If the pH has changed, more NaOH should be added to make the pH $\geq$ 11 and the sample extracted for several more hours.

7.1.16 Once samples are cool to the touch, the CLLE apparatus can be disassembled. The round bottom flask is removed, covered foil and placed in the interim extract refrigerator. The remaining sample in the CLLE body is poured in the "N-Hi" satellite.

Proceed to Step 7.3 for sample extract concentration procedures.

7.2 SEPARATORY FUNNEL EXTRACTION (Modified Method 3510)

If an emulsion prevents acceptable recovery or client history indicates samples may demonstrate matrix interference, then samples should be extracted by continuous liquid-liquid extraction (CLLE).

7.2.1 Rinse all glassware, including teflon separatory funnels, three times with methylene chloride prior to use.

7.2.2 Label 2 L separatory funnels and amber collection bottles clearly. Each label should include: sample number (or QC indicator number), analyte (SVOA), matrix (Aq), extraction date.

7.2.3 A method blank and a laboratory control sample (LCS) must be prepared for every 20 samples or with each extraction batch, whichever is more frequent. To prepare method blank and LCS, add 1 L reagent water to a separatory funnel. If combined SIM-SVOA analysis is requested, a separate LCS must be prepared for each analysis. This blank and LCS are carried through the entire extraction and analytical procedure.

7.2.4 Measure the initial volume by comparing the meniscus of the sample with the reference bottle of the same bottle type. Please refer to SOP CA-108, "Basic Laboratory Technique", for the reference bottle verification procedure. Record the volume and any notable characteristics (e.g. color, presence of sediment, or odor) in the extraction logbook.

7.2.5 If the batch requires a MS/MSD, transfer two 1 L portions of the sample selected/designated for MS/MSD to separatory funnels for preparation of a matrix spike/matrix spike duplicate if required. If combined SIM-SVOA analysis is requested, a separate MS/MSD must be prepared for each analysis. If extra MS/MSD aliquots of sample are unavailable, a laboratory control sample duplicate (LCSD) may be substituted.

7.2.6 To all samples, method blank, LCS/LCSD, and MS/MSD add 1.0 mL base/neutral and acid (SVOA) surrogate spiking solution using a 1.0 mL or 2.5 mL gas tight syringe. Record surrogate spike volume and identification code in extraction logbook. Thoroughly rinse syringe with acetone before and after each use.

7.2.6.1 If the request is for SVOA, use the SVOA Surrogate Solution.

7.2.6.2 If the request is for SIM, use the SIM Surrogate Solution.

7.2.6.3 If the request is for SIM-SVOA, use the SIM surrogate solution as well as SVOA surrogate solution. NOTE: Separate LCS/LCSD and/or MS/MSD are needed for each analysis and should be spiked with the appropriate surrogate.

7.2.7 To LCS/LCSD and MS/MSD add 1.0 mL base/neutral and acid (SVOA) matrix spike/LCS spiking solution using a 1.0 mL or 2.5 mL gas tight syringe. Record matrix spike/LCS spiking solution volume and identification code in the extraction logbook. Thoroughly rinse syringe with methanol before and after each use.

7.2.7.1 If the request is for SVOA, use the SVOA Spiking Solution.

7.2.7.2 If the request is for SIM, use the SIM Spiking solution.

7.2.7.3 If the request is for SVOA Appendix IX, use the SVOA Appendix IX Spiking solution as well as the SVOA spiking solution

7.2.8 For each sample, rinse the original sample container with 60 mL of methylene chloride. Add this rinse to the separatory funnel.

7.2.9 Adjust the pH of the samples (including method blank, LCS/LCSD, and MS/MSD) to pH $\geq$ 11 with 10N NaOH after addition of surrogates and spikes. Stir with a glass stirring rod and check pH by tapping the glass stirring rod onto wide range pH paper. The pH must be $\geq$ 11. If the pH test strip does not clearly indicate the pH is greater than 11, narrow range pH paper must be used.

7.2.10 Add 60 mL of methylene chloride directly to the method blank and LCS/LCSD separatory funnels.

7.2.11 Extract the samples by shaking the funnel for two minutes, venting often, but gently, in a hood to release pressure. A mechanical shaker may be used, where samples are shaken for 3 minutes. Following each shake, allow phases to separate for at least 10 minutes. Drain the methylene chloride layer into an amber collection bottle.

7.2.12 If an emulsion forms, mechanical techniques must be employed to achieve maximum separation. Such means include swirling, centrifugation, and draining through a small separatory funnel. In certain instances, transferring the entire sample into a continuous liquid-liquid extractor (CLLE) may be the only alternative. If any such techniques are used, they must be noted in the

extractions logbook, and the batch transferred to a CLLE batch with its own batch ID.

7.2.13 Add a second 60 mL aliquot of methylene chloride to the separatory funnel and extract for the second time (see 7.2.12 – 7.2.13). Collect the methylene chloride layer in the same amber collection bottle.

7.2.14 Repeat the extraction for a third time as described in 7.2.14.

7.2.15 Following the third shake, using a glass stirring rod, check the pH to ensure that it has remained at $\geq$ 11. If the pH has changed back to neutral range, it must be readjusted to $\geq$ 11 and the sample must be extracted at least one more time, adding the methylene chloride to the same amber bottle, that was previously used. If the pH has remained at a value $\geq$ 11, the pH is then adjusted to $\leq$ 2 with 1:1 H_2SO_4. Add enough 1:1 H_2SO_4 to adjust the pH to $\leq$ 2 with stirring. Use glass stirring rods to stir.

7.2.16 Add 60 mL methylene chloride and extract the samples three times in the same manner described in 7.2.11 – 7.2.13. Collect the methylene chloride layer in the same amber collection bottle used to collect the acid fraction.

7.2.17 Sample waste should be poured into the "n-lo" sattalite.

7.2.18 Proceed to Section 7.3 for extract concentration procedures.

7.3 CONCENTRATING THE EXTRACTS

For Methods 3510 and 3520, the combined fractions are concentrated to a final volume of 1.0 mL.

7.3.1 Rinse the K-D glassware (flask, concentration tube, and snyder column, including the ground glass joints on the flask and columns) three times with methylene chloride. Add two boiling chips to the K-D prior to final rinse. Also rinse the assembled funnels, filter paper, and granular sodium sulfate used for drying the extracts.

7.3.2 Transfer the methylene chloride extract to a K-D concentrator setup through a short stem funnel filled with 1-2 inches of sodium sulfate in fluted filter paper. This is the drying step, which is required to remove residual water from the extracts. Any large water layers must be removed by other means, prior to pouring through the sodium sulfate. After pouring all of the extract volume through the sodium sulfate, rinse the extract flask three times with ~ 2 – 3 mls of methylene chloride. Add the rinsings through the sodium

sulfate to complete a quantitative transfer. Rinse the sodium sulfate with ~ 15 mls of methylene chloride and allow to drain

7.3.3 Transfer the label from the collection bottle or round bottom flask (for CLLE) to a K-D. Remove the funnel and attach a 3- or 4-ball macro Snyder column. Pre-wet the Snyder column with 1 mL of methylene chloride.

7.3.4 Place the K-D in a hot water bath (75-85°C). Gently swirl K-D in the water until boiling begins. At the proper distillation rate, the Snyder balls should chatter but the chambers should not flood with condensed solvent. The K-D should be kept in a vertical orientation while on the bath. When the apparent volume in the concentrator tube reaches ≈ 6 mL, remove the K-D from the water bath. Allow the K-D to cool for 10 minutes. Rinse the Snyder column lower joint with ≈ 1 mL of methylene chloride. Remove the Snyder column. Wipe off any water from the neck above the lower joint of the flask. Separate the K-D flask from the concentrator tube, rinsing the ground glass joint with ≈ 1 mL methylene chloride.

7.3.5 Reduce the methylene chloride extract in the concentrator tube to approximately 1 mL using the nitrogen blow-down apparatus. The bath temperature must be no higher than the boiling point of the solvent (39°C for methylene chloride). Turn the gas to 3 psi. Be careful not to splash the extract out of the tube. During concentration on the N-evap, the internal wall of the concentrator tube and the N-evap sparging pipet must be rinsed down at least once or twice with ≈1 mL of methylene chloride. The solvent level in the concentrator tube must be positioned below the level of the water bath as much as possible to prevent water from condensing into the sample extract. As the extract volume is reduced, lower the N_2 sparging pipet closer to the surface of the extract to expedite the concentration. Note any problems or extract losses, if they occur, in the extractions logbook.

7.3.6 Reduce each extract to slightly less than 1 mL and then, using a 5 ¾" pasteur pipet, transfer the final extract and label to a 1.8 mL vial with PTFE-lined cap.

7.3.7 If at any time during the concentration process the concentrator tube goes dry, reextraction must occur immediately.

7.3.8 Using methylene chloride for a quantitative transfer, adjust the final volume of each extract to 1 mL. Use the 1 mL oil-filled reference vial for volume comparison.

7.3.9 Store in refrigerator until GC/MS analysis.

TITLE: PREPARATION OF AQUEOUS SAMPLES FOR EXTRACTABLE SEMIVOLATILE ANALYSIS

8.0 QUALITY CONTROL AND ACCEPTANCE CRITERIA

A method blank must be extracted for each and every item listed below:

- Each sample matrix (soil, water)
- Each day of extraction (24 hours midnight - midnight)
- Each extraction method or level
- Every 20 samples extracted in a 24-hour period

A laboratory control sample (LCS) is required for each and every item listed below:

- Each sample matrix
- Each extraction method or level
- Every extraction batch of twenty or fewer samples

Refer to the current revision of the applicable Katahdin SOP for analysis of semivolatiles for quality control acceptance criteria.

9.0 METHOD PERFORMANCE

Refer to the applicable analytical SOP.

10.0 APPLICABLE DOCUMENTS/REFERENCES

Test Methods for Evaluating Solid Waste-Physical/Chemical Methods, Methods 3510 and 3520 (current revisions), SW-846 Third Edition, Updates I, II, IIA, and IIB, Revised January 1995, US EPA.

LIST OF TABLES AND FIGURES

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Figure 1 Example of Semivolatiles Logbook Page
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Figure 3 LCS/Matrix Spike Component List
Figure 4 Appendix Ix LCS/Matrix Spike Component List

TITLE: PREPARATION OF AQUEOUS SAMPLES FOR EXTRACTABLE SEMIVOLATILE ANALYSIS

TABLE 1

SUMMARY OF METHOD MODIFICATIONS (METHOD 3510, current revision)

TOPIC	KATAHDIN SOP CA-502-06	METHOD 3510, current revision
Apparatus/Materials	1) 250 mL amber bottle or flask 2) 1.0 mL syringe 3) short stem funnels	1) 250 mL Erlenmeyer flask 2) 5.0 mL syringe 3) drying columns
Reagents		
Sample preservation/ handling		
Procedures	1) extract collection in amber bottle or Erlenmeyer flask 2) Add surrogate/spike to sample in CLLE 3) Extract for 3 minutes on mechanical shaker 4) extract three times at pH $\geq$ 11, then extract three times at pH $\leq$ 2. 5) extract dried using Na_2SO_4 in short stem funnels 6) Rinse the extract flask three times with ~ 2 – 3 mLs of methylene chloride then rinse the sodium sulfate with ~ 15 mLs of methylene chloride to complete a quantitative transfer 7) water bath temp 75-85 deg C 8) no apparatus height specification for concentration on water bath 9) sample removed from water bath when volume reaches ~6 mL 10) N bath temp no higher than 39 deg C	1) extract collection in Erlenmeyer flask 2) Add surrogate/spike directly to sample bottle 3) Extract by shaking vigorously for 1 - 2 minutes with periodic venting 4) extract three times at pH $\leq$ 2, then extract three times at pH $\geq$ 11. 5) extract dried using Na_2SO_4 in drying columns 6) Rinse the Erlenmeyer flask, which contained the solvent extract, with 20 - 30 mL of methylene chloride to complete the quantitative transfer 7) water bath temp 15-20 deg C above solvent boiling temp 8) partially immerse concentrator tube in water and lower apparatus to complete concentration in 10-20 min 9) sample removed from water bath when volume reaches 1 mL 10) N bath temp 35 deg C
QC - Spikes	1) Acid surrogate and spike components at 100 ug/mL; base/neutral surrogate and spike components at 50 ug/mL	1) Acid surrogate and spike components at 200 ug/mL; base/neutral surrogate and spike components at 100 ug/mL
QC - LCS	1) Acid surrogate and spike components at 100 ug/mL; base/neutral surrogate and spike components at 50 ug/mL	1) Acid surrogate and spike components at 200 ug/mL; base/neutral surrogate and spike components at 100 ug/mL

TITLE: PREPARATION OF AQUEOUS SAMPLES FOR EXTRACTABLE SEMIVOLATILE ANALYSIS

TABLE 1, continued

SUMMARY OF METHOD MODIFICATIONS (METHOD 3520, current revision)

TOPIC	KATAHDIN SOP CA-502-06	METHOD 3520, current revision
Apparatus/Materials	1) short stem funnels	1) drying columns
Reagents		
Sample preservation/ handling		
Procedures	1) Add surrogate/spike to sample in CLLE 2) Add approximately 500 - 600 mL of methylene chloride to the CLLE body 3) CLLE for 22 ± 2 hours 4) Extract dried using Na_2SO_4 in short stem funnels 5) Rinse the extract flask three times with ~ 2 – 3 mLs of methylene chloride then rinse the sodium sulfate with ~ 15 mLs of methylene chloride to complete a quantitative transfer 6) water bath temp 75-85 deg C 7) no apparatus height specification for concentration on water bath 8) sample removed from water bath when volume reaches ~6 mL 9) N bath temp no higher than 39 deg C	1) Add surrogate/spike directly to sample bottle 2) Add 300 - 500 mL of methylene chloride to the distilling flask of the extractor 3) CLLE for 18 - 24 hours 4) Extract dried using Na_2SO_4 in drying columns 5) Rinse the Erlenmeyer flask, which contained the solvent extract, with 20 - 30 mL of methylene chloride to complete the quantitative transfer 6) water bath temp 15-20 deg C above solvent boiling temp 7) partially immerse concentrator tube in water and lower apparatus to complete concentration in 10-20 min 8) sample removed from water bath when volume reaches 1 mL 9) N bath temp 35 deg C
QC - Spikes	1) Acid surrogate and spike components at 100 ug/mL; base/neutral surrogate and spike components at 50 ug/mL	1) Acid surrogate and spike components at 200 ug/mL; base/neutral surrogate and spike components at 100 ug/mL
QC - LCS	1) Acid surrogate and spike components at 100 ug/mL; base/neutral surrogate and spike components at 50 ug/mL	1) Acid surrogate and spike components at 200 ug/mL; base/neutral surrogate and spike components at 100 ug/mL

TITLE: PREPARATION OF AQUEOUS SAMPLES FOR EXTRACTABLE SEMIVOLATILE ANALYSIS

FIGURE 1

EXAMPLE OF SEMIVOLATILES LOGBOOK PAGE

SVBLM
Sep

KATAHDIN ANALYTICAL SERVICES, INC.
ORGANIC EXTRACTIONS LOG - AQUEOUS SEMI-VOLATILES

Extraction Method: (check one)	SW846 3520 (CLLE)		SW846 3510 (SEP) ✓		SW846 3535 (SPE)	
Analytical Method: (check one)	SW846 8270 ✓	EPA 625	CLP OLM04.2	CLP OLC02.1	CLP SOM01.2	
Standards	Surrogate ID (1): SV2350		Spike ID (1): SV852		Spike ID (3):	
	Surrogate ID (2): SV2349		Spike ID (2): SV2351			
Solvents/Acid/Base	Solvent Lot # (Mec12): H90631		H_2SO_4 # 635026		NaOH Lot # H22101	
Consumables	Filter Paper Lot # K11472365		$NaSO_4$ Lot # 27969003		Vial Lot # 00094428	
Nitrogen Water Bath Temperature 35°C			pH (1st Extraction) ≥11		pH (2nd Extraction) ≤2	
Prep Start Time: 0930	Prep End Time: 1230	CLLE Acid Start:	CLLE Acid End:		CLLE B/N Start:	CLLE B/N End:

QAEX173

Date Extracted	Ext. Init.	Sample ID	Initial Vol. mL	Surr. Vol.	Spike Vol.	Fraction SV	Fraction SW	Final Vol. mL	Date Conc.	Tray Location	Initials	Comments
10/24/09	CB	W670483-1 W670483-1	1000	1mL each	NR	✓	✓	1mL	10/26/09	SV492 B8	CB	R_{spike} R112490
↓	↓	W670483-2	↓	1mL	1mL		↓	↓		B9	↓	R_{surr} R112487
		-3	980	↓	↓		↓			B10		W6SC6526-11k
		-4	1000				✓			B1		MSD -11L
		W670484-2	1000			✓				C2		
↓	↓	-3	↓	↓	↓	↓		↓	↓	C3	↓	
					CB	10/26/09						

0000089

Date Extracted	Ext. Init.	Sample ID	Initial Vol. mL	Surr. Vol.	Spike Vol.	Fraction SV	Fraction SW	Final Vol. mL	Date Conc.	Tray Location	Initials	Comments
10/24/09	CB	SC6526-1a	1060	1mL	NR		✓	1mL	10/26/09	SV492 C4	CB	
↓	↓	-3c	1010	↓	↓		↓	↓	↓	C5	↓	
		-5d	1030							C6		
		-7c	1060							C7		less double sand.
		-9c	1030							C8		
		-11h	1030							C9		MSD
		-13c	1020							C10		
		-15d	1010							D1		
		-17c	1060							D2		
		-19d	↓							D3		
		-21c	↓							D4		
		-23c	1020							D5		
↓		-25c	1040				✓			D6		
		SC6525-2e	1060			✓				D7		
		-3c	↓			↓				D8		
		-4e	↓							D9		
		-5d	1040							D10		
↓	↓	-6d	1040	↓	↓	↓		↓	↓	E1	↓	

QAEX173

Reviewed By_____ Date_____

0000090

TITLE: PREPARATION OF AQUEOUS SAMPLES FOR EXTRACTABLE SEMIVOLATILE ANALYSIS

FIGURE 2

SOLVENT/REAGENT LOT CHECK LOGBOOK

SOLVENT:

LOT#:

DATE RECEIVED:

DATE CONCENTRATED:

CONCENTRATED BY:

PREP METHOD:

TRAY LOCATION:

ANALYZED BY:

PASS/FAIL:

TITLE: PREPARATION OF AQUEOUS SAMPLES FOR EXTRACTABLE SEMIVOLATILE ANALYSIS

FIGURE 3

LCS/MATRIX SPIKE COMPONENT LIST

BASE/NEUTRALS	
1-Methylnaphthalene	Bis (2-chloroethoxy) methane
1,1-Biphenyl	Bis (2-chloroethyl) ether
1,2,4-Trichlorobenzene	Bis (2-Chloroisopropyl) ether)
1,2-Dichlorobenzene	Bis(2-Ethylhexyl)adipate
1,3-Dichlorobenzene	Bis (2-ethylhexyl) phthalate
1,4-Dichlorobenzene	Butylbenzyl phthalate
1,4-Dioxane	Caprolactam
2,4-Dinitrotoluene	Carbazole
2,6-Dinitrotoluene	Chrysene
2-Chloronaphthalene	Dibenz (a, h) anthracene
2-Methylnaphthalene	Dibenzofuran
2-Nitroaniline	Diethyl phthalate
3,3'-Dichlorobenzidine	Diethyl adipate
3-Nitroaniline	Dimethyl phthalate
4-Bromophenylphenyl ether	Di-n-butylphthalate
4-Chloroaniline	Di-n-octyl phthalate
4-Chlorophenylphenyl ether	Fluoranthene
4-Nitroaniline	Fluorene
Acenaphthene	Hexachlorobenzene
Acenaphthylene	Hexachlorobutadiene
Acetophenone	Hexachlorocyclopentadiene
Aniline	Hexachloroethane
Anthracene	Indeno (1,2,3-cd) pyrene
Atrazine	Isophorone
Azobenzene	Naphthalene
Benzaldehyde	Nitrobenzene
Benzidine	N-Nitrosodimethylamine
Benzo (a) Anthracene	N-Nitroso-di-n-propylamine
Benzo (a) pyrene	N-Nitrosodiphenylamine
Benzo (b) fluoranthene	Phenanthrene
Benzo (ghi) perylene	p-toluidine
Benzo (k) fluoranthene	Pyrene
Benzyl alcohol	Pyridine

ACIDS		
2, 3, 4, 6-Tetrachlorophenol	2-Chlorophenol	Benzoic acid
2,4,5-Trichlorophenol	2-Methylphenol	Ethyl methanesulfonate
2,4,6-Trichlorophenol	2-Nitrophenol	Methyl methanesulfonate
2,4-Dichlorophenol	4,6-Dinitro-2-methylphenol	Pentachlorophenol
2,4-Dimethylphenol	4-Chloro-3-methylphenol	Phenol
2,4-Dinitrophenol	4-Methylphenol	
2,6-Dichlorophenol	4-Nitrophenol	

TITLE: PREPARATION OF AQUEOUS SAMPLES FOR EXTRACTABLE SEMIVOLATILE ANALYSIS

FIGURE 4

APPENDIX IX LCS/MATRIX SPIKE COMPONENT LIST

1,2,4,5-Tetrachlorobenzene	Hexachloropropene
1,3,5-Trinitrobenzene	Isodrin
1,4-Naphthoquinone	Isosafrole
1-Chloronaphthalene	Kepone
1-Naphthylamine	m-Dinitrobenzene
2,4-D	Methapyrilene
2-Acetyl aminofluorene	Methyl parathion
2-Naphthylamine	n-Nitrosodiethylamine
2-Picoline	n-Nitrosodi-n-butylamine
3,3-Dimethylbenzidine	n-Nitrosomethylethylamine
3-Methylcholanthrene	n-Nitrosomorpholine
4-Aminobiphenyl	n-Nitrosopyrrolidine
4-Nitroquinoline-1-oxide	n-Nitrotrosopiperidine
5-Nitro-o-toluidine	O,O,O-Triethyl phosphorothioate
7,12-Dimethylbenz(a)anthracene	o-Toluidine
a,a-Dimethylphenethylamine	Parathion
Acetophenone	p-Dimethylaminoazobenzene
Aramite	Pentachlorobenzene
Chlorobenzilate	Pentachloronitriobenzene
Diallate	Phenacetin
Dibenz(a,j)acridine	Phorate
Dimethoate	p-Phenylenediamine
Dinoseb	Pronamide
Diphenylamine	Safrole
Disulfoton	Silvex (2,4,5-TP)
Famphur	Sulfotep
Hexachlorophene	Thionazin

TITLE: EXTRACTION OF PETROLEUM HYDROCARBONS FROM SAMPLES FOR ANALYSIS BY MADEP - EPH METHODS

Prepared By: Mike Thomas Date: 4/98

Approved By:

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General Manager: Dennis P. Hughes Date: 2/1/01

Revision History:

SOP Revision	Changes	Approval Initials	Approval Date	Effective Date
01	Format changes, added pollution prevention. Changed from tabular to paragraph format (procedure section).	DN	1.31.01	1/31/01
02	Minor changes in sections 4, 5 and 7. Changes to Table 3.	DN	4.2.02	4.2.02
03	Changed HPLC to SPE. Updated extract methods, procedure and fractionation to concur with Method. Updated Tables 1 & 2, and Figures 1 & 2. Removed (old) Figures 2 & 3.	LAD	051305	051305
04	Added variances between SOP and method updated fractionation procedure. updated logbook	LAD	04/06	04/06
05	Updated solvent exchange procedure. Added fractionation solution and fractionation surrogate to Sect. 5. Added cartridge interference. Added waste disposal. Updated method reference.	LAD	09/07	09/07

TITLE: EXTRACTION OF PETROLEUM HYDROCARBONS FROM SAMPLES FOR ANALYSIS BY MADEP - EPH METHODS

SOP Revision	Changes	Approval Initials	Approval Date	Effective Date
06	Changed the addition of fractionation surrogate from after KD process to immediately before fractionation, weights from 0.1 to 0.05 g, soxhlet extraction time from 16 – 24 to 18 ± 2, addition of hexane from 18 to 17 mL. Added the final volume in LB should be 2 mL, and to record hexane and methylene chloride volumes used in LB. Added KAS SOP CA-108 reference for additional subsampling information.	LAD	03/09	03/09
07	Added fractionation by HPLC to all applicable sections. Added HPLC Maintenance Logbook and Run log examples. Added HPLC instrument parameters. Change surrogate Chloro-octadecane to 5-alpha Androstane. Added references.	LAD	04/10	04/10

TITLE: EXTRACTION OF PETROLEUM HYDROCARBONS FROM SAMPLES FOR ANALYSIS BY MADEP - EPH METHODS

Please acknowledge receipt of this standard operating procedure by signing and dating both of the spaces provided. Return the bottom half of this sheet to the QA Department.

I acknowledge receipt of copy _____ of document **SOP CA-511-07**, titled **EXTRACTION OF PETROLEUM HYDROCARBONS FROM SAMPLES FOR ANALYSIS BY MADEP-EPH METHODS.**

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STANDARD OPERATING PROCEDURE

I acknowledge receipt of copy _____ of document **SOP CA-511-07**, titled **EXTRACTION OF PETROLEUM HYDROCARBONS FROM SAMPLES FOR ANALYSIS BY MADEP-EPH METHODS.**

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TITLE: EXTRACTION OF PETROLEUM HYDROCARBONS FROM SAMPLES FOR ANALYSIS BY MADEP - EPH METHODS

1.0 SCOPE AND APPLICATION

This document describes the protocols of the Massachusetts Department of Environmental Protection Method used for the Determination of Extractable Petroleum Hydrocarbons (EPH), including sample collection, sample extraction and cleanup. The MADEP EPH method is designed to measure the collective concentrations of extractable aliphatic hydrocarbons within the ranges C_9 through C_{18} and C_{19} through C_{36}. This method is also designed to measure the collective aromatic hydrocarbons within the C_{11} through C_{22} range and to measure the individual concentrations of targeted polynuclear aromatic hydrocarbons (PAHs) in water and soil. These aliphatic and aromatic hydrocarbon ranges correspond to a boiling point range between approximately 150°C and 265°C. Petroleum products suitable for evaluation by this method include kerosene, fuel oil #2, fuel oil #4, fuel oil #6, diesel fuel, jet fuel and certain lubricating oils. This method, in and of itself, is not suitable for the evaluation of gasoline, mineral spirits, petroleum napthas, and other petroleum products which contain a significant percentage of hydrocarbons lighter than C_9 or for petroleum products which contain a significant percentage of hydrocarbons heavier than C_{36}.

1.1 Definitions

Extractable Petroleum Hydrocarbons (EPH) - all hydrocarbon compounds eluting from n-nonane to n-hextriacontane, excluding Targeted PAH Analytes. EPH is comprised of C_9 through C_{18} Aliphatic Hydrocarbons, C_{19} through C_{36} Aliphatic Hydrocarbons, and C_{11} through C_{22} Aromatic Hydrocarbons. EPH concentration data are reported as a toxicologically-weighted summation of the aliphatic and aromatic hydrocarbon fractions.

C_{11} through C_{22} Aromatic Hydrocarbons - all aromatic hydrocarbon compounds eluting from naphthalene through benzo(g,h,i)perylene, excluding Targeted PAH Analytes.

C_9 through C_{18} Aliphatic Hydrocarbons - all aliphatic hydrocarbon compounds eluting from n-nonane to just before n-nonadecane (n-C_{19}).

C_{19} through C_{36} Aliphatic Hydrocarbons - all aliphatic hydrocarbon compounds eluting from n-nonadecane through n-hexatriacontane (n-C_{36}).

Targeted PAH Analytes - the 17 polynuclear aromatic hydrocarbon (PAH) compounds listed in Table 3.

1.2 Responsibilities

Implementation of this SOP requires sufficiently trained analysts and properly functioning instrumentation. Samples must be properly extracted following Katahdin Analytical Quality Assurance/Quality Control requirements. Only analysts/technicians

qualified and experienced with this method may perform these procedures. Each analyst or technician must be familiar with Katahdin Analytical safety procedures. Refer to Katahdin SOP QA-805, "Personnel Training & Documentation of Capability," current revision.

It is the responsibility of all Katahdin technical personnel involved in the determination of Extractable Petroleum Hydrocarbons to read and understand this SOP, to adhere to the procedures outlined, and to properly document their data in the appropriate lab notebook. Any deviations from the test or irregularities with the samples should also be recorded in the lab notebook and reported to the Department Manager or designated qualified data reviewer responsible for EPH data.

It is the responsibility of the Department Manager to oversee that members of their group follow this SOP, to ensure that their work is properly documented and to initiate periodic review of the associated logbooks.

1.3 Safety

Users of this procedure must be cognizant of inherent laboratory hazards, proper disposal procedures for contaminated materials and appropriate segregation of hazardous wastes. The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical should be treated as a potential health hazard. A reference file of material safety data sheets is available to all personnel involved in the chemical analysis. Everyone involved with the procedure must be familiar with the MSDS's for all the materials used in this procedure.

Each qualified analyst or technician must be familiar with the Katahdin Analytical Environmental Health and Safety Manual including the Katahdin Hazardous Waste Management Plan and must follow appropriate procedures. These include the use of appropriate personal protective equipment (PPE) such as safety glasses, gloves and lab coats when working with chemicals or near an instrument and not taking food or drink into the laboratory. Each analyst should know the location of all safety equipment. Each analyst shall receive a safety orientation from their Department Manager, or designee, appropriate for the job functions they will perform.

All standards should be prepared in a hood.

0.3 Pollution Prevention/Waste Disposal

Whenever possible, laboratory personnel should use pollution prevention techniques to address their waste generation. Refer to the current revision of the Katahdin Hazardous Waste Management Plan for further details on pollution prevention techniques.

TITLE: EXTRACTION OF PETROLEUM HYDROCARBONS FROM SAMPLES FOR ANALYSIS BY MADEP - EPH METHODS

Wastes generated during the preparation of samples must be disposed of in accordance with the Katahdin Hazardous Waste Management Plan and Safety Manual and SOP SD-903, "Sample Disposal," current revision. Expired standards are lab packed, placed in the Katahdin hazardous waste storage area, and disposed of in accordance with this SOP.

Any methylene chloride solvent waste generated during the rinsing of glassware etc. should be disposed of in the "D" waste stream satellite accumulation area nearest the point of generation. Acetone and hexane are considered flammable waste, and should be disposed of in the "O" waste stream satellite accumulation area nearest the point of generation. Post-extraction soil samples, as well as cartridges used for the fractionation of EPH samples, should be disposed of in the soil with organics "I" waste stream satellite accumulation area nearest the point of generation. Please refer to the current revision of SOP CA-107 for the location of satellite waste accumulation areas.

2.0 SUMMARY OF METHOD

A soil or water sample is extracted with methylene chloride, dried with sodium sulfate, solvent exchanged into hexane, and then concentrated using a Kuderna-Danish apparatus. Sample fractionation into aliphatic and aromatic fractions is conducted using a preparative HPLC column and Foxy fraction collector. The two extracts produced are then re-concentrated to final volumes of 1 mL each. The resulting extracts (an aliphatic extract and an aromatic extract) are analyzed separately for EPH using a GC equipped with a flame ionization detector (FID).

3.0 INTERFERENCES

Method interferences are minimized by using high purity reagents and by washing all glassware with hot soapy water and then rinsing with warm tap water, acetone and methylene chloride.

Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interference will vary from one source to another. A preparative HPLC column cleanup and fractionation procedure is used to overcome many of these interferences, but some samples may require additional cleanup approaches that are beyond the scope of this method.

Certain organic compounds not associated with releases of petroleum products, including chlorinated hydrocarbons, phenols, and phthalate esters, will be quantitated as Extractable Petroleum Hydrocarbons. If necessary or desirable, additional sample cleanup or analytical procedures may be employed to minimize or document the presence of such compounds.

TITLE: EXTRACTION OF PETROLEUM HYDROCARBONS FROM SAMPLES FOR ANALYSIS BY MADEP - EPH METHODS

The leaching of plasticizers and other compounds has been observed from commercially available silica gel cartridges used to fractionate EPH sample extracts. Concerns of this nature must be continuously monitored and documented by the analysis of laboratory method blanks.

4.0 APPARATUS AND MATERIALS

4.1 1-L amber glass bottles

4.2 4 oz. (120 mL) glass wide-mouth jars

4.3 Vials: 4 mL glass vials with silicone/PTFE septa in open top caps

4.4 Vials: 1.8 mL with silicone/PTFE septa in open-top caps

4.5 Glass funnels

4.6 2-L Separatory teflon FEP funnels with screw closures

4.7 Kuderna-Danish apparatus including 10-mL concentrator tube, 500-mL Evaporative flask and 3-ball Snyder column

4.8 250 mL amber bottles with Teflon-lined screw covers

4.9 Disposable pipettes: Pasteur, 5 ¾"

4.10 25-mL graduated cylinder

4.11 1-L graduated cylinder

4.12 400-mL beakers

4.13 A top-loading balance capable of weighing to the nearest 0.1 g must be used for weighing soil samples

4.14 Nitrogen blowdown apparatus, Organomation N-EVAP

4.15 Water bath: heated with a concentric ring cover, capable of temperature control (±2° C). The bath should be used in a hood

4.16 Syringes, gas tight, 1.0mL, Hamilton or equivalent, and 10mL Luer-Lok syringe (Popper or equivalent)

4.17 Boiling Chips, silicon carbide (carborundum), 12 mesh

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4.18 Soxhlet extraction apparatus, or apparatus for equivalent technique such as ASE (accelerated solvent extractor)

4.19 Voa vials, 40 mL

4.20 Filter paper, 18.5 cm diameter

4.21 Wide range pH test strips, CF-type, pH0-14

4.22 Solid Phase Extraction (SPE) cartridges with silica gel (5g/20mL)

4.23 Waters HPLC system, or equivalent, consisting of an autosampler and gradient pump.

4.24 ISCO foxy 200 fraction collector, or equivalent.

4.25 Restek HPLC column, or equivalent, 150mm X 10mm.

5.0 REAGENTS

5.1 Laboratory reagent grade water: organic free water (Culligan reagent grade water).

4.1 Solvents: hexane, methylene chloride, and acetone; pesticide grade or better.

5.3 Sodium sulfate: (ACS) granular, anhydrous. Purify by heating at 400°C for 4 hours in a shallow tray (sodium sulfate may be purchased pre-purified by the manufacturer).

5.4 Sand: free of extractable petroleum hydrocarbons, purified by heating at 400 °C for four hours

5.5 Matrix Spike/Lab Control Sample Spiking Solution: Refer to Table 3

5.6 Surrogate Spiking Solution: 5-alpha androstane and ortho-terphenyl (OTP) at concentrations of 90 ug/mL in acetone

5.7 Fractionation check standard: See Table 3.

5.8 Fractionation surrogate standards: 2-Fluorobiphenyl and 2-Bromonaphthalene at 90 ug/mL in hexane.

5.9 <u>Hydrochloric acid solution</u> (1:1 HCl: H_2O) - slowly add 500 mL of HCl to 500 mL reagent water.

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6.0 SAMPLE COLLECTION, PRESERVATION AND HANDLING

6.1 Aqueous samples are collected in 1 liter amber glass bottles with Teflon-lined screw caps.

6.2 Soil and sediment samples are collected in 4 oz. (120 mL) wide-mouth glass jars with Teflon-lined screw caps.

6.1 Sample container, preservation and holding times are summarized in Table 4.

6.1 A chain of custody form must accompany all aqueous, soil and sediment samples, documenting the date and time of sampling and any preservatives added.

7.0 PROCEDURES

Samples are extracted using methylene chloride, and solvent-exchanged into hexane. The recommended extraction procedure for water samples is a separatory funnel liquid-liquid extraction technique based upon SW-846 Method 3510A. For soil or sediment samples, use of a Soxhlet extraction technique based on SW846 Method 3540C is employed. Alternative extraction procedures are acceptable such as 3541 automated Soxhlet extraction procedure, provided that the laboratory can document acceptable performance. Sonication (3550) may only be used for the extraction of highly contaminated (free product) non-soil/sediments.

WATER EXTRACTION

7.1 Mark the meniscus on the 1-liter sample bottle (for later volume determination) and transfer it to a 2-liter separatory funnel.

7.2 A method blank must be prepared with each extraction batch, not to exceed 20 client samples. To prepare method blank, pour 1 liter of laboratory reagent grade water into a 2-liter separatory funnel.

7.3 A laboratory control sample (LCS) and laboratory control sample duplicate (LCSD) must be prepared with each extraction batch, not to exceed 20 client samples. To prepare LCS/LCSD, pour 1-liter of laboratory reagent grade water into each of two 2-liter separatory funnels.

7.4 A matrix spike/matrix spike duplicate (MS/MSD) is prepared per client request. To prepare MS/MSD, mark the meniscus on each 1-liter sample bottle designated for MS/MSD (for later volume determination) and transfer each to a 2-liter separatory funnel.

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7.5 To all samples, method blank, LCS/LCSD, and MS/MSD add 1.0 mL of EPH surrogate spiking solution using a pre-rinsed 1.0 mL gas tight syringe. Record surrogate spike volume and identification code in extraction logbook. Thoroughly rinse syringe with solvent prior to using it for another spiking solution.

7.6 To LCS/LCSD and MS/MSD add 1.0 mL of the EPH matrix spike/LCS spiking solution using a 1.0 mL gas tight syringe. Record matrix spike/LCS spiking solution volume and identification code in extraction logbook. Thoroughly rinse syringe with solvent when spiking is completed.

7.7 Check the pH of the sample with wide-range pH paper. Note the pH in the laboratory notebook. The pH of the sample must be adjusted to pH<2. Adjust all samples and quality control samples as needed with 1:1 HCl.

7.8 Add 60 mL methylene chloride to the sample bottle to rinse the inner walls of the container, then add this solvent to the separatory funnel. Add 60 mL methylene chloride directly to separatory funnel for blank, LCS/LCSD.

7.9 Seal and shake the separatory funnel vigorously for 3 minutes with periodic venting to release excess pressure.

NOTE: Methylene chloride creates excessive pressure very rapidly; therefore, venting should be done immediately after the separatory funnel has been sealed and shaken once.

7.10 Allow the organic layer to separate from the water phase for a minimum of 5 minutes. If the emulsion interface between layers is more then one-third the size of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample and may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods. Collect the solvent extract in a 250 mL amber bottle with a Teflon-lined screw-cap.

7.11 Repeat the extraction two more times using additional 60 mL portions of solvent. Combine the three solvent extracts in the amber bottle. (Steps 7.5 to 7.10)

CONCENTRATION OF EXTRACTS

7.12 For sample volume determination add water to the sample bottle to the level of the meniscus previously marked then transfer this water to a graduated cylinder. Record sample volumes in extraction logbooks to the nearest 10 mLs.

7.13 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporation flask.

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7.14 Add approximately 50 mL Hexane directly to the KD body to allow for a solvent exchange.

7.15 Dry the extract by passing it through a glass powder funnel containing anhydrous sodium sulfate. Collect the dried extract in a K-D concentrator. Rinse the amber bottle, which contained the solvent extract, with 20 to 30 mL of methylene chloride and add it to the funnel to complete the quantitative transfer.

7.16 Add one or two clean boiling chips to the K-D flask and attach a three ball Snyder column. Pre-wet the Snyder column by adding about 1 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (80-90°C). Gently swirl K-D in water until boiling begins. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood. . The K-D should be kept in a vertical orientation while on the bath. When the apparent volume of liquid reaches 4 - 6 mLs, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes. Rinse the Snyder column lower joint with ~ 1 mL of methylene chloride. Remove the Snyder column. Wipe off any water from the neck above the lower joint of the flask. Separate the K-D flask from the concentrator tube, rinsing the ground glass joint with ~1 mL methylene chloride.

7.1 Reduce the hexane extract in the concentrator tube to approximately 1 mL using the nitrogen blow-down apparatus. The bath temperature must be no higher than the boiling point of the solvent (45°C for hexane). Turn the gas to 3 psi. Be careful not to splash the extract out of the tube. During concentration on the N-evap, the internal wall of the concentrator tube and the N-evap sparging pipette must be rinsed down at least once or twice with ~1 mL of hexane. The solvent level in the concentrator tube must be positioned below the level of the water bath as much as possible to prevent water from condensing into the sample extract. As the extract volume is reduced, lower the N_2 sparging needle closer to the surface of the extract to expedite the concentration. Note any problems or extract losses, if they occur, in the extractions logbook.

7.1 Concentrate the extract as described in Step 7.17, using hexane to rinse the internal wall of the concentrator tube. Be sure to lower the bath temperature back to 39°C when the solvent exchange is complete. Reduce the extract to 1 mL and place in a 4.0 mL vial. Record the "pre-fractionation" final volume as 1 mL in the extractions logbook.

7.1 Record the sample preparation information for the extraction and concentration steps. As a minimum, record the date, sample laboratory number, sample volume, volume and concentration of added surrogates, fractionation surrogates, and matrix spike solutions, and any deviations for problems associated with the extraction of the samples.

7.20 The 1 mL extract is now ready to be cleaned and fractionated using HPLC or SPE fractionation. Proceed to section 7.35.

SOIL EXTRACTION

7.1 Rinse the Soxhlet extractors and 500 mL flat-bottom boiling flasks three times with methylene chloride. Be sure that the solvent rinses through the large vapor tube and smaller siphon tubes of the Soxhlet. Inspect these for tiny cracks. Also rinse the 24/40 lower joint.

7.2 Add ~ 250 mLs of methylene chloride to the 500 mL boiling flask. Add several boiling stones. Using stainless steel forceps and working in a hood, place a plug of the pre-baked glass wool at the bottom of the Soxhlet so that the siphon tube hole is covered. Insert the 24/40 joint of the Soxhlet extractor into the 500 mL boiling flask and secure with a metal clip. Cover the top of the Soxhlet extractor with a piece of aluminum foil until ready to begin loading the sample.

7.3 Samples should be prepped as follows:

7.23.1 Sediment/soil samples - Decant and discard any water layer on a sediment sample. Mix the sample thoroughly with the stainless steel spatula. If the sample container is full to the extent that stirring the sample is impractical, try to remove the "best representative" aliquot from the jar based on color, particle size, moisture, etc. Discard any foreign objects such as sticks, leaves, and rocks.

7.23.2 Gummy, fibrous, or oily materials not amenable to mixing should be cut, shredded, or otherwise reduced in size to allow for maximum exposure of the sample surfaces to the extraction solvent. Materials such as glass, rubber, metal, etc. may not require mixing with powdered sodium sulfate to disperse the sample. Plastic materials must be tested for degradation (melting) in methylene chloride prior to Soxhlet extraction.

7.23.3 Please refer to the current revision of Katahdin Analytical Services SOP CA-108, "Basic Laboratory Technique", for more detailed guidance on subsampling to ensure reproducibility.

7.4 The following steps should be performed <u>rapidly to avoid loss of the more volatile extractables</u>. Weigh out a 10.0 ± 0.05 g portion of sample into a labeled 400-mL beaker. Record sample weight to the nearest 0.01 g in appropriate extraction logbook. Add between 10 g and 20 g of anhydrous powdered sodium sulfate as required to produce a "free-flowing" mixture. The amount of sodium sulfate added will depend upon the moisture content of the sample (e.g., low moisture content will require less sodium sulfate). Mix well with a spatula. Keep the spatula in the sample beaker and <u>cover</u> the beaker with aluminum foil.

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7.1 A method blank must be prepared with each extraction batch, not to exceed 20 client samples. To prepare method blank, weigh out one 10.0 ± 0.05 g portion of purified sand in a labeled 400 mL beaker. Add 20 g sodium sulfate and mix well. Although a "free-flowing" mixture can be achieved with less than 20 g sodium sulfate, the method blank must contain 20g in order to evaluate the sodium sulfate as a potential source of contamination.

7.2 A laboratory control sample (LCS) and laboratory control sample duplicate (LCSD) must be prepared with each extraction batch, not to exceed 20 client samples. To prepare LCS/LCSD, weigh out two 10.0 ± 0.05 g portions of purified sand in labeled 400 mL beakers. Add 10 g sodium sulfate to each and mix well.

7.24 To prepare MS/MSD, weigh out 10 ± 0.05 g portions of the sample designated for MS/MSD into each of two labeled 400 mL beakers. Record sample weights to nearest 0.01 g in appropriate extraction logbook. Add between 10 g and 20 g sodium sulfate to each to produce a free-flowing mixture, and mix well.

7.24 Once all of the QC and field samples have been weighed and mixed with sodium sulfate, begin adding each to the assembled and appropriately labeled Soxhlet extractors using the stainless steel spatulas. Carefully scrape all of the mixtures from the beaker walls so that no more than 1% remains behind in the beaker. Be careful not to have any of the solid material fall into the extract flask through the large vapor tube.

7.24 To all samples, method blank, LCS/LCSD, and MS/MSD add 1.0 mL of EPH surrogate spiking solution using a pre-rinsed 1.0 mL gas tight syringe. Record surrogate spike volume and identification code in extraction logbook. Thoroughly rinse syringe with solvent prior to using it for another spiking solution.

7.24 To LCS/LCSD and MS/MSD add 1.0 mL of the EPH matrix spike/LCS spiking solution using a 1.0 mL gas tight syringe. Record matrix spike/LCS spiking solution volume and identification code in extraction logbook. Thoroughly rinse syringe with solvent when spiking is completed.

7.24 Place each of the Soxhlet extractors in a heating mantle and lower the Allihn cooling water condensers into the 45/50 joints of the extractors. Save the pieces of aluminum foil for covering the flat-bottom flasks when the extraction is complete. Switch on the individual heating mantles and be sure that the Rheostat of the variable transformer is set to 45-50% of the output voltage. Once the methylene chloride begins to boil and the Soxhlet begins to cycle (solvent will immerse the sample and collect in the Soxhlet until the level reaches that of the small siphon tube and then begin to spill over into the extract flask), re-check the apparatus' for leaks. Allow the samples to extract for 18 ±2 hours. Be sure the chiller/recirculator temperature is set low enough to provide enough cooling capacity for the number of extractions in the batch.

7.8 When the extraction is complete, allow the extracts to cool before dismantling. Remove the Allihn condenser. Tilt each extractor slightly to cause any remaining solvent in the sample chamber to drain through the siphon tube into the extract flask. This will help to cool the extract flask and make the apparatus easier to dismantle. Move the extractors to a hood and detach the extractor from the extract flask. Try to drain as much solvent as possible from the extractor into the flask. Cover the flask with aluminum foil and store in the interim extract storage refrigerator unless the extracts are to be concentrated the same day.

7.9 Immediately remove the extracted soil/sodium sulfate mixtures from the extractors using a square edge spatula, and dispose of in an appropriate solid waste container. It is important to do this soon after the extractors are dismantled, as the sample mixture will tend to "freeze" into a solid mass in the Soxhlet as the solvent dries.

7.10 See sections 7.13 through 7.20 for the concentration of the extracts.

Fractionation

NOTE: If using the SPE cartridges: The Fractionation step is a critical yet highly sensitive procedure. Small changes in the volumes of eluting solvents, fractionation equipment, and/or fractionation techniques can significantly impact the proportion of hydrocarbons segregated in either the aliphatic or aromatic fractions. Considerable care and attention is required to ensure satisfactory results.

7.11 Fractionation checks are analyzed by HPLC on a daily basis before any samples are fractionated. For SPE cartridges: fractionation checks are run with each new lot of SPE cartridges or every three months. A fractionation check is made by adding 1mL fractionation check solution to the previously concentrated 1 mL extract. The fractionation checks are labeled with the lot number and date of fractionation. These checks are to be performed before sample fractionation to confirm the amount of hexane necessary to prevent aromatic breakthrough into the aliphatic fraction.

7.12 Add 1.0 mL of the fractionation surrogate spiking solution with a gas tight syringe to the 1 mL hexane extract.

HPLC FRACTIONATION

7.13 Make sure the methylene chloride and hexane bottles are full. All solvents need to be filtered and sonicated for at least 15 minutes prior to putting on the HPLC.

7.14 Turn pump on at 1.00 mL/min by pressing the home button and then typing 1.00 and enter. Make sure the solvent flowing is hexane. The %A under the flow rate

should be at 100%. If it is not hit enter until the %A line is highlighted and type in 100 then enter until sparge is highlighted.

7.15 Next prime the pumps.

7.16 Take a 5 mL disposable syringe and connect to the prime valve on the front bottom of the pump. Turn knob until it reads draw and then draw the syringe fairly slowly. You should see bubbles coming through the clear tubing into the syringe. Repeat at least three more times or until there is no more air coming through the lines.

7.17 Repeat 7.40 for the methylene chloride . You must put solvent B at 100% before priming.

7.18 When finished priming change pump back to 100% hexane following 7.38.

7.19 Let equilibrate for about 5 minutes then purge the autosampler.

7.20 At the autosampler, on the front screen, hit the purge page button and then start purge. The settings are already there for an 8 minute purge.

7.21 When the purge is finished go to the pump hit the home button and change the flow rate to 4.00 mL/min. Let equilibrate for at least 5 minutes.

7.22 At the pump push the program table button and select table 1. Parameters are shown in table 5.

7.23 Now push the program method button and scroll over to enter the starting and ending vial numbers that correspond to the samples that are in the autosampler.

7.24 Push the operate methods button twice and wait for the start run prompt at the bottom of the screen.

7.25 Turn on the Isco Foxy 200 fraction collector using the power button.

7.26 Load the Foxy tray with 40 mL VOA vials. You will need two vials per sample, the first being for the aliphatic and the second for the aromatic. Start with position one and put a waste VOA vial after every aromatic fraction due to the fact the collector skips a space after every injection.

7.27 After the vials are on the tray push the run A button on the front of the Foxy. The sampling arm should move to the ready position waiting for the injection to occur.

7.28 Push the start run button on the pump which will prompt the autosampler to start the injection. Most injection are 1.0 mL, however you can inject a smaller volume as long as you make sure there is enough sample in the vial to inject. When the

injection occurs the sampling arm of the Foxy will position itself over the aliphatic vial and start collecting. When the aliphatic portion finishes the arm automatically moves to the second vial and immediately starts collecting the aromatic fraction.

7.29 The total run time for one sample is 16.50 minutes followed by a 6 minute equilibration time in hexane.

7.30 Place all fractions on the N-evap once the fractionation is complete. The aliphatic fraction should be transferred into a 12 mL conical vial. The aromatic fraction should be left in the VOA vial until it reaches a suitable volume to transfer into a 12 mL conical vial.

7.31 Blow all fractions down to the volume at which they were injected (if 1.0 mL was injected, the final volume will be 1 mL, if 0.5 mL was injected the final volume will be 0.5 mL). All aliphatic fractions are in Hexane, while all aromatic fractions are in methylene chloride.

7.32 Transfer all samples to a 2.0 mL screw top vial.

7.33 Samples are now ready for analysis.

7.34 All samples fractionated on the HPLC should be written in the HPLC03 logbook (figure 2).

SPE CARTRIDGE FRACTIONATION

7.35 Place SPE cartridges on the sample collection apparatus. With the valve under the sample in the open position, rinse each SPE cartridge with 30mL of hexane, using a 10mL syringe. Close the valve when approximately 0.5cm of solvent remains above the cartridge frit. Do not allow the silica gel cartridges to dry out after the solvent has passed through. Empty the collection apparatus of eluted solvent.

7.36 Place a 40mL VOA vial, labeled as the aliphatic fraction, under each SPE cartridge in the sample collection apparatus. Add 1mL of the fractionation check or sample to the top of the SPE cartridge. Open the valve. Just as the sample/solvent layer reaches the frit, add ~17mL of hexane by syringe. (The amount of hexane is determined by the fractionation check done on each lot or every three months.) The solvent should be added slowly, however, the cartridge must not be allowed to go dry. Rinsing the sides of the cartridge when adding the hexane may help improve recoveries. Close the valve when approximately 0.5cm of solvent remains. Remove the test tubes.

7.37 Place a new 40mL VOA vial, labeled as the aromatic fraction, under the sample collection apparatus. Open the valve. Just as the hexane layer reaches the frit, add 20mL of methylene chloride, by syringe, to collect the aromatic fraction. Rinsing

the sides of the cartridge when adding the methylene chloride may help improve recoveries. Remove the test tubes.

7.24 All fractions should be placed on the N-EVAP bath and blown down to the volume at which they were fractionated (if 1.0mL was fractionated, the final volume will be 1mL). The final volume recorded in the logbook and computer, however, should be 2.0 mL since this is what the actual final volume is. All aliphatic fractions are in hexane, while all aromatic fractions are in $MeCl_2$.

7.24 Record the sample preparation information for the fractionation and concentration steps. At a minimum, record the SPE cartridges lot#, fractionation date, fractionation initials, volumes of hexane and methylene chloride added for each fraction, concentration volume, concentration initials, and any deviations or problems associated with the fractionation of the samples.

8.0 QUALITY CONTROL AND ACCEPTANCE CRITERIA

A method blank must be extracted for each and every item listed below:

- Each sample matrix (soil, water)
- Each day of extraction (24 hours midnight - midnight)
- Each extraction method
- Every 20 samples extracted in a 24-hour period

A laboratory control sample (LCS) and laboratory control sample duplicate (LCSD) is required for each and every item listed below:

- Each sample matrix
- Each extraction method
- Every extraction batch of twenty or fewer samples

Sample specific matrix spikes (MS) and matrix spike duplicates (MSD) are extracted per client request or per project requirements.
Refer to Katahdin SOP CA-322, Method for the Analysis of Extractable Petroleum Hydrocarbons (MADEP - EPH), current revision, for other Quality Control parameters and acceptance criteria.

9.0 METHOD PERFORMANCE

Refer to Katahdin SOP CA-322, Method for the Analysis of Extractable Petroleum Hydrocarbons (MADEP - EPH), current revision.

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10.0 APPLICABLE DOCUMENTS/REFERENCES

Method for the Determination of Extractable Petroleum Hydrocarbons (EPH), Massachusetts DEP, May 2004, revision 1.1.

Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, USEPA SW846, 3rd Edition, Final Updates I, II, IIA, IIB, III, IIIA, IIIB and IV, February 2007, Office of Solid Waste and Emergency Response, U.S. EPA

Department of Defense Quality Systems Manual for Environmental Laboratories (DOD QSM), Version 4.1, 04/22/09.

Katahdin Analytical Services, Inc. SOP CA-322, current revision, Method for the Analysis of Extractable Petroleum Hydrocarbons (MADEP - EPH)

Katahdin SOP CA-101, Equipment Maintenance and Troubleshooting, current revision.

Katahdin SOP QA-806, Method Detection Limit, Instrument Detection Limit and Reporting Limit Studies and Verifications, current revision.

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TABLE 1

QC REQUIREMENTS

Parameter/ Method	QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action
Sample Prep for waters and soils for EPH determination	Method blank	One per prep batch or 20 samples whichever is more frequent.	Refer to analytical method.	Refer to analytical method.
	LCS/LCSD	One each per prep batch	Refer to analytical method.	Refer to analytical method.
	Matrix Spike/Matrix Spike Duplicate	Per client request	Refer to analytical method.	Refer to analytical method.
	Sample Duplicate/ Matrix Spike	Per client request	Refer to analytical method.	Refer to analytical method.
	Demonstration of analyst proficiency; accuracy and precision	One time per analyst performing the method, then yearly	Must pass all applicable QC for method	Repeat analysis until able to perform passing QC; document successful performance in personal training file
	MDL and-or LOD/LOQ verification study	Refer to KAS SOP QA-806, "Method Detection Limit, Instrument Detection Limit and Reporting Limit Studies and Verifications", current revision.		

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TABLE 2

SUMMARY OF METHOD MODIFICATIONS

TOPIC	KATAHDIN SOP CA-511-07	MADEP METHOD, current revision
Apparatus/Materials	Automated HPLC and Fraction Collector	SPE cartridges
Reagents		
Sample preservation/ handling		
Procedures	0) Initial solvent exchange with addition of 50 mLs hexane to KD body prior to sample addition, and solvent exchange a second time into hexane via the addition of 10 mLs of hexane during the nitrogen blowdown. 0) 7.15 ...with 20 to 30 mL of methylene chloride ...to complete the quantitative transfer. 0) 7.16... Place the K-D apparatus on a hot water bath (80-90°C). Gently swirl K-D in water until boiling begins. 0) Fractionate samples using HPLC.	0) Addition of 50 mLs of hexane to KD body after concentration of extract in methylene chloride to 1mL to accomplish solvent exchange. 0) 9.1.2.5 ...with 100 to 125 mL of methylene chloride to complete the quantitative transfer. 0) 9.1.10 Place the K-D apparatus on a hot water bath (80-90 °C) so that... 0) Fractionate samples with SPE cartridges.
QC - Spikes	1) Surrogate, spike and fractionation surrogate all prepared at 90 ug/mL for use in a 2 mL or prefractionated volume. 2) Fractionation check solution: aliphatics, aromatics, 5-alpha androstane, and o-terphenyl at 200ug/mL each	1) Surrogate at 40 ug/mL, matrix spike at 50-150 ug/mL, fractionation surrogate at 40 ug/mL. 2) Fractionation check solution: aliphatics and aromatics at 200ug/mL each
QC - LCS		
QC - Accuracy/Precision		
QC - MDL		

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TABLE 3

RECOMMENDED STOCK, FRACTIONATION CHECK SOLUTION, AND MATRIX SPIKE CONCENTRATIONS - MADEP - EPH METHOD

ANALYTE	Stock * Standards (ng/uL)	Fractionation** Check Solution (ng/uL)	Matrix Spike Standard *** (ng/uL)
Naphthalene	1,000	200	90
2-Methylnaphthalene	1,000	200	90
Acenaphthylene	1,000	200	90
Acenaphthene	1,000	200	90
Fluorene	1,000	200	90
Phenanthrene	1,000	200	90
Anthracene	1,000	200	90
Fluoranthene	1,000	200	90
Pyrene	1,000	200	90
Benzo(a)Anthracene	1,000	200	90
Chrysene	1,000	200	90
Benzo(b)Fluoranthene	1,000	200	90
Benzo(k)Fluoranthene	1,000	200	90
Benzo(a)Pyrene	1,000	200	90
Indeno(1,2,3-cd)Pyrene	1,000	200	90
Dibenzo(a,h)Anthracene	1,000	200	90
Benzo(g,h,i)Perylene	1,000	200	90
o-Terphenyl (surr)	1,000	200	90
Nonane	1,000	200	90
Decane	1,000	200	90
Dodecane	1,000	200	90
Tetradecane	1,000	200	90
Hexadecane	1,000	200	90
Octadecane	1,000	200	90
Nonadecane	1,000	200	90
Eicosane	1,000	200	90
Docosane	1,000	200	90
Tetracosane	1,000	200	90
Hexacosane	1,000	200	90
Octacosane	1,000	200	90
Triacontane	1,000	200	90
Hexatriacontane	1,000	200	90
5-alpha androstane(surr)	1,000	200	90
Petroleum Reference Std	1,000	------	------

* The Aromatic Hydrocarbon Stock Standards (17 PAH compounds and o-terphenyl) should be prepared in methylene chloride. The Aliphatic Hydrocarbon (consisting of 14 normal alkanes and 5-alpha androstane) should be prepared in hexane.

** The Fractionation Check Standard should be prepared in hexane.

*** The Matrix Spike Solution should be prepared in acetone. The o-terphenyl and 5-alpha androstane surrogate solution should also be prepared in acetone.

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TABLE 4

HOLDING TIMES AND PRESERVATIVES FOR EPH SAMPLES

MATRIX	CONTAINER	PRESERVATION	HOLDING TIME
Aqueous Samples	1 Liter amber glass bottle with Teflon- lined screw cap	Add 5 mL of 1:1 HCl; cool to 4 (±2) °C	Samples must be extracted within14 days and extracts analyzed within40 days of extraction
Soil/Sediment Samples	4-oz. (120 mL) wide-mouth glass jar with Teflon-lined screw cap	Cool to 4 (±2) °C	Samples must be extracted within14 days and extracts analyzed within40 days of extraction
Soil/Sediment Samples	4-oz. (120 mL) wide-mouth glass jar with Teflon-lined screw cap. Jar should be filled to only 2/3 capacitiy to avoid breakage if expansion occurs during freezing.	Freeze at -10 °C in the field or in the laboratory*	Samples must be extracted within 14 days of the date thawed and extracts analyzed within 40 days of extraction*

*Samples processed in the laboratory must be preserved at 4 (±2) °C and frozen within 48 hours of the time of collection. Frozen samples may be held for up to one year prior to analysis and must be extracted within 24 hours of thawing.

TITLE: EXTRACTION OF PETROLEUM HYDROCARBONS FROM SAMPLES FOR ANALYSIS BY MADEP - EPH METHODS

TABLE 5

HPLC PROGRAM 1 RUN PARAMETERS

RUN TIME(Min)	FLOW RATE (mL/min)	%A (Hexane)	%B $MeCl_2$	CURVE #
Initial	4.00	100	0	*
3.00	4.00	0	100	11
10.50	4.00	100	0	11
16.50	4.00	100	0	11
22.50	0.00	100	0	11

TITLE: EXTRACTION OF PETROLEUM HYDROCARBONS FROM SAMPLES FOR ANALYSIS BY MADEP - EPH METHODS

TABLE 6

ISCO FOXY 200 FRACTION COLLECTOR

- Use the time windows function
- Collect Vial 1 from 0.00 min – 3.00 min
- Collect Vial 2 from 3.00 min – 10.50 min
- Total fraction size is 10.50 min
- There is a 6 minute equilibration time in hexane where it diverts the hexane to waste until the new injection.

TITLE: EXTRACTION OF PETROLEUM HYDROCARBONS FROM SAMPLES FOR ANALYSIS BY MADEP - EPH METHODS

FIGURE 1

EXAMPLE OF EXTRACTION LOGBOOK PAGE

EPH Sep

KATAHDIN ANALYTICAL SERVICES, INC.
ORGANIC EXTRACTIONS LOG - MADEP EPH

Extraction Method:	SW846 3520 (CLLE)	SW846 3510 (SEP) ✓	SW846 3540 (SOX)	SW846 3545 (ASE)
Surrogate ID: G10777 / G10784	Spike ID: G10736	Frac. Surrogate ID: G10734		
MeCL2 Lot # H48358	Hexane Lot # H47603	NaSO4 Lot # 27946004	HCL Lot #	SPE Lot #
KD Filler Paper Lot # K1167726		Nitrogen Water Bath Temp.		

Start: 9:20 End: 10:30

Date Extracted	Ext. Init.	Sample ID	Wt/Vol g/mL	Surr Vol.	Spike Vol.	Final Vol Pre-Frac. mL	Date Conc. Pre-Frac.	Conc. Init. Pre-Frac.	Tray Location	Frac. Init.	Frac. Surr Vol.	Final Vol. Post-Frac.	Date Conc Post-Frac.	Tray Location	Conc. Init Post-Frac.	Comments
4/5/10	WS	W47358 7-1	1000	1mL	NR	1mL	4/5/10	WS	EPH-101 B6	JLP	1mL	2mL	4-9-10	E4	KT	R123744
↓	↓	↓ -2	↓	↓	1mL	↓	↓	↓	B7	↓	↓	↓	↓	E5	↓	
↓	↓	↓ -3	↓	↓	↓	↓	↓	↓	B8	↓	↓	↓	↓	E6	↓	

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Date Extracted	Ext. Init.	Sample ID	Wt/Vol g/mL	Surr Vol.	Spike Vol.	Final Vol pre-Frac. mL	Date Conc. pre-Frac.	Conc. Init. Pre-Frac.	Tray Location	Frac. Init.	Frac. Surr Vol.	Final Vol. Post-Frac.	Date Conc post-Frac.	Tray Location	Conc. Init Post-Frac.	Comments
4/5/10	WS	SD13790-2 @ RE	1020	1mL	NR	1mL	4/5/10	WS	EPH-101 B9	JLP	1mL	2mL	4-9-10	E7	KT	
↓	↓	-4 @	1010	↓	↓	↓	↓	↓	B10	↓	↓	↓	↓	E8	↓	
↓	↓	-6 b	1010	↓	↓	↓	↓	↓	B11	↓	↓	↓	↓	E9	↓	
↓	↓	-8 b	1050	↓	↓	↓	↓	↓	B12	↓	↓	↓	4-10-10	E10	JLP	
↓	↓	-10 b	1060	↓	↓	↓	↓	↓	C1	↓	↓	↓	↓	A1	↓	
↓	↓	-12 b	1060	↓	↓	↓	↓	↓	C2	↓	↓	↓	↓	A2	↓	
↓	↓	SD13791-6a	1060	↓	↓	↓	↓	↓	C3	↓	↓	↓	↓	A3	↓	

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Reviewed By_____ Date_____

TITLE: EXTRACTION OF PETROLEUM HYDROCARBONS FROM SAMPLES FOR ANALYSIS BY MADEP - EPH METHODS

FIGURE 2

EXAMPLE OF HPLC03 LOGBOOK PAGE

Katahdin Analytical Services
HPLC03 Logbook

Analytical Method:	MA-EPH: X	Other:	Flow: 4.0 ml/min.
MeCl2 Lot #: H49E58		Hexane Lot #: H47E07	

Tray Pos. No.	Sample Identification	Date	Initials	Inj. Volume	Dilution	Comments
2	SS-13	3-29-10	JLP	1mL	1	
3	-14					No cap
3	-15					
3	-16					
1	FC-17	3-31-10	JLP	1mL	1	
2	WG75404-1					
3	-2					
4	-3					
5	WG75297-4					filtered
6	-5					
7	SD1390-2					
8	-4					
9	-8					
10	-6					
11	-10					
12	-12					
13	FC-18					
1	FC-19	4-1-10	JLP	1mL	1	
2	WG75404-4					filtered
3	-5					
4	SD1391-6					
5	SD1425-3					
6	-4					
7	WG75456-1					
8	-2					

JP03/31/10

Reviewed by: Review Date:

TITLE: EXTRACTION OF PETROLEUM HYDROCARBONS FROM SAMPLES FOR ANALYSIS BY MADEP - EPH METHODS

FIGURE 3

EXAMPLE OF HPLC03 MAINTENANCE LOGBOOK PAGE

KATAHDIN HPLC MAINTENANCE LOG — INSTRUMENT: HPLC03

DATE	INITIALS	MAINTENANCE PERFORMED
040810	KT	performed purge and compression check
		flow rate at 1.0 ml/min purge set for 9.7 min.
		+ compression check passed!
		performed an autozero of the autosampler passed
		purged system twice at 1ml/min w/ 100% pure
		degassed mesh.
		Calibrated seal PAK:
		Down seal count 76
		up seal count 327 passed
		seal width count 72

HP-002 - Revision 1 - 02/15/2010

TITLE: PREPARATION OF SEDIMENT/SOIL SAMPLES BY SONICATION USING METHOD 3550 FOR SUBSEQUENT EXTRACTABLE SEMI-VOLATILES ANALYSIS

Prepared By: Mike Thomas Date: 09/96

Approved By:

Group Supervisor: Michael F. Thomas Date: 11/15/00

Operations Manager: J C Bruton Date: 10/25/00

QA Officer: Deborah J. Nadeau Date: 10·24·00

General Manager: Dennis C. Hufnagel Date: 11/16/00

Revision History:

SOP Revision	Changes	Approval Initials	Approval Date	Effective Date
01	Minor changes throughout. Clarifications to procedure section.	DN	10·24·00	10/24/00
02	Addition of compounds to Figure 2.	DN	3·28·02	3·28·02
03	Definitions added to section 1.1. Wording was added or changed to clarify sections 4, 5, 6, 7, 8 + 9. Minor changes throughout. New figures.	HRC	11.08.04	11.08.04
04	Updated Sect. 5.0 with current spike solutions prep. Removed section on medium level soil extraction. Replaced figure 3 and 4 with current LCS/MS spike components. Minor corrections to sect. 1.3, 4.24, 6.0 and 7.12. Updated logbook	LAD	04/06	04/06
05	Many changes made throughout, including but not limited to, waste information, updated spikes and surrogates, added SIM LCS/D and MS/D information, updated Table 1. Please refer to the QAM/SOP change form filed w/ SOP in QA for a detailed list of changes.	LAD	09/07	09/07

TITLE: **PREPARATION OF SEDIMENT/SOIL SAMPLES BY SONICATION USING METHOD 3550 FOR SUBSEQUENT EXTRACTABLE SEMI-VOLATILES ANALYSIS**

SOP Revision	Changes	Approval Initials	Approval Date	Effective Date
06	Updated logbook example. Added adipate compounds to fig. 2. Added necessity of recording lot numbers of consumables in logbook. Added to record the temperature of the nitrogen evaporation water bath.	LAD	07/08	07/08
07	Added requirement to add spike before Na_2SO_4. Changed N_2 water bath temperature from <39°C to <30°C. Removed respirator reference. Added KAEHS manual. Added KAS SOP CA-108 reference for additional subsampling information.	LAD	02/09	02/09
08	Removed targeting sample weights. Added KAT. SOP SD-902 reference. Updated logbook page example. Added GPC cleanup is required for all samples. Removed decanting samples	LAD	08/10	08/10

TITLE: **PREPARATION OF SEDIMENT/SOIL SAMPLES BY SONICATION USING METHOD 3550 FOR SUBSEQUENT EXTRACTABLE SEMI-VOLATILES ANALYSIS**

Please acknowledge receipt of this standard operating procedure by signing and dating both of the spaces provided. Return the bottom half of this sheet to the QA Department.

I acknowledge receipt of copy ___ of document **SOP CA-512-08**, titled **PREPARATION OF SEDIMENT/SOIL SAMPLES BY SONICATION USING METHOD 3550 FOR SUBSEQUENT EXTRACTABLE SEMI-VOLATILES ANALYSIS.**

Recipient: _____ Date: _____

KATAHDIN ANALYTICAL SERVICES, INC.
STANDARD OPERATING PROCEDURE

I acknowledge receipt of copy ___ of document **SOP CA-512-08**, titled **PREPARATION OF SEDIMENT/SOIL SAMPLES BY SONICATION USING METHOD 3550 FOR SUBSEQUENT EXTRACTABLE SEMI-VOLATILES ANALYSIS.**

Recipient: _____ Date: _____

TITLE: **PREPARATION OF SEDIMENT/SOIL SAMPLES BY SONICATION USING METHOD 3550 FOR SUBSEQUENT EXTRACTABLE SEMI-VOLATILES ANALYSIS**

1.0 SCOPE AND APPLICATION

The purpose of this SOP is to describe the procedures and requirements for the preparation of solid samples for analysis of extractable semivolatile organic compounds. This SOP is specifically applicable to EPA Method 3550B in accordance with SW-846 Method 8270, current revision.

1.1 Definitions

METHOD BLANK (laboratory reagent blank): An artificial sample designed to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus. For aqueous samples, reagent water is used as a blank matrix; for soil samples, baked organic-free sand is used as a blank matrix. The blank is taken through the appropriate steps of the process.

LABORATORY CONTROL SAMPLE (LCS): A blank that has been spiked with the analyte(s) from an independent source, and is analyzed exactly like a sample. Its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements. The matrix used should be phase matched with the samples and well characterized.

MATRIX SPIKE/MATRIX SPIKE DUPLICATE (MS/MSD): Predetermined quantities of stock solutions of certain analytes are added to a sample matrix prior to sample extraction and analysis. Samples are split into duplicates, spiked and analyzed. Percent recoveries are calculated for each of the analytes detected. The relative percent difference between the samples is calculated and used to assess analytical precision.

SURROGATES: Organic compounds which are similar to analytes of interest in chemical composition, extraction and chromatography, but which are not normally found in environmental samples. These compounds are spiked into all blanks, standards, samples and spiked samples prior to analysis. Percent recoveries are calculated for each surrogate.

1.2 Responsibilities

This method is restricted to use by, or under the supervision of analysts experienced in the extraction of samples for semivolatile analysis. Each analyst must demonstrate and document their ability to generate acceptable results with this method. Refer to Katahdin SOP QA-805, current revision, “Personnel Training”.

It is the responsibility of all Katahdin technical personnel involved in the extraction of samples for semivolatile analysis to read and understand this SOP, adhere to the procedures outlined, and to properly document their data in the appropriate lab

notebook. Any deviations from the test or irregularities with the samples should also be recorded in the lab notebook and reported to the Department Manager or designated qualified data reviewer responsible for this data.

It is the responsibility of the Department Manager to oversee that members of their group follow this SOP, to ensure that their work is properly documented and to indicate periodic review of the associated logbooks.

1.3 Safety

Users of this procedure must be cognizant of inherent laboratory hazards, proper disposal procedures for contaminated materials and appropriate segregation of hazardous wastes. The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical should be treated as a potential health hazard. A reference file of material safety data sheets is available to all personnel involved in the chemical analysis. Everyone involved with the procedure must be familiar with the MSDSs for all the materials used in this procedure.

Each qualified analyst or technician must be familiar with Katahdin Analytical Environmental Health and Safety Manual including the Katahdin Hazardous Waste Plan and must follow appropriate procedures. These include the use of appropriate personal protective equipment (PPE) such as safety glasses, gloves and lab coats when working with chemicals or near an instrument and not taking food or drink into the laboratory. Each analyst should know the location of all safety equipment. Each analyst shall receive a safety orientation from their Department Manager, or designee, appropriate for the job functions they will perform.

1.4 Waste Disposal

Wastes generated during the preparation of samples must be disposed of in accordance with the procedures described in the current revision of the Katahdin Analytical Environmental Health and Safety Manual and SOP SD-903, “Sample Disposal,” current revision. Expired standards are lab packed, placed in the Katahdin hazardous waste storage area, and disposed of in accordance with this SOP.

Any methylene chloride solvent waste generated during the rinsing of glassware etc. should be disposed of in the “D” waste stream satellite accumulation area nearest the point of generation. Acetone and methanol are considered flammable waste, and should be disposed of in the “O” waste stream satellite accumulation area nearest the point of generation. Post-extraction soil samples and sodium sulfate waste should be disposed of in the soil with organics “I” waste stream satellite accumulation area nearest the point of generation. Please refer to the current revision of SOP CA-107 for the location of satellite waste accumulation areas.

TITLE: **PREPARATION OF SEDIMENT/SOIL SAMPLES BY SONICATION USING METHOD 3550 FOR SUBSEQUENT EXTRACTABLE SEMI-VOLATILES ANALYSIS**

2.0 SUMMARY OF METHOD

An approximate, greater than 30 gram portion of sediment/soil is mixed with anhydrous powdered sodium sulfate and extracted with 1:1 methylene chloride/acetone (v/v) using an ultrasonic probe. The methylene chloride extract is dried and concentrated to a volume of 1.0 mL.

3.0 INTERFERENCES

Contaminants in solvents, reagents, glassware, and other sample processing hardware may cause method interferences such as discrete artifacts and/or elevated baselines in the total ion current profiles (TICPs). All of these materials routinely must be demonstrated to be free from interferences under the conditions of the analysis by running laboratory method blanks. Interferences caused by phthalate esters can pose a major problem in semivolatile organics analysis because many phthalates are also target analytes. Common flexible plastics contain varying amounts of phthalates that are easily extracted during laboratory operations, so cross-contamination of glassware frequently occurs when plastics are handled. Interferences from phthalates can best be minimized by avoiding the use of such plastics in the laboratory.

At no time may gloves that have not been tested for phthalates or gloves known to contain phthalates be used or stored in the organic extraction lab. Additionally, whenever possible plastic items in this lab must be replaced with metal or Teflon or other non-phthalate plastic substitute.

Special care should be taken to ensure clean glassware and apparatus are used, pre-rinsed with the appropriate solvent prior to use. Solvents should be analyzed prior to use to demonstrate that each lot is free of contaminants that may interfere with the analysis. Interferences coextracted from the samples will vary considerably from source to source. If analysis of an extracted sample is prevented due to inteferences, further cleanup of the sample extract may be needed to minimize interferences.

4.0 APPARATUS AND MATERIALS

Prior to use, all glassware must be rinsed three times with methylene chloride. Brand names and catalog numbers are included below for illustration purposes only.

4.1 Syringe - gas tight, 1.0 mL, solvent rinsed between each use.

4.2 Sonicator ultrasonic processor XL – Misonix (or equivalent) equipped with dual titanium 3/4" horn extenders for extracting two samples at a time.

4.3 Powder funnels, 100 mm diameter, 35 mm stem

4.4 Kuderna-Danish (KD) apparatus - Concentrator tube - 10 mL
Evaporative flask - 500 mL
Snyder column - 3-ball macro

4.5 Filter paper, 7.0 cm, Whatman #4

4.6 Vacuum filtration flask - 500 mL Erlenmeyer

4.7 Buchner funnel, porcelain, Coors® with 85 mm plate diameter (or equivalent)

4.8 Beakers - 400 mL

4.9 Boiling chips - approximately 12 mesh, silicon carbide (carborundum or equivalent). Soxhlet extract overnight in methylene chloride.

4.10 Water bath - eight position concentric ring bath, or equivalent, equipped with a calibrated thermometer. The bath should be used in a hood.

4.11 Balance - capable of accurately weighing ± 0.01 g.

4.12 Vials and caps – 1.8 mL with PTFE/silicone septa and 12 mL with Teflon-lined caps for extracts designated for GPC cleanup.

4.13 Filter paper, 18.5 cm, Fisherbrand or Whatman 114V (or equivalent)

4.14 Pasteur pipets - disposable, 5 ¾ ".

4.15 Nitrogen evaporation apparatus.

4.16 Muffle oven – capable of maintaining 400 °C for baking glass wool and organic-free sand.

4.17 Gel Permeation Chromatograph (GPC) - J2 Scientific AccuPrep MPS™ with internal UV detection

5.0 REAGENTS

5.1 Sodium Sulfate - anhydrous powdered and granular crystals, reagent grade, certified by the manufacturer/vendor as purified heating to 400°C prior to receipt by the laboratory. Solvent rinse immediately prior to use by rinsing three times with pesticide grade methylene chloride. (Jost Chemical anhydrous powder, catalog #2797 or equivalent, and Jost Chemical granular crystals, catalog #2796 or equivalent).

5.2 Methylene chloride, methanol, and acetone - pesticide residue analysis grade or equivalent. Methylene chloride and acetone are evaluated by lot prior to use by concentration of approximately 400 mL to 1.0 mL followed by GC/MS analysis. The lot numbers of all solvents used during an extraction must be recorded in the extraction logbook.

5.3 Organic-free sand, purified by baking at 400 °C. Method blanks serve as checks on the baked sand.

5.4 Base/Neutral and Acid (SVOA) Surrogate Spiking Solution - Surrogate standards are added to all samples and calibration solutions. Prepare a surrogate standard spiking solution that contains the following compounds at the indicated concentrations in acetone.

Compound	Conc.
phenol-$_{d6}$	100 ug/mL
2,4,6-tribromophenol	100 ug/mL
2-fluorophenol	100 ug/mL
nitrobenzene-$_{d5}$	50 ug/mL
p-terphenyl-$_{d14}$	50 ug/mL
2-fluorobiphenyl	50 ug/mL

Store the spiking solution at -10°C to -20°C in Teflon-sealed containers. These solutions must be replaced after six months or sooner if comparison with quality control check samples indicates a problem. If reanalysis of a method blank still indicates surrogates out of criteria, a new surrogate solution must be used.

5.5 SIM Surrogate Spiking Solution- Surrogate Standards are added to all samples and calibration solutions. Prepare a surrogate solution that contains the following compounds at a concentration of 2 ug/mL in acetone.

Compound	Conc. ug/mL
Fluorene-d10	2.0 ug/mL
2-Methylnaphthalene-d10	2.0 ug/mL
Pyrene-d10.	2.0 ug/mL
2,4-Dibromophenol	2.0 ug/mL

Store the spiking solution at -10°C to -20°C in Teflon-sealed containers. These solutions must be replaced after six months, or sooner if comparison with quality control check samples indicates a problem. If reanalysis of a method blank still indicates surrogates out of criteria, a new surrogate solution must be used.

5.6 Base/Neutral and Acid (SVOA) Matrix Spike/Lab Control Sample Spiking Solution - Prepare a spiking solution in methanol that contains the compounds listed in Figure 2 at a concentration of 50 ug/mL for base/neutrals and 100 ug/mL for acids. Store the

spiking solution at -10°C to -20°C in Teflon-sealed containers. These solutions must be replaced after six months, or sooner if comparison with quality control check samples indicates a problem.

5.7 Base/Neutral and Acid (SVOA APPENDIX IX) Matrix Spike/Lab Control Sample Spiking Solution. Prepare a spiking solution in methanol that contains the compounds listed in Figure 3 at a concentration of 100 µg/mL for each compound. Store the spiking solution at -10°C to -20°C in Teflon-sealed containers. These solutions must be replaced after six months, or sooner if comparison with quality control check samples indicates a problem

5.8 Base/Neutral (SIM) Matrix Spike/ Lab Control Sample Spike Solution for SIM-SVOA. Prepare a spiking solution in methanol that contains the compounds listed in Figure 2 at a concentration of 2 ug/mL for base/neutral. Take out 1.0 mL of Base/Neutral and Acid Matrix Spike/Lab Control Spiking Solution for SVOA and dilute it to 25.0 mL in methanol. Store the solution Spiking at -10°C to -20°C in Teflon-sealed containers. These solutions must be replaced after six months, or sooner if comparison with quality control check samples indicates a problem.

6.0 SAMPLE COLLECTION, PRESERVATION AND HANDLING

Sediment/soil samples must be collected in a soil jar and must be maintained at 4°C (±2°C).

Holding time for extraction of sediment/soil samples for Method 3550 is 14 days from date of sample collection, although the analyst should be aware that actual holding times employed may be project/program specific.

Store all extracts at 4°C (±2°C) in the dark in labeled Teflon-sealed containers. See SOP SD-902, "Sample Receipt and Internal Control," current revision, for storage areas and temperature maintenance procedures.

7.0 PROCEDURES

The following information must be recorded in the extraction logbook.

- Extraction method
- Surrogate and spike IDs
- Lot numbers of all solvents, acids and bases, sodium sulfate, filter paper
- Nitrogen evaporation water bath temperature
- pH if appicable
- Sonicator horns tuned
- Extraction and Concentration dates

- Extraction and Concentration analyst
- Sample ID or QC sample ID
- Initial and final volumes or weight
- Surrogate and spike amounts
- Final extract tray location
- Any comments regarding the sample extraction (ie. Emulsion)

All solid samples should be cleaned using gel permeation chromatography (GPC) to reduce matrix interferences.

The organic department manager should be consulted to determine if a particular sample should be subjected to further cleanup procedures; the decision should consider sample history, sample appearance, and project/client needs.

Samples need to be “swiped” out when removing and “swiped” in when replacing samples in storage locations to maintain the internal chain of custody. Refer to Katahdin SOP, Sample Receipt and Internal Control, current revision, for the proper procedure for removal and return samples. Fill out the sample preparation/extraction log with the necessary information before starting the extraction. Prerinse all glassware three times with methylene chloride.

7.1 Do not decant any water layer on a sediment sample. Mix with a stainless steel spatula to ensure homogeneity of the sample. If the sample container is full to the extent that stirring the sample is impractical, try to remove the “best representative” aliquot from the jar based on color, particle size, moisture, etc. Remove any foreign objects such as sticks, leaves, and rocks, and note actions taken in the appropriate extraction logbook. Please refer to the current revision of Katahdin Analytical Services SOP CA-108, “Basic Laboratory Technique “, for more detailed guidance on subsampling to ensure reproducibility.

7.2 The following steps should be performed <u>rapidly</u> <u>to</u> <u>avoid</u> <u>loss</u> <u>of the</u> <u>more</u> <u>volatile</u> <u>extractable</u>. Weigh out an approximate, greater than 30g portion of sample into a labeled 400-mL beaker. Record sample weight to the nearest 0.01 g in appropriate extraction logbook. Add between 30 g and 60 g of anhydrous powdered sodium sulfate as required for producing a “free-flowing” mixture. The amount of sodium sulfate added will depend upon the moisture content of the sample (e.g., low moisture content will require less sodium sulfate). Mix well with a spatula. Keep the spatula in the sample beaker and <u>cover</u> the beaker with aluminum foil.

7.3 A method blank must be prepared with each extraction batch, not to exceed 20 client samples. To prepare a method blank, weigh out one, greater than 30 g portion of purified sand in a labeled 400 mL beaker. Refer to sections 7.7 and 7.7 for spike and surrogate addition instructions. Add 60 g sodium sulfate and mix well. Although a “free-flowing” mixture can be achieved with less than 60 g sodium

sulfate, the method blank must contain 60 g in order to evaluate the sodium sulfate as a potential source of contamination.

7.4 A laboratory control sample (LCS) must be prepared with each extraction batch, not to exceed 20 client samples. To prepare LCS, weigh out one 30 g portion of purified sand in a labeled 400 mL beaker. Refer to sections 7.7 and 7.7 for spike and surrogate addition instructions. Add 30 g sodium sulfate and mix well. If combined SIM-SVOA analysis is requested, a separate LCS must be prepared for each analysis. If an MS/MSD pair is not extracted on a particular day, an LCS/LCSD pair may be required in order to meet client-specific or program-specific requirements. This information will be disseminated from the project manager or Department Manager.

7.5 A matrix spike/matrix spike duplicate (MS/MSD) set must be prepared for every 20 samples. To prepare MS/MSD, weigh out two approximate, greater than 30 g portions of the sample designated for MS/MSD into each of two labeled 400 mL beakers. Record sample weights to nearest 0.01 g in appropriate extraction logbook. Refer to sections 7.7 and 7.7 for spike and surrogate addition instructions. Add 30 - 60 g sodium sulfate to each to produce a free-flowing mixture, and mix well. If combined SIM-SVOA analysis is requested, a separate MS/MSD must be prepared for each analysis.

7.6 To all samples, method blank, LCS/LCSD, and MS/MSD add 1.0 mL of the appropriate base/neutral and acid surrogate spiking solution listed below using the pre-rinsed 1.0 mL gas tight syringe. The surrogate spike should be added **prior** to the addition of the sodium sulfate. Record surrogate spike volume and identification code in extraction logbook. Thoroughly rinse syringe with solvent prior to using it for another spiking solution.

7.6.1 If the request is for SVOA or SVOA Appendix IX, use the SVOA surrogate solution (sect. 5.4).

7.6.2 If the request is for SIM, use the SIM surrogate solution (sect. 5.5).

7.6.3 If the request is for SIM-SVOA, use both the SIM and SVOA surrogate solutions. NOTE: Separate LCS/LCSD and/or MS/MSD are needed for each analysis and should be spiked with the appropriate surrogate.

7.7 To the LCS/LCSD and the MS/MSD add 1.0 mL of the appropriate base/neutral and acid (SVOA) matrix spike/LCS spiking solution listed below using a 1.0 mL gas tight syringe. The LCS/MS spike should be added **prior** to the addition of the sodium sulfate. Record the matrix spike/LCS spiking solution volume and identification code in extraction logbook. Thoroughly rinse the syringe with solvent when spiking is completed.

7.7.1 If the request is for SVOA, add 1 mL of SVOA Spiking Solution (sect 5.6).

7.7.2 If the request is for SIM, add 1 mL SIM Spiking solution (sect 5.8).

7.7.3 If the request is for SVOA and SIM, add 1mL of SVOA Spiking Solution and 1 mL SIM Spiking solution (sect 5.6 and 5.8).

7.7.4 If the request is for SVOA Appendix IX, add 1mL of SVOA Spiking Solution and 1 mL of SVOA Appendix IX Spiking solution (sect 5.6 and 5.7).

7.8 To assure optimum operation and maximum energy output, the sonicators must be tuned daily prior to extracting samples. The following tuning procedure must be performed with the sonicator probes vibrating in air.

7.8.1 Turn OUTPUT CONTROL knob counter-clockwise to zero. This automatically switches the duty cycle to continuous mode.

7.8.2 Press and hold down the power switch to on.

7.8.3 Press and hold down the TUNE switch. Check if the counter is less or equal to 20%; otherwise, rotate the Tuning Knob (tuning button) clockwise until a reading of 20%or less is obtained.

7.8.4 Release the TUNE switch.

7.8.5 Turn OUTPUT CONTROL KNOB counter-clockwise to 50 and the power switch off.

7.8.6 Confirm that the sonicators were tuned by recording the date and/or percent in the extractions logbook.

7.9 Prior to extracting any samples, ensure that the sonicator probes are decontaminated by rinsing three times with a methylene chloride wash bottle. Collect the waste in a waste beaker. It may sometimes be necessary to wipe the upper part of each probe with a methylene chloride dampened KimWipe. Repeat this decontamination step between each sample on each probe.

7.10 To the mixed and spiked blank and LCS, add 100 mL of the 1:1 methylene chloride/acetone (V/V) solution and proceed with steps 7.11 through 7.14. Record the lot numbers of the solvents in the extraction logbook.

7.11 It may be necessary at this time to stir the sample/sodium sulfate mixture with the spatula to loosen up the mixture prior to extracting. Rinse the spatula with methylene chloride and collect the rinsing into a correspondent beaker. Position the beaker in the ultrasonic cell disruptor so that the bottom surface of the tip of the 3/4

inch disruptor horn is about halfway below the surface of the solvent and above the sediment layer.

7.12 Sonicate for 3 minutes with the output control knob set at 10, and mode switch on "pulsed" and % duty cycle knob set at 50%. While the mixture is sonicating, one should be able to see all, or most of the material, moving in the beaker under the influence of the energized probes. If not, stir the mixture again.

7.13 Prepare a filter flask fitted with a Buchner funnel. The Buchner funnel should contain a 7.0 cm Whatman #4 filter. Prerinse the flask, funnel and filter with methylene chloride and discard rinsings into solvent waste container. Decant extract into the filter flask and Buchner funnel. A vacuum pump may be used to facilitate filtration or the extract may be gravity filtered. The lot number of the filter paper must be written ti the extraction logbook.

7.14 Repeat the extraction two more times (sec 7.11 – 7.14) using 100 mL portions of 1:1 methylene chloride: acetone. Before each extraction, make certain that the sodium sulfate is still free-flowing and not a consolidated mass. As required, break up large lumps with the spatula. Decant the extraction solvent into the Buchner funnel after each sonication. On the final sonication, pour the entire sample contents into the Buchner funnel and rinse thoroughly with methylene chloride to complete the quantitative transfer of the extract. Use the vacuum pump to pull all the extract into the flask

CONCENTRATION OF LOW LEVEL EXTRACTS

7.15 Rinse the K-D glassware (flask, concentration tube, and Snyder column, including the ground glass joints on the flask and columns) three times with methylene chloride before assembling. Add two boiling chips to the K-D. Insert fluted 18.5 cm filter papers into short stem powder funnels and add ~ 2 inches of sodium sulfate crystals. Rinse the sodium sulfate in the assembled funnels with ~20-30 mLs of methylene chloride. Place the assembled K-D's under the funnels. The lot number of the filter paper must be written ti the extraction logbook.

7.16 Transfer the extracts to the K-D concentrator setups through the sodium sulfate in the funnels. This is the drying step, which is required to remove residual water from the extracts. Any large water layers must be removed by other means, prior to pouring through the sodium sulfate. After pouring all of the extract volume through the sodium sulfate, rinse the extract flask three times with ~ 2 – 3 mls of methylene chloride. Add the rinsings through the sodium sulfate to complete a quantitative transfer. Rinse the sodium sulfate with ~ 15 mls of methylene chloride and allow to drain.

7.17 If samples are to be GPC'd, refer to the current revision of Katahdin SOP CA-513, Extract Cleanup Using Gel Permeation Chromatography, for appropriate concentrating procedures.

7.18 If samples are not to be GPC'd, follow Steps 7.19 through 7.24 to concentrate extracts to final volume of 1 mL. Otherwise proceed to GPC cleanup procedure as described in the current revision of Katahdin SOP CA-513.

7.19 Transfer the labels from the extract flasks to the K-Ds. Remove the funnel and attach a 3-ball macro Snyder column. Pre-wet the Snyder column with 1 mL of methylene chloride.

7.20 Place the K-D in a hot water bath (75-85°C). Gently swirl K-D in the water until boiling begins. At the proper distillation rate, the Snyder balls should chatter but the chambers should not flood with condensed solvent. The K-D should be kept in a vertical orientation while on the bath. When the apparent volume in the concentrator tube reaches ≈ 6 mL, remove the K-D from the water bath. **Do not allow the evaporator to go dry. If the sample extract does go dry, re-extraction must occur immediately.** Allow the K-D to cool for 10 minutes. Rinse the Snyder column lower joint with ≈ 1 mL of methylene chloride. Remove the Snyder column. Wipe off any water from the neck above the lower joint of the flask. Separate the K-D flask from the concentrator tube, rinsing the ground glass joint with ≈ 1 mL methylene chloride.

7.21 Reduce the extract in the concentrator tube to approximately 1 mL using the nitrogen blow-down apparatus. The bath temperature must be < 30°C. Turn the gas to 3 psi. Be careful not to splash the extract out of the tube. During concentration on the N-evap, the internal wall of the concentrator tube and the N-evap sparging pipet must be rinsed down at least once or twice with ≈1 mL of methylene chloride. The solvent level in the concentrator tube must be positioned below the level of the water bath as much as possible to prevent water from condensing into the sample extract. As the extract volume is reduced, lower the N_2 sparging pipet closer to the surface of the extract to expedite the concentration. Record the temperature of the water in the nitrogen evaporation water bath in the logbook also note any problems or extract losses, if they occur, in the extractions logbook.

7.22 When the apparent volume reaches slightly less than 1 mL, remove the concentrator tube and allow it to cool.

7.23 Complete the quantitative transfer of the extract to a 1.8 mL vial by using methylene chloride. Adjust the volume of the methylene chloride extract to 1.0 mL using the 1.8 mL reference vial for volume comparison.

7.24 Label the vial with lab sample number, extraction date, matrix and analysis. Store extract vials at a temperature of 4 ± 2 °C until ready for analysis. Indicate in the extraction logbook the box number and "tray location" of the individual extract vials.

8.0 QUALITY CONTROL AND ACCEPTANCE CRITERIA

A method blank must be extracted for each and every item listed below:

- Each sample matrix
- Each extraction method or level
- Every extraction batch of twenty or fewer samples

A laboratory control sample (LCS) is required for each and every item listed below:

- Each sample matrix
- Each extraction method or level
- Every extraction batch of twenty or fewer samples

Refer to the current revision of the applicable Katahdin SOP for analysis of Semivolatile Organics for quality control acceptance criteria.

Each extractions analyst must demonstrate proficiency in performing the extractions that prepare samples for analysis. Demonstration consists of preparation (extraction), by the analyst, of at least four aliquots which are then analyzed according to the analytical method in question. These QC samples must meet all quality control acceptance limits. Demonstration must be documented by use of a form which summarizes the results of the analysis of these aliquots, calculated percent recoveries, and standard deviation. Demonstration of proficiency must be done one time per analyst initially and then annually thereafter. Refer to SOPs QA-805 and QA-807, current revision.

If, upon analysis of the extracted samples, it is discovered that quality control acceptance criteria have not been met, all associated samples must be evaluated against all the QC. In some cases data may be reported, perhaps with narration, while in other cases, other corrective action may be taken. The corrective actions may include re-extraction of the samples associated with the quality control sample that did not meet acceptance criteria, or may include making new reagents and standards if the standardization is suspect. These decisions are based on holding time considerations, client and project specific Data Quality Objectives and on review of chromatograms. The supervisor, Operations Manager, and/or Quality Assurance Officer may be consulted to evaluate data. Some samples may not be able to be reanalyzed within hold time. In these cases "qualified" data with narration may be advisable after consultation with the client.

Much of the work performed at the lab is analyzed in accordance with specific QC requirements spelled out in a project specific Quality Assurance Project Plan (QAPP) or in a program specific Quality Systems Manual (QSM). The reporting limits, acceptance criteria and/or corrective actions may be different than those specified in this SOP. In these cases the appropriate information will be communicated to the Department Manager and/or senior chemists before initiation of the analyses so that specific product codes can be produced for the project. In addition, the work order notes for each project will describe the specific QAPP or QSM to be followed.

9.0 METHOD PERFORMANCE

The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. The MDLs are determined per type of instrument and filed with the Organic Department Manager and with the QAO. Refer to the current revision of Katahdin SOP QA-806, Method Detection Limit, Instrument Detection Limit and Reporting Limit Studies and Verifications, for procedures on determining the MDL.

Refer to the applicable analytical SOP for other method performance parameters and requirements.

10.0 APPLICABLE DOCUMENTS/REFERENCES

Test Methods for Evaluating Solid Waste-Physical/Chemical Methods, Method 3550C, USEPA SW-846, Third Edition, Update IV, February 2007.

Department of Defense Quality Systems Manual for Environmental Laboratories (DOD QSM), Version 4.1, 04/22/09.

The National Environmental Laboratory Accreditation Conference (NELAC) Standards, June 2003.

Katahdin SOP QA-806, Method Detection Limit, Instrument Detection Limit and Reporting Limit Studies and Verifications, current revision.

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Figure 2 LCS/Matrix Spike Component List
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TITLE: **PREPARATION OF SEDIMENT/SOIL SAMPLES BY SONICATION USING METHOD 3550 FOR SUBSEQUENT EXTRACTABLE SEMI-VOLATILES ANALYSIS**

TABLE 1

SUMMARY OF METHOD MODIFICATIONS

TOPIC	KATAHDIN SOP CA-512-08	METHOD 3550, current revision
Apparatus/Materials	1) short stem funnels	1) drying columns
Reagents		
Sample preservation/ handling		
Procedures	1) extract dried using Na_2SO_4 in short stem funnels 2) place sonicator horns ½ way between the surface of the solvent and the sediment layer 3) no apparatus height specification for concentration on water bath 4) water bath at 75-85 deg C 5) sample removed from water bath when volume reaches ~6 mL	1) extract dried using Na_2SO_4 in drying columns 2) place sonicator horns ½ inch below the solvent surface but above sediment layer 3) partially immerse concentrator tube in water and lower apparatus to complete concentration in 10-15min 4) water bath at 80-90 deg C 5) sample removed from water bath when volume reaches 1-2 mL
QC - Spikes	1) Acid surrogate and spike components at 100 ug/mL; base/neutral surrogate and spike components at 50 ug/mL	1) Acid surrogate and spike components at 200 ug/mL; base/neutral surrogate and spike components at 100 ug/mL
QC - LCS	1) Acid surrogate and spike components at 100 ug/mL; base/neutral surrogate and spike components at 50 ug/mL	1) Acid surrogate and spike components at 200 ug/mL; base/neutral surrogate and spike components at 100 ug/mL
QC - Accuracy/Precision		
QC - MDL		

TITLE: **PREPARATION OF SEDIMENT/SOIL SAMPLES BY SONICATION USING METHOD 3550 FOR SUBSEQUENT EXTRACTABLE SEMI-VOLATILES ANALYSIS**

FIGURE 1

EXAMPLE OF LOGBOOK PAGE

EX-008 - Revision 1 - 12/20/2009

SV
SOW

KATAHDIN ANALYTICAL SERVICES, INC.
ORGANIC EXTRACTIONS LOG - SOIL SEMIVOLATILE

Extraction Method: (check one)	SW846 3550 (SONIC.) ✓	SW846 3540 (SOX)	SW846 3545 (ASE)
	SW846 3580 (OIL / WIPES)	OTHER	
Analytical Method: (check one)	SW846 8270 ✓	OTHER	
Standards	Surrogate ID (1): SV2401	Spike ID (1): SV2399	Spike ID (3):
	Surrogate ID (2):	Spike ID (2):	
Solvents / Chemicals / Consumables	Solvent Lot # (Mecl2): J22E10	Solvent Lot # (Acetone): H26E28	Sodium Sulfate (granular) Lot # 2796002
	Filter Paper Lot # (SON) R1558982	Filter Paper Lot # (KD) F6000494	Sodium Sulfate (powder) Lot # 2797001
Misc.	Nitrogen Bath Temperature: 37C	Sonicator Horns Tuned: ✓ 20%	Balance ID: Mettler 6140

Start: 9:55 End: 12:00

QAEX183

Ext. Date	Ext. Init.	Sample ID	Initial Weight (g)	Surr. Vol. (mL)	Spk. Vol. (mL)	Fraction SOX	Fraction SE	Pre-GPC Date Conc.	Pre-GPC Conc. Init.	Pre-GPC Final Vol. (mL)	Post-GPC Date Conc.	Post-GPC Conc. Init.	Post-GPC Final Vol. (mL)	Tray Loc. (SVOC)	Comments
7/29/10	WS	WW30267-1	29.98	1mL	NR	✓		7/29/10	KF	5mL	7/30/10	WS	1mL	C9	R133081
↓	↓	↓ -2	29.98	↓	1mL	↓		↓	↓	↓	↓	↓	↓	C10	
↓	↓	↓ -3	29.97	↓	↓	↓		↓	↓	↓	↓	↓	↓	D1	
↓		GPC Blank									↓	↓	↓	E2	
															WS 7/30/10

0000147

EX-008 - Revision 1 - 12/20/2009

QAEX183

Ext. Date	Ext. Init.	Sample ID	Initial Weight (g)	Surr. Vol. (mL)	Spk. Vol. (mL)	Fraction SOX	Fraction SE	Pre-GPC Date Conc.	Pre-GPC Conc. Init.	Pre-GPC Final Vol. (mL)	Post-GPC Date Conc.	Post-GPC Conc. Init.	Post-GPC Final Vol. (mL)	Tray Loc. (SVOC)	Comments
7/29/10	WS	SO4560-1	31.65	1mL	NR	✓		7/29/10	KF	5mL	7/30/10	WS	1mL	D2	
↓	↓	↓ -2	31.44	↓	↓	↓		↓	↓	↓	↓	↓	↓	D3	
↓	↓	↓ -3	31.81	↓	↓	↓		↓	↓	↓	↓	↓	↓	D4	
↓	↓	↓ -4	32.35	↓	↓	↓		↓	↓	↓	↓	↓	↓	D5	
		SO4481-1	30.00											D6	
		SO4581-1	31.25											D7	
		↓ -2	30.48											D8	
		↓ -3	33.15											D9	
		↓ -4	30.70											D10	
↓	↓	↓ -5	30.79	↓	↓	↓		↓	↓	↓	↓	↓	↓	E1	
															WS 7/30/10

0000148

Reviewed By_____ Date_____

TITLE: **PREPARATION OF SEDIMENT/SOIL SAMPLES BY SONICATION USING METHOD 3550 FOR SUBSEQUENT EXTRACTABLE SEMI-VOLATILES ANALYSIS**

FIGURE 2

LCS/MATRIX SPIKE COMPONENT LIST

BASE/NEUTRALS	
1-Methylnaphthalene	Bis (2-chloroethoxy) methane
1,1-Biphenyl	Bis (2-chloroethyl) ether
1,2,4-Trichlorobenzene	Bis (2-Chloroisopropyl) ether)
1,2-Dichlorobenzene	Bis (2-ethylhexyl) adipate
1,3-Dichlorobenzene	Bis (2-ethylhexyl) phthalate
1,4-Dichlorobenzene	Butylbenzyl phthalate
1,4-Dioxane	Caprolactam
2,4-Dinitrotoluene	Carbazole
2,6-Dinitrotoluene	Chrysene
2-Chloronaphthalene	Dibenz (a, h) anthracene
2-Methylnaphthalene	Dibenzofuran
2-Nitroaniline	Diethyl adipate
3,3'-Dichlorobenzidine	Diethyl phthalate
3-Nitroaniline	Dimethyl phthalate
4-Bromophenylphenyl ether	Di-n-butylphthalate
4-Chloroaniline	Di-n-octyl phthalate
4-Chlorophenylphenyl ether	Fluoranthene
4-Nitroaniline	Fluorene
Acenaphthene	Hexachlorobenzene
Acenaphthylene	Hexachlorobutadiene
Acetophenone	Hexachlorocyclopentadiene
Aniline	Hexachloroethane
Anthracene	Indeno (1,2,3-cd) pyrene
Atrazine	Isophorone
Azobenzene	Naphthalene
Benzaldehyde	Nitrobenzene
Benzidine	N-Nitrosodimethylamine
Benzo (a) Anthracene	N-Nitroso-di-n-propylamine
Benzo (a) pyrene	N-Nitrosodiphenylamine
Benzo (b) fluoranthene	Phenanthrene
Benzo (ghi) perylene	p-toluidine
Benzo (k) fluoranthene	Pyrene
Benzyl alcohol	Pyridine

ACIDS		
2, 3, 4, 6-Tetrachlorophenol	2-Chlorophenol	Benzoic acid
2,4,5-Trichlorophenol	2-Methylphenol	Ethyl methanesulfonate
2,4,6-Trichlorophenol	2-Nitrophenol	Methyl methanesulfonate
2,4-Dichlorophenol	4,6-Dinitro-2-methylphenol	Pentachlorophenol
2,4-Dimethylphenol	4-Chloro-3-methylphenol	Phenol
2,4-Dinitrophenol	4-Methylphenol	
2,6-Dichlorophenol	4-Nitrophenol	

TITLE: **PREPARATION OF SEDIMENT/SOIL SAMPLES BY SONICATION USING METHOD 3550 FOR SUBSEQUENT EXTRACTABLE SEMI-VOLATILES ANALYSIS**

FIGURE 3

APPENDIX IX LCS/MATRIX SPIKE COMPONENT LIST

1,2,4,5-Tetrachlorobenzene	Hexachloropropene
1,3,5-Trinitrobenzene	Isodrin
1,4-Naphthoquinone	Isosafrole
1-Chloronaphthalene	Kepone
1-Naphthylamine	m-Dinitrobenzene
2,4-D	Methapyrilene
2-Acetyl aminofluorene	Methyl parathion
2-Naphthylamine	n-Nitrosodiethylamine
2-Picoline	n-Nitrosodi-n-butylamine
3,3-Dimethylbenzidine	n-Nitrosomethylethylamine
3-Methylcholanthrene	n-Nitrosomorpholine
4-Aminobiphenyl	n-Nitrosopyrrolidine
4-Nitroquinoline-1-oxide	n-Nitrotrosopiperidine
5-Nitro-o-toluidine	O,O,O-Triethyl phosphorothioate
7,12-Dimethylbenz(a)anthracene	o-Toluidine
a,a-Dimethylphenethylamine	Parathion
Acetophenone	p-Dimethylaminoazobenzene
Aramite	Pentachlorobenzene
Chlorobenzilate	Pentachloronitriobenzene
Diallate	Phenacetin
Dibenz(a,j)acridine	Phorate
Dimethoate	p-Phenylenediamine
Dinoseb	Pronamide
Diphenylamine	Safrole
Disulfoton	Silvex (2,4,5-TP)
Famphur	Sulfotep
Hexachlorophene	Thionazin

KATAHDIN ANALYTICAL SERVICES, INC.
STANDARD OPERATING PROCEDURE

SOP Number: CA-515
Revision History
Cover Page
Page 1

TITLE: PREPARATION OF AQUEOUS SAMPLES FOR PESTICIDES/PCBs ANALYSIS

Prepared By: Mike Thomas Date: 8/96

Approved By:

Group Supervisor: Michael F. Thomas Date: 11/15/00

Operations Manager: JCBurton Date: 10/25/00

QA Officer: Deborah J. Nadeau Date: 10·23·00

General Manager: Dennis F. Hulgan Date: 11/16/00

Revision History:

SOP Revision	Changes	Approval Initials	Approval Date	Effective Date
01	Minor changes throughout. Clarifications to procedure section.	DN	10·23·00	
02	Addition of SPE Procedure. Minor changes through out Added wording to Sections 6 and 8	LAD	013105	013105
03	Added separate QC for Pest. and PCB. Updated concentration procedure to reflect current practices. Changes in wording for clarification. Update Logbook page	LAD	04/06	04/06
04	Added waste generated and disposal info. Added missing definitions. Updated SPE extraction procedure. Updated Table 1 and 2. Added Table 3.	LAD	09/07	09/07
05	Updated logbook example. Added logbook requirements	LAD	09/08	09/08

TITLE: PREPARATION OF AQUEOUS SAMPLES FOR PESTICIDES/PCBs ANALYSIS

Revision History:

SOP Revision	Changes	Approval Initials	Approval Date	Effective Date
06	Added information for determining initial volume. Added reference to CA-108. Added clarification for LCS/D and MS/D sets for PEST/PCB analysis. Minor changes to reflect current techniques.	LAD	10/09	10/09
07	Added additional solvent exchange procedure. Updated logbook example.	LAD	08/10	08/10

TITLE: PREPARATION OF AQUEOUS SAMPLES FOR PESTICIDES/PCBs ANALYSIS

Please acknowledge receipt of this standard operating procedure by signing and dating both of the spaces provided. Return the bottom half of this sheet to the QA Department.

I acknowledge receipt of copy _____ of document **SOP CA-515-07,** titled **PREPARATION OF AQUEOUS SAMPLES FOR PESTICIDES/PCBs ANALYSIS**.

Recipient: _____Date:_____

KATAHDIN ANALYTICAL SERVICES, INC.
STANDARD OPERATING PROCEDURE

I acknowledge receipt of copy _____ of document **SOP CA-515-07,** titled **PREPARATION OF AQUEOUS SAMPLES FOR PESTICIDES/PCBs ANALYSIS**.

Recipient: _____Date:_____

1.0 SCOPE AND APPLICATION

The purpose of this SOP is to describe the procedures utilized by Katahdin Analytical Services, Inc. laboratory personnel for the preparation of aqueous samples prior to analysis for pesticides/PCBs by GC/ECD. It includes extraction of water samples by separatory funnel, continuous liquid-liquid, and solid phase extraction methods (EPA Methods 3510, 3520, 3535A, and EPA Method 608 current revisions).

1.1 Definitions

METHOD BLANK (laboratory reagent blank): An artificial sample designed to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus. For aqueous samples, reagent water is used as a blank matrix; for soil samples, baked organic-free sand is used as a blank matrix. The blank is taken through the appropriate steps of the process.

LABORATORY CONTROL SAMPLE (LCS): A blank that has been spiked with the analyte(s) from an independent source, and is analyzed exactly like a sample. Its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements. The matrix used should be phase matched with the samples and well characterized.

MATRIX SPIKE/MATRIX SPIKE DUPLICATE (MS/MSD): Predetermined quantities of stock solutions of certain analytes are added to a sample matrix prior to sample extraction and analysis. Samples are split into duplicates, spiked and analyzed. Percent recoveries are calculated for each of the analytes detected. The relative percent difference between the samples is calculated and used to assess analytical precision.

SURROGATES: Organic compounds which are similar to analytes of interest in chemical composition, extraction and chromatography, but which are not normally found in environmental samples. These compounds are spiked into all blanks, standards, samples and spiked samples prior to analysis. Percent recoveries are calculated for each surrogate.

1.2 Responsibilities

This method is restricted to use by, or under the supervision of, analysts experienced in the extraction of aqueous samples for pesticides/PCBs analysis. Each analyst must demonstrate the ability to generate acceptable results with this method. Refer to Katahdin SOP QA-805, current revision, “Personnel Training”.

It is the responsibility of all Katahdin personnel involved in the preparation of aqueous samples for pesticides/PCBs analysis to read and understand this SOP, adhere to the procedures outlined, and to properly document their data in the appropriate lab notebook. Any deviations from the test or irregularities with the

samples should also be recorded in the lab notebook and reported to the Department Manager or designated qualified data reviewer responsible for the data.

It is the responsibility of the Supervisor to oversee that members of their group follow this SOP, that their work is properly documented and to initiate periodic review of the associated logbooks.

1.3 Safety

Users of this procedure must be cognizant of inherent laboratory hazards, proper disposal procedures for contaminated materials and appropriate segregation of hazardous wastes. The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical should be treated as a potential health hazard. A reference file of material safety data sheets is available to all personnel involved in the chemical analysis. Everyone involved with the procedure must be familiar with the MSDSs for all the materials used in this procedure.

Each qualified analyst or technician must be familiar with Katahdin Analytical Health and Safety Manual including the Katahdin Hazardous Waste Management Plan and must follow appropriate procedures. These include the use of appropriate personal protective equipment (PPE) such as safety glasses, gloves and lab coats when working with chemicals or near an instrument and not taking food or drink into the laboratory. Each analyst should know the location of all safety equipment. Each analyst shall receive a safety orientation from their supervisor, or designee, appropriate for the job functions they will perform.

1.4 Waste Disposal

Wastes generated during the preparation of samples must be disposed of in accordance with the procedures described in the current revision of the Katahdin Hazardous Waste Management Plan and Safety Manual and SOP SD-903, “Sample Disposal,” current revision. Expired standards are lab packed, placed in the Katahdin hazardous waste storage area, and disposed of in accordance with this SOP.

Any methylene chloride solvent waste generated during the rinsing of glassware etc. should be disposed of in the “D” waste stream satellite accumulation area nearest the point of generation. This includes the methylene chloride waste layer generated during CLLE extraction. Special care should be taken to pour this layer off into the appropriate waste stream, leaving the sample waste to be disposed of as follows. Since Pesticide/PCB samples are at a neutral pH, SEP funnel or CLLE sample waste may be dumped into either the “N-Hi” or “N-low” satellite accumulation area. Acetone and hexane are considered flammable waste, and should be disposed of in the “O” waste stream satellite accumulation area nearest the point of generation. Acid waste generated during the cleanup of PCB samples should be disposed of in the “O” satellite accumulation area nearest the point of generation. Please refer to

the current revision of SOP CA-107 for the location of satellite waste accumulation areas

2.0 SUMMARY OF METHOD

Pesticides/PCBs are extracted from aqueous samples using methylene chloride and separatory funnel, continuous liquid-liquid apparatus or Automated Extractor System (SPE), following EPA Methods 3510, 3520, 3535A and EPA Method 608. The methylene chloride is exchanged with hexane for the final extract. Method detection limit studies must be performed annually for pesticides/PCBs using all extraction methods, if the extraction lab wishes to use either or all techniques. Method 3510 (separatory funnel) is generally preferred for pesticides/PCBs since organochlorine pesticides may dechlorinate if under elevated pH conditions for an extended period of time. (Section 3.2, Method 3510B, Rev. 2, 9/94)

3.0 INTERFERENCES

Solvents, reagents, glassware, and other sample preparation apparatus may yield interferences to GC analysis due to the presence of contaminants. These contaminants can lead to discrete artifacts or elevated baselines in chromatograms. Routinely, all of these materials must be demonstrated to be free from interferences under the conditions of the analysis by running reagent blanks. Interferences caused by phthalate esters can pose a major problem in pesticide analysis. Common flexible plastics contain varying amounts of phthalates which are easily extracted during laboratory operations, so cross-contamination of glassware frequently occurs when plastics are handled. Interferences from phthalates can best be minimized by avoiding the use of such plastics in the laboratory. At no time may gloves which have not been tested for phthalates or gloves known to contain phthalates be used or stored in the organic extraction lab. Additionally, whenever possible plastic items in this lab must be replaced with metal or Teflon or other non-phthalate plastic substitute.

Special care should be taken to ensure clean glassware and apparatus are used, pre-rinsed with the appropriate solvent prior to use. Solvents should be analyzed prior to use to demonstrate that each lot is free of contaminants that may interfere with the analysis.

Interferences coextracted from the samples will vary considerably from source to source. If analysis of an extracted sample is prevented due to inteferences, further cleanup of the sample extract may be needed to minimize interferences.

4.0 APPARATUS AND MATERIALS

Prior to use, all glassware must be rinsed three times with the solvent to be used for extraction.

4.1 Separatory Funnel - 2000 mL capacity, Nalgene Teflon FEP separatory funnels with Nalgene Tefzel® screw-cap closures (or equivalent)

4.2 Concentrator tube - 10 mL, graduated

4.3 Evaporative flask - Kuderna-Danish, 500 mL capacity attached to concentrator with neck clips

4.4 Snyder column - Kuderna-Danish, three ball macro

4.5 Graduated cylinders - 100 mL, 1000 mL, or 2000 mL

4.6 Short Stem Funnels

4.7 250 mL amber collection bottles with Teflon-lined caps

4.8 12 mL and/or 16 mL glass vials with Teflon-lined caps

4.9 Continuous liquid-liquid extractors (CLLE) including body, 500 mL flat bottom boiling flask and Alhin condensers

4.10 Filter paper, 18.5 cm, Fisherbrand or Whatman 114V (or equivalent)

4.11 Nitrogen evaporation apparatus.

4.12 Boiling chips - approximately 10/40 mesh, Teflon or selenized carborundum, 12 mesh (or equivalent). Cleaned by Soxhlet.

4.13 Water bath - eight position concentric ring bath or equivalent, equipped with a calibrated thermometer.

4.14 Vials, 60 mL with PTFE – lined screw caps.

4.15 Horizon SPE-DEX 4790 Automated Extractor System.

4.16 Atlantic DVB disks, or equivalent.

4.17 1-L amber bottles

5.0 REAGENTS

5.1 Laboratory reagent grade water - water in which an interferent is not observed at or above the PQL for any parameter of interest (carbon filtered ASTM Type II water or equivalent)

5.2 Sodium Hydroxide (10N) – Purchased from vendor, “Baker-analyzed”, or equivalent

5.3 Sodium Sulfate (ACS) - Granular, anhydrous. Bake at 400°C for 4 hours (may be done by vendor). Purify by rinsing three times with pesticide grade methylene chloride. Allow residual methylene chloride to evaporate before use. Stored in a Teflon capped glass bottle.

5.4 Sulfuric Acid Solution (1:1) - Add 500 mL concentrated sulfuric acid (certified ASC grade or better) slowly to 500 mL laboratory reagent grade water. Prepare as needed and store in a ground glass stoppered bottle.

5.5 Methylene Chloride ($MeCL_2$) - Pesticide grade or better. Lot must be verified by concentrating 300-400 mL to 1.0 mL and evaluating by GC/MS.

5.6 Acetone and Hexane - Pesticide grade or better. Lot must be verified by concentrating approximately 20-30 mL to 1.0 mL and evaluating by GC/ECD.

5.7 Pesticide/PCB Surrogate spiking solution - Prepare a solution of decachlorbiphenyl (DCB) and tetrachloro-meta-xylene (TCMX) at a concentration of 1.0 ug/mL ea in acetone. Store the solution at –10 to -20 °C in a Teflon sealed container. Solution must be verified by GC/ECD prior to use, and must be replaced every 6 months or sooner if degradation is evident.

5.8 Pesticide Matrix Spike/Lab Control Sample spiking solution - Prepare a matrix spiking solution in pesticide grade methanol that contains all target analytes listed below:

ANALYTE	ug/mL
4,4’-DDT	0.5
4,4’-DDD	0.5
4,4’-DDE	0.5
Aldrin	0.5
Dieldrin	0.5
Endrin	0.5
Endrin Aldehyde	0.5
Endrin Ketone	0.5
Endosulfan I	0.5
Endosulfan II	0.5
Endosulfan Sulfate	0.5
alpha-BHC	0.5

ANALYTE (cont.)	ug/mL
beta-BHC	0.5
delta-BHC	0.5
gamma-BHC (Lindane)	0.5
Heptachlor	0.5
Heptachlor epoxide	0.5
Methoxychlor	0.5
alpha-Chlordane	0.5
gamma-Chlordane	0.5

5.9 PCB Matrix Spike/Lab Control Sample spiking solution - Prepare a matrix spiking solution in pesticide grade acetone that contains 5.0ug/ml ea of Aroclor® 1016/1260 mix (Restek catalog# 32039).

5.10 Store the spiking solutions at –10 to -20 °C in a Teflon sealed container. The solutions must be verified by GC/ECD prior to use, and must be replaced every 6 months or sooner if degradation is evident.

6.0 SAMPLE COLLECTION, PRESERVATION AND HANDLING

Samples are collected in 1 L amber bottles and held at 4 (±2) °C until time of extraction.

Holding time for extraction of aqueous samples for Methods 3510, 3520, and 3535 is 7 days from date of sample collection, although the analyst should be aware that actual holding times employed might be project/program specific.

7.0 PROCEDURES

The following information must be recorded in the extraction logbook.

- Extraction method
- Surrogate and spike IDs
- Lot numbers of all solvents, acids and bases, sodium sulfate, filter paper
- Nitrogen evaporation water bath temperature
- Sample pH if appicable
- Extraction and Concentration dates
- Extraction and Concentration analyst
- Sample ID or QC sample ID
- Initial and final volumes or weight
- Surrogate and spike amounts
- Any sample cleanup preformed
- Final extract tray location
- Any comments regarding the sample extraction (ie. Emulsion)

- Prep batch start time and end time
- CLLE start time and end time
- Lot numbers of the vials the concentrated extracts are stored in.

SEPARATORY FUNNEL SAMPLE EXTRACTION

If an emulsion prevents acceptable recovery or client history indicates samples may demonstrate matrix interence, then samples should be extracted by continuous liquid-liquid extraction (CLLE).

7.1 Rinse all glassware three times with methylene chloride prior to use.

7.2 Label a 2 L Teflon separatory funnel and a 250 mL amber collection bottle clearly. Label should include laboratory sample number, matrix, analyte, and extraction date. Be sure that the detachable stopcocks are secured to the separatory funnels before adding samples.

7.3 Measure the initial volume by comparing the meniscus of the sample with the reference bottle of the same bottle type. Please refer to SOP CA-108, “Basic Laboratory Technique”, for the reference bottle verification procedure. Record the volume and any notable characteristics (e.g. color, presence of sediment, or odor) in the extraction logbook.

7.4 Transfer the contents of the sample bottle to a 2 L separatory funnel.

7.5 Transfer 1 L of laboratory reagent grade water to a 2 L separatory funnel. This serves as a method blank for the extraction batch. A method blank must be prepared for every daily extraction batch of twenty or fewer samples.

7.6 Transfer 1 L of laboratory reagent grade water to a 2 L separatory funnel for each analysis to be performed (pesticide and/or PCB). This will serve as a Laboratory Control Sample (LCS). When Pesticides and PCBs are extracted together, a LCS and LCSD set must be extracted for each analysis. An LCS is required for every daily extraction batch of twenty or fewer samples and each analysis. If an MS/MSD pair is not extracted on a particular day, an LCS/LCSD pair may be required in order to meet client-specific or program-specific requirements. This information will be disseminated from the project manager or Department Manager.

7.7 A matrix spike/matrix spike duplicate (MS/MSD) is to be prepared as requested by a client or, at a minimum, one pair per 20 samples or every 14 days and each analysis(refer to the logbook page, “date QC expires”). Transfer two additional 1 L aliquots of sample to 2 L separatory funnels for a matrix spike and matrix spike duplicate (MS/MSD) for each analysis. When Pesticides and PCBs are extracted together, a MS and MSD set must be extracted for each analysis. Note: Sufficient sample volume should be available without depleting all remaining sample aliquots.

7.8 Check the pH of the samples. If it is not between pH 5 and 9, adjust the pH with 10N sodium hydroxide or 1:1 sulfuric acid solution. Note the addition of NaOH or H_2SO_4 in the extraction logbook.

7.9 Using a gas-tight syringe, add 1.0 mL of surrogate spiking solution to all samples the blank, LCS/LCSD(s) and MS/MSD(s), if performed.

7.10 Using a gas-tight syringe, add 1.0 mL of pesticide or PCB matrix spiking solution to the appropriate LCS, LCSD, MS and MSD if performed.

7.11 To each empty sample bottle add 60 mLs of methylene chloride, rinse the bottle and transfer the solvent into the appropriate separatory funnel. Add 60 mL of methylene chloride directly to the blank and LCS/LCSD(s).

7.12 Ensure that each screw cap is secured tightly to the separatory funnel to prevent leaks. Shake briefly and vent in hood to release pressure. Extract the sample by shaking the funnel on mechanical shaker for 3 minutes. Allow phases to separate for at least 10 minutes. Drain the methylene chloride layer into the 250 mL amber collection bottle.

7.13 If an emulsion forms, mechanical techniques must be employed to achieve maximum separation and solvent recovery. Such means include swirling and centrifugation and draining through a small separatory funnel. In certain instances, transferring the entire sample into a continuous liquid-liquid extractor may be the only alternative. If any such techniques are used, they must be noted in the extractions logbook.

7.14 Add a second 60 mL aliquot of methylene chloride to the separatory funnel and extract for the second time (see 7.10 - 7.12). Collect the methylene chloride layer in the same 250 mL amber collection bottle.

7.15 Repeat the extraction for a third time as described in 7.13.

7.16 Proceed to Section 7.53 for extract concentration procedures.

CONTINUOUS LIQUID-LIQUID SAMPLE EXTRACTION (CLLE)

7.17 Set up the CLLE apparatus. All glassware should be rinsed three times with methylene chloride and the extract flasks properly labeled.

7.18 Add 2-3 boiling stones to the round bottom flask and approximately 500 - 600 mL of methylene chloride to the CLLE body.

7.19 Add 1 L laboratory reagent grade water to a CLLE body. This is the method blank for this extraction batch. Be sure that no water leaks into the round bottom flask. A method blank is required for every extraction batch of twenty or fewer samples.

7.20 Mark the sample level (meniscus) on the sample bottle with a wax crayon so that the volume can be measured (this may be done prior to removal from the walk-in cooler). Transfer the sample to a CLLE body, being sure that no water leaks into the round bottom flask.

7.21 Prepare an LCS for every daily extraction batch of twenty or fewer samples and each analysis (pesticide and/or PCB). Add 1 L of laboratory reagent grade water to a CLLE body. If an MS/MSD pair is not extracted on a particular day, an LCS/LCSD pair may be required in order to meet client-specific or program-specific requirements. This information will be disseminated from the project manager or Department Manager. When Pesticides and PCBs are extracted together, a LCS and LCSD set must be extracted for each analysis.

7.22 Mark the sample levels on the sample bottles. Transfer the samples to the CLLE bodies.

7.23 Check the pH of the samples. If it is not between pH 5 and 9, adjust the pH with 10N sodium hydroxide or 1:1 sulfuric acid solution. Note the addition of NaOH or H_2SO_4 in the extraction logbook.

7.24 Transfer two 1 L portions of a sample to CLLE bodies for each analysis for preparation of a matrix spike/matrix spike duplicate if required. An MS/MSD is required if requested by the client or per 20 samples, whichever occurs first. When Pesticides and PCBs are extracted together, a MS and MSD set must be extracted for each analysis. Note: Sufficient sample volume should be available without depleting all remaining sample aliquots.

7.25 For each sample, rinse the original sample container with approximately 30 mL of methylene chloride. Add this rinse to the CLLE body.

7.26 Determine the initial volume of the samples by comparing the grease marking where the sample meniscus was to the reference bottle located in the lab. Please refer to SOP CA-108, “Basic Laboratory Technique”, for the reference bottle verification procedure. Record the volume and any notable characteristics (e.g. color, presence of sediment, or odor) in the extraction logbook.

7.27 Add 1.0 mL of the Pesticide/PCB Surrogate Spike to each sample including the blank, LCS/LCSD and MS/MSD, if performed.

7.28 Add 1.0 mL of Pesticide or PCB Matrix Spike to the appropriate LCS/LCSD and MS/MSD pair, if performed, and stir.

7.29 Attach cooling water Allihn condensers, after first rinsing each 45/50 joint with methylene chloride. Turn on the heating mantles and allow the samples to extract for at least 18 hours, total extract time may go up to 20 hours. Turn off the mantles and let samples cool.

7.30 Proceed to Section 7. 53 for sample extract concentration procedures.

EXTRACTION WITH AUTOMATED EXTRACTOR SYSTEM (SPE)

Alternatively, samples may be extracted using the Horizon Automated Extractor System (Figure 2)

Purging the Extractor Vessels

7.31 Check and fill all necessary solvent bottles (acetone, laboratory reagent grade water and hexane) as needed. Check and empty the two waste containers as needed.

7.32 Turn on nitrogen tank to 60 psi. Turn the instrument pressure on top of the controller to 50 psi. Turn the solvent bottle pressure to 10 psi.

7.33 Turn on the Horizon controller (switch in the back).

7.34 Check the lubrication oil on the air pump. Fill as needed. Turn the air pump on.

7.35 Clean the glass sensors that are located on the back of the dispensing stems of the extractors using a Kim Wipe. This is to remove any residue that may interfere with the sensors.

7.36 Attach 19/22 adapters to 40-mL vials and attach beneath the disk holder platforms of the extractors. Assembly per owner's manual and place empty Horizon disk holder assemblies on top of the disk holder platforms. There should be roughly 1 cm separating the speedisk from the extractor downtube.

7.37 Check to be sure that all extractors have empty sample bottles loaded on top. If not, use a Horizon cap on a one liter empty bottle and firmly place the bottlenose down into the extractor.

7.38 Press *select* on the control panel to designate an extractor (1, 2, 3, 4 or "." for all), then press *enter*.

7.39 Type 8081.9, and press enter to select pesticide/PCB purge method. Once the method is loaded, start the extractors by pressing the *start* buttons on the individual extractors. The red LED will blink when the method is complete.

7.40 Repeat this process 2-3 times before using the Horizon autoextractors.

ANALYSIS OF SAMPLES WITH AUTOEXTRACTOR

7.41 Label a 60 ml vial with the sample to be extracted. Attach 19/22 adapter to vial and attach beneath the disk holder platforms of the extractors.

7.42 Place an Atlantic DVB disk (or equivalent) into a Horizon disk holder assembly and assemble per owner's manual. Place the disk holder assemble on top of the disk holder platform. There should be roughly 1 cm separating the speedisk from the extractor downtube

7.43 Mark the volume level of liquid in each sample on the outside using a grease pencil.

7.44 Add 1 L laboratory reagent grade water to 1 L amber bottle. This is the method blank for this batch. A method blank is required for every extraction batch of twenty or fewer samples.

7.45 Prepare an LCS for every daily extraction batch of twenty or fewer samples and each analysis, pesticide and/or PCB. Add 1 L of laboratory reagent grade water to a 1 L amber bottle. If an MS/MSD pair is not extracted on a particular day, an LCS/LCSD pair may be required to meet client specific or program specific requirements. This information will be disseminated from the project manager or department manager.

7.46 Add 1.0 mL of Pesticide/PCB surrogate spike to each sample including the blank, LCS/LCSD and MS/MSD, if required. Recap samples and shake well.

7.47 Add 1.0 mL of pesticide or PCB matrix spike to the appropriate LCS/LCSD and MS/MSD samples. Recap and shake well.

7.48 Remove cap and add 5.0 mL of 1:1 H_2SO_4 to each sample including the blank, LCS/LCSD and MS/MSD set immediately prior to extracting the sample.

7.49 Remove the cap from each sample bottle and cover with tin foil. Screw a Horizon adapter cap over the tin foil. Invert the bottle and check for leaks.

7.50 Load the sample bottle on the holder and twist ¾ of a rotation. Stop twisting when air bubbles rise to the top of the sample bottle. Do not twist completely around. The foil may loosen and jam the valve.

7.51 Press *select* on the control panel to designate an extractor (1, 2 or "." for both), then press *enter*.

7.52 Type in 8081.3 for the method and press enter. Once the method is loaded, start the extractors by pressing the *start* buttons on the individual extractors. The red LED will blink when the method is complete. The extract will be collected in the 60 ml vial.

7.53 Sample is now ready to reduce to 10 mL final volume.

NOTE: The instrument methods stated above apply specifically to the Atlantic DVB disk. Instrument methods may need to be modified with the usage of different filters and/or to increase recoveries. See instrument logbook for current methods in use.

CONCENTRATION OF WATER SAMPLE EXTRACTS

7.54 Rinse the K-D glassware (flask, concentration tube, funnel and Snyder column, including the ground glass joints on the flask and columns) three times with methylene chloride (or hexane for samples extracted with the Autoextractor) before assembling. Add two boiling chips to the K-D. Insert fluted 18.5 cm filter papers into short stem powder funnels and add ~ 2 inches of sodium sulfate crystals. Rinse the sodium sulfate in the assembled funnels with ~20-30 mLs of methylene chloride (hexane for samples extracted with the Autoextractor). Place the assembled K-D's under the funnels.

7.55 For methylene chloride extracts, add approximately 50 mL Hexane to funnel and let drain through. Since methylene chloride has a lower boiling point than Hexane, this will result in a final extract in hexane only.

Note: For Pesticide / PCB samples originating from South Carolina (see worknotes) do not add the hexane at this step. Solvent exchange will be during the nitrogen blow down procedure.

7.56 Transfer the methylene chloride or hexane extracts to the K-D concentrator setups through the sodium sulfate in the funnels. This is the drying step, which is required to remove residual water from the extracts. Any large water layers must be removed by other means, prior to pouring through the sodium sulfate. After pouring all of the extract volume through the sodium sulfate, rinse the extract bottle three times with ~ 2 – 3 mLs of methylene chloride (or hexane for samples extracted with the Autoextractor). Add the rinsings through the sodium sulfate to complete a quantitative transfer. Rinse the sodium sulfate with ~ 15 mLs of methylene chloride (or hexane for samples extracted with the Autoextractor) and allow to drain.

7.57 Transfer the labels from the collection bottles or round bottom flasks (from the CLLE extraction) to the K-Ds. Remove the funnel and attach a 3-ball macro Snyder column. Pre-wet the Snyder column with 1 mL of methylene chloride (or hexane for samples extracted with the Autoextractor).

7.58 Place the K-D in a hot water bath (85-90°C). Gently swirl K-D in the water until boiling begins. At the proper distillation rate, the Snyder balls should chatter but the chambers should not flood with condensed solvent. The K-D should be kept in a vertical orientation while on the bath. When the apparent volume in the concentrator tube reaches ≈ 5-6 mL, remove the K-D from the water bath. Allow the K-D to cool for 10 minutes. Rinse the Snyder column lower joint with ≈ 1 mL of hexane (methylene chloride for samples that have not gone through solvent exchange (ie. South Carolina samples). Remove the Snyder column. Wipe off any

water from the neck above the lower joint of the flask. Separate the K-D flask from the concentrator tube, rinsing the ground glass joint with ≈ 1 mL hexane.

7.59 Reduce the extracts to ≈ 1 mL using Nitrogen blow-down apparatus. The bath temperature must be no higher than the boiling point of the solvent (45 °C for hexane). Turn the gas to 3 psi. Be careful not to splash the extract out of the tube. During concentration on the N-evap, the internal wall of the concentrator tube and the N-evap sparging pipet must be rinsed down at least once or twice with ≈1 mL of hexane (methylene chloride for samples not yet solvent exchanged). The solvent level in the concentrator tube must be positioned below the level of the water bath as much as possible to prevent water from condensing into the sample extract. As the extract volume is reduced, lower the N_2 sparging needle closer to the surface of the extract to expedite the concentration. Note any problems or extract losses, if they occur, in the extractions logbook. Transfer extract to a 12 or 16 mL vial. Using a reference vial for volume comparison, adjust the final extract volume to 10 mL by rinsing sides of tube with hexane and transferring rinsings to vial.

7.60 For samples that still need to be solvent exchanged, reduce the methylene chloride extract to ~ 1 mL. Add 10 mL of hexane to the concentrator tube and reduce to ~ 1 mL again on the N-evap. Adjust final extract to 10 mL by rinsing sides of tube with hexane and transferring rinsings to vial.

7.61 If at any point in the concentration procedure the concentrator tube goes dry – reextract the sample immediately.

7.62 Transfer the label from the concentrator tube to the vial. Store extract vials at a temperature of 4 ± 2 °C until ready for analysis. Indicate in the extractions logbook the box number and “tray location” of the individual extract vials.

7.63 All sample extracts for 8082 PCB analysis must undergo a sulfuric acid wash (cleanup) prior to analysis. All sample extracts for 8081 pesticide analysis do not undergo further cleanup unless requested by the client. Therefore, all sample extracts for combined 8081/8082 analyses must be split. Prior to splitting, mix contents of vial well. One portion must be acid cleaned for 8082 analysis. The associated method blank must be split and acid-cleaned in the same fashion. PCB LCSs and matrix spikes are acid cleaned also. Pesticide LCSs and matrix spikes are not subjected to further cleanup. Please refer to Katahdin SOP CA525 (current revision), Extract Cleanup Using Sulfuric Acid, for further instructions.

8.0 QUALITY CONTROL AND ACCEPTANCE CRITERIA

Each extractions analyst must demonstrate proficiency in performing the extractions that prepare samples for analysis. Demonstration consists of preparation (extraction), by the analyst, of at least four aliquots which are then analyzed according to the analytical method in question. These QC samples must meet all quality control acceptance limits. Demonstration

must be documented by use of a form which summarizes the results of the analysis of these aliquots, calculated percent recoveries, and standard deviation. Demonstration of proficiency must be done one time per analyst initially and then annually thereafter. Refer to SOPs QA-805 and QA-807, current revision.

If, upon analysis of the extracted samples, it is discovered that quality control acceptance criteria have not been met, all associated samples must be evaluated against all the QC. In some cases data may be reported, perhaps with narration, while in other cases, other corrective action may be taken. The corrective actions may include re-extraction of the samples associated with the quality control sample that did not meet acceptance criteria, or may include making new reagents and standards if the standardization is suspect. These decisions are based on holding time considerations, client and project specific Data Quality Objectives and on review of chromatograms. The supervisor, Operations Manager, and/or Quality Assurance Officer may be consulted to evaluate data. Some samples may not be able to be reanalyzed within hold time. In these cases "qualified" data with narration may be advisable after consultation with the client.

Much of the work performed at the lab is analyzed in accordance with specific QC requirements spelled out in a project specific Quality Assurance Project Plan (QAPP) or in a program specific Quality Systems Manual (QSM). The reporting limits, acceptance criteria and/or corrective actions may be different than those specified in this SOP. In these cases the appropriate information will be communicated to the Department Manager and/or senior chemists before initiation of the analyses so that specific product codes can be produced for the project. In addition, the work order notes for each project will describe the specific QAPP or QSM to be followed.

A method blank must be extracted for <u>each</u> and <u>every</u> item listed below:

- Each day of extraction (24 hours midnight - midnight)
- Each extraction method
- Every 20 samples extracted in a 24-hour period

A laboratory control sample (LCS) is required for <u>each</u> and <u>every</u> item listed below:

- Each extraction method
- Every extraction batch of twenty or fewer samples
- Each analysis (pesticide and/or PCB) to be performed

Refer to the current revision of the applicable Katahdin SOP for analysis of Pesticides and PCBs for quality control acceptance criteria.

9.0 METHOD PERFORMANCE

Refer to the applicable analytical SOP.

10.0 APPLICABLE DOCUMENTS/REFERENCES

Test Methods for Evaluating Solid Waste - Physical/Chemical Methods, Methods 3510C and 3520C, USEPA SW-846, Third Edition, Final Update III, December 1996.

40 CFR 136, Appendix A, "Test Procedures for Analysis of Organic Pollutants," Method 608, June, 1998 edition.

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TABLE 1

SUMMARY OF METHOD MODIFICATIONS (METHOD 3510, current revision)

TOPIC	KATAHDIN SOP CA-515-07	METHOD 3510, current revision
Apparatus/Materials	1. 12 or 16 mL vials used for final extract 2. 250 mL amber bottle or flask used 3. 1.0 mL syringe 4. short stem funnels	1. 2 mL vials used for final extract 2. 250 mL Erlenmeyer flask 3. 5.0 mL syringe 4. drying column
Reagents		
Sample preservation/ handling	1. entire contents of 1 L sample bottle transferred to separatory funnel	1. one liter graduated cylinders used to transfer initial sample volume to separatory funnel
Procedures	1. extract collection in amber bottle or Erlenmeyer flask 2. extract dried using Na_2SO_4 in short stem funnels 3. no apparatus height specification for concentration on water bath 4. sample removed from water bath when volume reaches ~10 mL 5. hexane added directly to K-D body at start of concentration process	1. extract collection in Erlenmeyer flask 2. extract dried using Na_2SO_4 in drying columns 3. partially immerse concentrator tube in water and lower apparatus to complete concentration in 10-15min 4. sample removed from water bath when volume reaches 1-2 mL 5. solvent exchange via large K-D with addition of 50 mL hexane after concentrating methylene chloride extract to 1 mL
QC - Spikes		
QC - LCS		
QC - Accuracy/Precision		
QC - MDL		

TABLE 2

SUMMARY OF METHOD MODIFICATIONS (METHOD 3520, current revision)

TOPIC	KATAHDIN SOP CA-515-07	METHOD 3520, current revision
Apparatus/Materials	1. short-stem funnels 2. 12 or 16 mL vials used for final extract	1. drying columns 2. 2 mL vials used for final extract
Reagents		
Sample preservation/ handling	1. entire contents of 1 L sample bottle transferred to CLLE	1. one liter graduated cylinders used to tranfer initial sample volume to CLLE
Procedures	1. CLLE for 18 $\pm$ 2 hours 2. extract dried using Na_2SO_4 in short stem funnels 3. no apparatus height specification for concentration on water bath 4. sample removed from water bath when volume reaches ~10 mL 5. hexane added directly to K-D body at start of concentration process	1. CLLE for 18-24 hours 2. extract dried using Na_2SO_4 in drying columns 3. partially immerse concentrator tube in water and lower apparatus to complete concentration in 10-15min 4. sample removed from water bath when volume reaches 1-2 mL 5. solvent exchange via macro K-D with addition of 50 mL hexane after concentrating methylene chloride extract to 1 mL
QC - Spikes		
QC - LCS		
QC - Accuracy/Precision		
QC - MDL		

TABLE 3

SUMMARY OF METHOD MODIFICATIONS (METHOD 3535, current revision)

TOPIC	KATAHDIN SOP CA-515-07	METHOD 3520, current revision
Apparatus/Materials	1. Horizon SPE-DEX 4790 Automated Extractor System.	1. Empore solid-phase extraction system
Reagents		
Sample preservation/ handling	1. entire contents of 1 L sample bottle transferred to separatory funnel	1. one liter graduated cylinders used to transfer initial sample volume to separatory funnel
Procedures	1. no methanol addition 2. extraction using Horizon SPE-DEX 4790 Automated Extractor System. 3. extract dried using Na_2SO_4 in short stem funnels 4. no apparatus height specification for concentration on water bath 5. sample removed from water bath when volume reaches ~10 mL 6. hexane added directly to K-D body at start of concentration process	1. 5mL methanol added to all samples and blanks 2. extraction using Empore solid-phase extraction system 3. extract dried using Na_2SO_4 in drying columns 4. partially immerse concentrator tube in water and lower apparatus to complete concentration in 10-15min 5. sample removed from water bath when volume reaches 1mL 6. solvent exchange via macro K-D with addition of 50 mL hexane after concentrating methylene chloride extract to 1 mL
QC - Spikes		
QC - LCS		
QC - Accuracy/Precision		
QC - MDL		

TITLE: PREPARATION OF AQUEOUS SAMPLES FOR PESTICIDES/PCBs ANALYSIS

FIGURE 1

EXAMPLE OF LOGBOOK PAGE

PIP
Sep

KATAHDIN ANALYTICAL SERVICES, INC.
ORGANIC EXTRACTIONS LOG - AQUEOUS PESTICIDE/PCB

Extraction Method: (check one)	SW846 3520 (CLLE)		SW846 3510 (SEP) ✓		SW846 3535 (SPE)	
Analytical Method: (check one)	SW846 8081 ✓	SW846 8082 ✓	EPA 608	CLP OLM04.2	CLP OLC2.1	Other:
Standards	Surrogate ID: G606654		Spike ID: G606654		Spike ID: G606663	
Solvents	Solvent Lot # (MeCl2): H40E31		Solvent Lot # (Hexane): H22E15		Solvent Lot # (Acetone): —	
Consumables	Filter Paper Lot # K11672365		Acid Lot # 435026		$NaSO_4$ Lot # 27969003	
Nitrogen Bath Temperature: 37°C		Vial Lot #: 00097808 / 00098146				
Prep Start Time: 1400		Prep End Time: 1500		CLLE Start Time:		CLLE End Time:

Date Extracted	Ext. Init.	Sample ID	Initial Vol. mL	Surr. Vol.	Spike Vol.	Fraction Pest	Fraction PCB	Final Vol. mL	Date Conc.	Tray Location	Initials	Clean-Up GPC	Clean-Up Flor.	Clean-Up Acid Wash	Clean-Up Other	Comments
10/22/09	OB	W470360-1 W470361-1	1000	1mL	NR	✓	✓	10mL	10-23-09	PP591 F4	GN			✓		Rpost=R112304
		W470360-2			1mL					F5						Rpub=R112305
		-3								F6						
		-4	200		NR	✓				F7						PP5923A-4 brought to volume in DI
		W470361-2	1000		1mL		✓			F8				✓		
		-3								F9				✓		
																10-23-09 GN

EX-002 – Revision 1 – 10/15/09

QAEX177 0000010

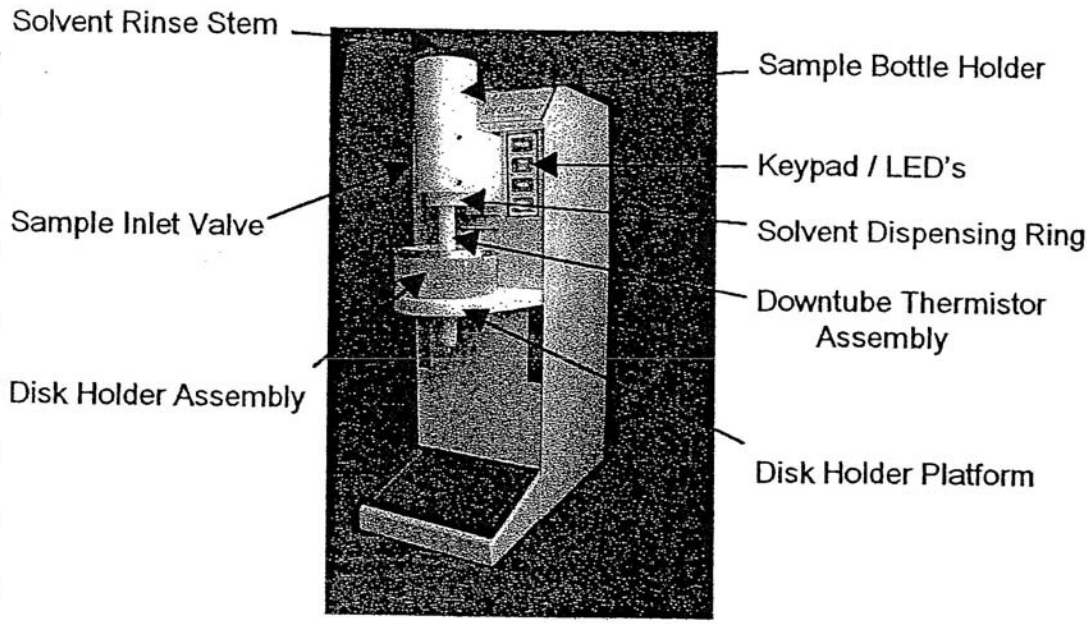
Date Extracted	Ext. Init.	Sample ID	Initial Vol. mL	Surr. Vol.	Spike Vol.	Fraction Pest	Fraction PCB	Final Vol. mL	Date Conc.	Tray Location	Initials	Clean-Up GPC	Clean-Up Flor.	Clean-Up Acid Wash	Clean-Up Other	Comments
10/22/09	OB	SC6328-1	200	1mL	NR	✓		10mL	10-23-09	F10	GN					TCLP extract brought to volume in DI
		SC6340-2								F11						
		-6								F12						
		-8								PP592 A1						
		SC6345-11								A2						
		SC6413-1								A3						
		SC6433-15a	1060				✓			A4				✓		
		-16j	1040							A5						
		SC6457-2L	1060							A6						
		-3L	970							A7						
		-4L	1040							A8						
																10-23-09 GN

EX-002 – Revision 1 – 10/15/09 QAEX177 0000011

TITLE: PREPARATION OF AQUEOUS SAMPLES FOR PESTICIDES/PCBs ANALYSIS

FIGURE 2

HORIZON AUTOEXTRACTOR SYSTEM DIAGRAM



KATAHDIN ANALYTICAL SERVICES, INC.
STANDARD OPERATING PROCEDURE

SOP Number: CA-524
Revision History
Cover Page
Page 1

TITLE: PREPARATION OF SEDIMENT/SOIL SAMPLES BY SOXHLET EXTRACTION USING METHOD 3540 FOR PESTICIDE/PCB ANALYSIS

Prepared By: Mike Thomas Date: 7/98

Approved By:

Group Supervisor: Michael F. Thomas Date: 11/15/00

Operations Manager: J Benton Date: 11/15/00

QA Officer: Deborah J. Nadeau Date: 11·15·00

General Manager: Dennis P. Hufnagel Date: 11/16/00

Revision History:

SOP Revision	Changes	Approval Initials	Approval Date	Effective Date
01	Minor changes throughout. Clarifications to procedure section.	DN	11.15.00	11/15/00
02	Added definitions to section 1.1. Wording changed or added to clarify sections 5, 6, 8, + 9. New figure	MRC	11.08.04	11.08.04
03	Sect. 7.1.2 - adding the step to rinse forceps also. 7.10 adding condenser temperature and output voltage of variable transformer	LAD	04/06	04/06
04	Added generated waste information. Updated spike list. Added LCSD. Reworded Sect. 7.10 and 7.11 for clarification. Updated Table 1 Replaced Figure 1	LAD	09/07	09/07
05	Changed "N-Lo" waste to "K" waste. Updated Logbook example. Sect. 7 - added wording instructing the recording of consumable lot #'s in Logbook.	LAD	07/08	07/08

TITLE: PREPARATION OF SEDIMENT/SOIL SAMPLES BY SOXHLET EXTRACTION USING METHOD 3540 FOR PESTICIDE/PCB ANALYSIS

SOP Revision	Changes	Approval Initials	Approval Date	Effective Date
06	Added balance criteria. Changed weight criteria to +/- 0.05g. Minor changes to section 7 to reflect current techniques. Clarified samples being GPC'd are not solvent exchanged into hexane. Updated logbook page. Added CA-108 reference for subsampling information	LAD	08/09	08/09
07	Removed targeting sample weights. Removed decanting samples prior to extraction.	LAD	08/10	08/10

TITLE: **PREPARATION OF SEDIMENT/SOIL SAMPLES BY SOXHLET EXTRACTION USING METHOD 3540 FOR PESTICIDE/PCB ANALYSIS**

Please acknowledge receipt of this standard operating procedure by signing and dating both of the spaces provided. Return the bottom half of this sheet to the QA Department.

I acknowledge receipt of copy ___ of document **SOP CA-524-07**, titled **PREPARATION OF SEDIMENT/SOIL SAMPLES BY SOXHLET EXTRACTION USING METHOD 3540 FOR PESTICIDE/PCB ANALYSIS.**

Recipient: _____ Date: _____

KATAHDIN ANALYTICAL SERVICES, INC.
STANDARD OPERATING PROCEDURE

I acknowledge receipt of copy ___ of document **SOP CA-524-07**, titled **PREPARATION OF SEDIMENT/SOIL SAMPLES BY SOXHLET EXTRACTION USING METHOD 3540 FOR PESTICIDE/PCB ANALYSIS.**

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TITLE: **PREPARATION OF SEDIMENT/SOIL SAMPLES BY SOXHLET EXTRACTION USING METHOD 3540 FOR PESTICIDE/PCB ANALYSIS**

1.0 SCOPE AND APPLICATION

The purpose of this SOP is to describe the procedure for extracting pesticides/PCBs from solids such as soils, sludges, and wastes using Method 3540. The Soxhlet extraction process ensures intimate contact of the sample matrix with the extraction solvent.

This method is applicable to the isolation and concentration of water-insoluble and slightly water-soluble organics in preparation for a variety of chromatographic procedures including methods 8081 for pesticides and 8082 for PCB's.

1.1 Definitions

METHOD BLANK (laboratory reagent blank): An artificial sample designed to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus. For aqueous samples, reagent water is used as a blank matrix; for soil samples, baked organic-free sand is used as a blank matrix. The blank is taken through the appropriate steps of the process.

LABORATORY CONTROL SAMPLE (LCS): A blank that has been spiked with the analyte(s) from an independent source, and is analyzed exactly like a sample. Its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements. The matrix used should be phase matched with the samples and well characterized.

MATRIX SPIKE/MATRIX SPIKE DUPLICATE (MS/MSD): Predetermined quantities of stock solutions of certain analytes are added to a sample matrix prior to sample extraction and analysis. Samples are split into duplicates, spiked and analyzed. Percent recoveries are calculated for each of the analytes detected. The relative percent difference between the samples is calculated and used to assess analytical precision.

SURROGATES: Organic compounds which are similar to analytes of interest in chemical composition, extraction and chromatography, but which are not normally found in environmental samples. These compounds are spiked into all blanks, standards, samples and spiked samples prior to analysis. Percent recoveries are calculated for each surrogate.

1.2 Responsibilities

This method is restricted to use by, or under the supervision of analysts experienced in the extraction of samples for pesticide/PCB analysis. Each analyst must demonstrate and document their ability to generate acceptable results with this method. Refer to Katahdin SOP QA-805, current revision, "Personnel Training and Documentation of Capability".

It is the responsibility of all Katahdin technical personnel involved in the extraction of samples for pesticide/PCB analysis to read and understand this SOP, adhere to the procedures outlined, and to properly document their data in the appropriate lab notebook. Any deviations from the test or irregularities with the samples should also be recorded in the lab notebook and reported to the Department Manager or designated qualified data reviewer responsible for this data.

It is the responsibility of the Department Manager to oversee that members of their group follow this SOP, to ensure that their work is properly documented and to indicate periodic review of the associated logbooks.

1.3 Safety

Users of this procedure must be cognizant of inherent laboratory hazards, proper disposal procedures for contaminated materials and appropriate segregation of hazardous wastes. The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical should be treated as a potential health hazard. A reference file of material safety data sheets is available to all personnel involved in the chemical analysis. Everyone involved with the procedure must be familiar with the MSDSs for all the materials used in this procedure.

Each qualified analyst or technician must be familiar with Katahdin Analytical Health and Safety Manual including the Katahdin Hazardous Waste Plan and must follow appropriate procedures. These include the use of appropriate personal protective equipment (PPE) such as safety glasses, gloves and lab coats when working with chemicals or near an instrument and not taking food or drink into the laboratory. Each analyst should know the location of all safety equipment. Each analyst shall receive a safety orientation from their Department Manager, or designee, appropriate for the job functions they will perform.

1.4 Waste Disposal

Wastes generated during the preparation of samples must be disposed of in accordance with the procedures described in the current revision of the Katahdin Hazardous Waste Plan and Safety Manual and SOP SD-903, “Sample Disposal,” current revision. Expired standards are lab packed, placed in the Katahdin hazardous waste storage area, and disposed of in accordance with this SOP.

Any methylene chloride solvent waste generated during the rinsing of glassware etc. should be disposed of in the “D” waste stream satellite accumulation area nearest the point of generation. Acetone and hexane are considered flammable waste, and should be disposed of in the “O” waste stream satellite accumulation area nearest the point of generation. Post-extraction soil samples, used glass wool, and sodium sulfate waste should be disposed of in the soil with organics “I” waste stream

satellite accumulation area nearest the point of generation. Acid waste generated during the cleanup of PCB samples should be disposed of in the "K" satellite accumulation area nearest the point of generation. Please refer to the current revision of SOP CA-107 for the location of satellite waste accumulation areas.

2.0 SUMMARY OF METHOD

2.1 The solid sample is mixed with anhydrous sodium sulfate, placed in a Soxhlet extractor and extracted with methylene chloride.

2.2 The extract is then dried, concentrated, and exchanged into hexane for GC analysis. Sulfuric acid cleanup is performed on extracts for 8082 PCB analysis.

3.0 INTERFERENCES

Solvents, reagents, glassware, and other sample preparation apparatus may yield interferences to GC analysis due to the presence of contaminants. These contaminants can lead to discrete artifacts or elevated baselines in chromatograms. Routinely, all of these materials must be demonstrated to be free from interferences under the conditions of the analysis by running reagent blanks. Interferences caused by phthalate esters can pose a major problem in pesticide analysis. Common flexible plastics contain varying amounts of phthalates that are easily extracted during laboratory operations, so cross-contamination of glassware frequently occurs when plastics are handled. Interferences from phthalates can best be minimized by avoiding the use of such plastics in the laboratory. At no time may gloves that have not been tested for phthalates or gloves known to contain phthalates be used or stored in the organic extraction lab. Additionally, whenever possible plastic items in this lab must be replaced with metal or teflon or other non-phthalate plastic substitute.

Special care should be taken to ensure clean glassware and apparatus are used, pre-rinsed with the appropriate solvent prior to use. Solvents should be analyzed prior to use to demonstrate that each lot is free of contaminants that may interfere with the analysis.

Interferences coextracted from the samples will vary considerably from source to source. If analysis of an extracted sample is prevented due to inteferences, further cleanup of the sample extract may be needed to minimize interferences.

4.0 APPARATUS AND MATERIALS

4.1 Soxhlet extractor – 45/50 top joint and 24/40 lower joint.

4.1.1 500 mL flat-bottom boiling flask

4.1.2 Allihn cooling water condenser

4.2 Powder Funnels – 100 mm top diameter, 35 mm stem

4.3 Kuderna-Danish (K-D) apparatus

4.3.1 Concentrator tube - 10-mL

4.3.2 Evaporation flask - 500-mL

4.3.3 Snyder column - Three-ball macro

4.4 Nitrogen evaporation (N-EVAP) apparatus.

4.5 Boiling stones, 12 mesh silicon carbide (carborundum) – pre-purified by Soxhlet extraction in methylene chloride

4.6 Water bath - Heated, with concentric ring cover, capable of temperature control (± 5°C). The bath should be used in a hood.

4.7 Vials - Glass, 4, 12, or 16 mL with Teflon-lined screw caps

4.8 Glass wool (fiberglass) - baked at 400°C for a minimum of 4 hours or overnight.

4.9 Heating mantles - Rheostat controlled.

4.10 Disposable glass Pasteur pipets, 5 ¾”, and bulbs.

4.11 Drying oven - capable of maintaining 105°C for glassware drying.

4.12 Muffle oven – capable of maintaining 400 °C for baking glass wool and organic-free sand.

4.13 Beakers, 250 or 400 mL

4.14 Top-loading balance - capable of weighing to 0.**01** g.

4.15 Spatulas, stainless-steel

4.16 Long forceps, stainless-steel

4.17 Metal clips – for securing Soxhlets to boiling flasks

TITLE: **PREPARATION OF SEDIMENT/SOIL SAMPLES BY SOXHLET EXTRACTION USING METHOD 3540 FOR PESTICIDE/PCB ANALYSIS**

4.18 Filter paper, 18.5 cm, Fisherbrand or Whatman 114V (or equivalent)

4.19 Gel Permeation Chromatograph (GPC) - J2 Scientific AccuPrep MPS™ with internal UV detection

5.0 REAGENTS

5.1 Sodium sulfate (granular, anhydrous and powdered, anhydrous) (ACS reagent grade), Na_2SO_4. Certified by the manufacturer/vendor as purified by heating at 400°C for 4 hours prior to receipt by the laboratory.

5.2 Methylene chloride - (pesticide grade or equivalent) purchased by lot, evaluated prior to use by concentration of 300 mL to 1 mL followed by GC/MS analysis.

5.3 Acetone and hexane – (pesticide grade or equivalent) purchased by lot, evaluated prior to use by concentration of 300 mL to 1 mL followed by GC/MS and GC analysis.

5.4 Organic-free sand, purified by baking at 400 °C at a minimum of 4 hours or overnight. Method blanks serve as checks on the baked sand.

5.5 Surrogate spiking solution - Prepare a solution of decachlorobiphenyl (DCB) and tetrachloro-meta-xylene (TCMX) at a concentration of 1 ug/mL in acetone.

5.6 Matrix Spike/Lab Control Sample spiking solution

5.6.1 Pesticide spike solution – prepare in pesticide grade methanol containing the analytes listed below at concentrations of 0.5 ug/mL.

4,4'-DDD	Endrin
4,4'-DDE	Endrin Aldehyde
4,4'-DDT	Endrin Ketone
Aldrin	gamma-BHC (Lindane)
alpha-BHC	Heptachlor
beta-BHC	Heptachlor Epoxide
delta-BHC	Methoxychlor
Dieldrin	alpha-Chlordane
Endosulfan I	gamma-chlordane
Endosulfan II	Endrin
Endosulfan Sulfate	Endrin Aldehyde

5.6.2 PCB spike solution – prepare Aroclor 1660 (Aroclor 1016 and 1260) in pesticide grade acetone at a concentration of 5.0 ug/mL each.

5.7 Store the solutions mentioned in sections 5.5 and 5.6 at -10 to -20 °C (±2 °C) in a Teflon sealed container. Solution must be verified by GC/ECD prior to use and must be replaced every 6 months or sooner if degradation is evident.

6.0 SAMPLE COLLECTION, PRESERVATION AND HANDLING

Sediment/soil samples must be collected in a soil jar and must be maintained at 4°C (±2°C).

Holding time for extraction of sediment/soil samples for Method 3540 is 14 days from date of sample collection, although the analyst should be aware that actual holding times employed may be project/program specific.

Store all extracts at 4°C (±2°C) in the dark in labeled Teflon-sealed containers. See SOP SD-902, "Sample Receipt and Internal Control," current revision, for storage areas and temperature maintenance procedures.

7.0 PROCEDURES

The following information must be recorded in the extraction logbook.

- Extraction method
- Surrogate and spike IDs
- Lot numbers of all solvents, acids and bases, sodium sulfate, filter paper
- Nitrogen evaporation water bath temperature
- pH if applicable
- Sonicator horns tuned
- Extraction and Concentration dates
- Extraction and Concentration analyst
- Sample ID or QC sample ID
- Initial and final volumes or weight
- Surrogate and spike amounts
- Final extract tray location
- Any comments regarding the sample extraction (ie. Emulsion)

Samples need to be “swiped” out when removing and “swiped” in when replacing samples in storage locations to maintain the internal chain of custody. Refer to Katahdin SOP, Sample Receipt and Internal Control, current revision, for the proper procedure for removal and return samples.

7.1 Preparing the Soxhlet Extraction Apparatus

7.1.1 Rinse the Soxhlet extractors and 500 mL flat-bottom boiling flasks three times with methylene chloride. Be sure that the solvent rinses through the large vapor tube and smaller siphon tubes of the Soxhlet. Inspect these for tiny cracks. Also rinse the 24/40 lower joint.

7.1.2 Add ~ 250 mLs of methylene chloride to the 500 mL boiling flask. Add several boiling stones. Rinse the stainless steel forceps and pre-baked glass wool with Methylene chloride. Working in a hood, place a plug of the glass wool at the bottom of the Soxhlet so that the siphon tube hole is covered. Insert the 24/40 joint of the Soxhlet extractor into the 500 mL boiling flask and secure with a metal clip. Cover the top of the Soxhlet extractor with a piece of aluminum foil until ready to begin loading the sample.

7.2 Sample Handling

7.2.1 Sediment/soil samples – Do not decant any water layer on a sediment sample. Mix the sample thoroughly with the stainless steel spatula. If the sample container is full to the extent that stirring the sample is impractical, try to remove the “best representative” aliquot from the jar based on color, particle size, moisture, etc. Discard any foreign objects such as sticks, leaves, and rocks.

7.2.2 Gummy, fibrous, or oily materials not amenable to mixing should be cut, shredded, or otherwise reduced in size to allow for maximum exposure of the sample surfaces to the extraction solvent. Materials such as glass, rubber, metal, etc. may not require mixing with powdered sodium sulfate to disperse the sample. Plastic materials must be tested for degradation (melting) in methylene chloride prior to Soxhlet extraction.

7.2.3 Please refer to Katahdin Analytical Services SOP CA-108, current revision, “Basic Laboratory Techniques” for more information of subsampling.

7.3 Weigh out an approximate, greater than 30 g portion of sample into a labeled 400 mL beaker. Record sample weight to nearest 0.01 g in appropriate extraction logbook. Add between 30 to 60 g of powdered sodium sulfate, as required, to produce a “free-flowing” mixture. The amount of sodium sulfate added will depend upon the moisture content of the sample (e.g., low moisture content will require less sodium sulfate). Mix well with a spatula. Keep the spatula in the sample beaker and <u>cover</u> the beaker with aluminum foil. Record sodium sulfate lot in logbook.

7.4 A method blank must be prepared with each extraction batch, not to exceed 20 client samples. To prepare method blank, weigh out one greater than 30 g portion of purified sand in a labeled 400 mL beaker. Record sample weights to nearest 0.01 g in

appropriate extraction logbook. Add 60 g sodium sulfate and mix well. (Although a "free-flowing" mixture can be achieved with less than 60 g sodium sulfate, the method blank must contain 60 g in order to evaluate the sodium sulfate as a potential source of contamination.)

7.5 A laboratory control sample (LCS) must be prepared with each extraction batch, not to exceed 20 client samples. To prepare LCS, weigh out one greater than 30 g portion of purified sand in a labeled 400 mL beaker. Record sample weights to nearest 0.01 g in appropriate extraction logbook. Add 30 g sodium sulfate and mix well. With extraction batches prepared for combined 8081/8082 Pesticide and PCB analysis, separate Pesticide and PCB LCS's must be prepared (refer to section 5.6). If an MS/MSD pair is not extracted on a particular day, an LCS/LCSD pair may be required in order to meet client-specific or program-specific requirements. This information will be disseminated from the project manager or Department Manager.

7.6 A matrix spike/matrix spike duplicate (MS/MSD) set must be prepared for every 20 samples. To prepare MS/MSD, weigh out two approximate, greater than 30g portions of the sample designated for MS/MSD into each of two labeled 400 mL beakers. Record sample weights to nearest 0.01g in appropriate extraction logbook. Add 30 g sodium sulfate to each to produce a free-flowing mixture, and mix well. With extraction batches prepared for combined 8081/8082 Pesticide and PCB analysis, separate Pesticide and PCB MS/MSD pairs must be prepared (refer to section 5.6).

7.7 Once all of the QC and field samples have been weighed and mixed with sodium sulfate, begin adding each to the assembled and appropriately labeled Soxhlet extractors using the stainless steel spatulas. Carefully scrape all of the mixtures from the beaker walls so that no more than 1% remains behind in the beaker. Be careful that none of solid material falls into the extract flask through the large vapor tube.

7.8 To all samples, method blank, LCS/LCSD, and MS/MSD add 1.0 mL of the pesticide/PCBs surrogate spiking solution using a 1.0 mL gas tight syringe. Record surrogate spike volume and identification code in the extraction logbook. Thoroughly rinse syringe with solvent between each use.

7.9 To LCS/LCSD and MS/MSD add 1.0 mL of either the pesticide or PCBs matrix spike/LCS spiking solutions using a 1.0 mL gas tight syringe. Record matrix spike/LCS spiking solution volume and identification codes in the extraction logbook. Thoroughly rinse syringe with solvent between each use.

7.10 Rinse the joints of the Allihn cooling condensers with Methylene Chloride, collecting the waste in a methylene chloride solvent waste container. Place each of the Soxhlet extractors in a heating mantle and lower the Allihn cooling water

condensers into the 45/50 joints of the extractors. The condensers should be set to a temperature of 15ºC. Save the pieces of aluminum foil for covering the Soxhlets when the extraction is complete. Switch on the individual heating mantles and be sure that the Rheostat of the variable transformer is set to 55% of the output voltage. Once the methylene chloride begins to boil and the Soxhlet begins to cycle (solvent will immerse the sample and collect in the Soxhlet until the level reaches that of the small siphon tube and then begin to spill over into the extract flask), re-check the apparatus' for leaks. Allow the samples to extract for 18-24 hours. Be sure the chiller/recirculator temperature is set low enough to provide enough cooling capacity for the number of extractions in the batch.

7.11 When the extraction is complete, allow the extracts to cool before dismantling. Remove the Allihn condenser and replace the aluminum foil on top of the extractor. Move the extractors to a hood and detach the extractor from the extract flask. Tilt each extractor slightly to cause any remaining solvent in the sample chamber to drain through the siphon tube into the extract flask. This will help to cool the extract flask and make the apparatus easier to dismantle. Try to drain as much solvent as possible from the extractor into the flask. **This is done by rinsing a glass tube in methylene chloride and pressing on the sample slightly so that as solvent as possible is drained into the extract flask.** Cover the flask with aluminum foil and store in the interim extract storage refrigerator unless the extracts are to be concentrated the same day.

7.12 Immediately remove the extracted soil/sodium sulfate mixtures from the extractors using a square edge spatula, and dispose of in an appropriate solid waste container. It is important to do this soon after the extractors are dismantled, as the sample mixture will tend to "freeze" into a solid mass in the Soxhlet as the solvent dries.

CONCENTRATION OF THE EXTRACTS

7.13 Rinse the K-D glassware (flask, concentration tube, and Snyder column, including the ground glass joints on the flask and columns) three times with methylene chloride before assembling. Add a few boiling chips to the K-D. Insert fluted 18.5 cm filter papers into short stem powder funnels and add ~ 2 inches of sodium sulfate crystals. Rinse the sodium sulfate in the assembled funnels with ~20-30 mLs of methylene chloride. Place the assembled K-D's under the funnels. Record the lot numbers of the solvent, sodium sulfate and filter papers in the extraction logbook.

7.14 If samples are to be GPC'd, refer to the current revision of Katahdin SOP CA-513, Extract Cleanup Using Gel Permeation Chromatography, for appropriate concentrating procedures. Samples that undergo GPC are not solvent exchanged into hexane.

7.15 If samples are not to be GPC'd follow Steps 7.16 through 7.23 to concentrate extracts to final volume of 10.0 mLs

7.16 For a solvent exchange, (for samples not being GPC'd), add approximately 50 mL hexane to funnel and let drain through. Since methylene chloride has a lower boiling point than Hexane, this will result in a final extract in hexane only. Record the lot number of the solvent in the extraction logbook.

7.17 Transfer the extracts to the K-D concentrator setups through the sodium sulfate in the funnels. This is the drying step, which is required to remove residual water from the extracts. Any large water layers must be removed by other means, prior to pouring through the sodium sulfate. After pouring all of the extract volume through the sodium sulfate, rinse the extract flask three times with ~ 2 – 3 mLs of methylene chloride. Add the rinsings through the sodium sulfate to complete a quantitative transfer. Rinse the sodium sulfate with ~ 15 mLs of methylene chloride and allow to drain.

7.18 Transfer the labels from the extract flasks to the K-Ds. Remove the funnel and attach a 3-ball macro Snyder column. Pre-wet the Snyder column with 1 mL of methylene chloride.

7.19 Place the K-D in a hot water bath (75-85°C). Gently swirl K-D in the water until boiling begins. At the proper distillation rate, the Snyder balls should chatter but the chambers should not flood with condensed solvent. The K-D should be kept in a vertical orientation while on the bath. When the apparent volume in the concentrator tube reaches ≈ 6 mL, remove the K-D from the water bath. Allow the K-D to cool for 10 minutes. Rinse the Snyder column lower joint with ≈ 1 mL of methylene chloride, hexane, if exchange is taking place. Remove the Snyder column. Wipe off any water from the neck above the lower joint of the flask. Separate the K-D flask from the concentrator tube, rinsing the ground glass joint with ≈ 1 mL methylene chloride, hexane, if exchange is taking place.

7.20 Reduce the extract in the concentrator tube to approximately 1-2 mL using the nitrogen blow-down apparatus to ensure all methylene chloride has been evaporated. The bath temperature must be no higher than the boiling point of the solvent (39°C for methylene chloride). Turn the gas to 3 psi. Be careful not to splash the extract out of the tube. <u>During concentration on the N-evap, the internal wall of the concentrator tube and the N-evap sparging pipet must be rinsed down at least once or twice with ≈1 mL of hexane. The solvent level in the concentrator tube must be positioned below the level of the water bath as much as possible to prevent water from condensing into the sample extract. As the extract volume is reduced, lower the N_2 sparging pipet closer to the surface of the extract to expedite the concentration.</u> Record the temperature of the water in the nitrogen evaporation

water bath in the extraction logbook, also note any problems or extract losses, if they occur.

7.21 Complete quantitative transfer of the extract to a vial by using hexane. Adjust the volume of the hexane extract to 10 mL in either a 12 or 16 mL vial using the appropriate "reference vial" for volume comparison.

7.22 Label the vial with lab sample number, extraction date, matrix and analysis. Store extract vials at a temperature of 4 ± 2 °C until ready for analysis. Indicate in the extractions logbook the box number and "tray location" of the individual extract vials.

7.23 All sample extracts for 8082 PCB analysis must undergo a sulfuric acid wash (cleanup) prior to analysis, unless it has been GPC'd. All sample extracts for 8081 pesticide analysis should undergo further cleanup using the GPC unless time is a factor. All sample extracts for combined 8081/8082 analyses must be split unless GPC'd. One portion must be acid cleaned for 8082 analysis. The associated method blank must be split and acid-cleaned in the same fashion. PCB LCSs and matrix spikes are acid cleaned also. Pesticide LCSs and matrix spikes are not subjected to further cleanup. Record the lot number of the acid in the extraction logbook. Please refer to Katahdin SOP CA525 (current revision), Extract Cleanup Using Sulfuric Acid, for further instructions.

8.0 QUALITY CONTROL AND ACCEPTANCE CRITERIA

A method blank must be extracted for <u>each</u> and <u>every</u> item listed below:

- Each sample matrix (soil, water)
- Each day of extraction (24 hours midnight - midnight)
- Each extraction method or level
- Every 20 samples extracted in a 24-hour period

A laboratory control sample (LCS) is required for <u>each</u> and <u>every</u> item listed below:

- Each sample matrix
- Each extraction method or level
- Every extraction batch of twenty or fewer samples
- Each analysis (pesticide and/or PCB) to be performed

Refer to the current revision of the applicable Katahdin SOP for analysis of Pesticides and PCBs for quality control acceptance criteria.

Each extractions analyst must demonstrate proficiency in performing the extractions that prepare samples for analysis. Demonstration consists of preparation (extraction), by the

analyst, of at least four aliquots which are then analyzed according to the analytical method in question. These QC samples must meet all quality control acceptance limits. Demonstration must be documented by use of a form which summarizes the results of the analysis of these aliquots, calculated percent recoveries, and standard deviation. Demonstration of proficiency must be done one time per analyst initially and then annually thereafter. Refer to SOPs QA-805 and QA-807, current revision.

If, upon analysis of the extracted samples, it is discovered that quality control acceptance criteria have not been met, all associated samples must be evaluated against all the QC. In some cases data may be reported, perhaps with narration, while in other cases, other corrective action may be taken. The corrective actions may include re-extraction of the samples associated with the quality control sample that did not meet acceptance criteria, or may include making new reagents and standards if the standardization is suspect. These decisions are based on holding time considerations, client and project specific Data Quality Objectives and on review of chromatograms. The supervisor, Operations Manager, and/or Quality Assurance Officer may be consulted to evaluate data. Some samples may not be able to be reanalyzed within hold time. In these cases “qualified” data with narration may be advisable after consultation with the client.

Much of the work performed at the lab is analyzed in accordance with specific QC requirements spelled out in a project specific Quality Assurance Project Plan (QAPP) or in a program specific Quality Systems Manual (QSM). The reporting limits, acceptance criteria and/or corrective actions may be different than those specified in this SOP. In these cases the appropriate information will be communicated to the Department Manager and/or senior chemists before initiation of the analyses so that specific product codes can be produced for the project. In addition, the work order notes for each project will describe the specific QAPP or QSM to be followed.

9.0 METHOD PERFORMANCE

The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. The MDLs are determined per type of instrument and filed with the Organic Department Manager and with the QAO. Refer to the current revision of Katahdin SOP QA-806, Method Detection Limit, Method Detection Limit, Instrument Detection Limit and reporting Limit Studies and Verifications, for procedures on determining the MDL.

Refer to the applicable analytical SOP for other method performance parameters and requirements.

TITLE: **PREPARATION OF SEDIMENT/SOIL SAMPLES BY SOXHLET EXTRACTION USING METHOD 3540 FOR PESTICIDE/PCB ANALYSIS**

10.0 APPLICABLE DOCUMENTS/REFERENCES

Test Methods for Evaluating Solid Waste-Physical/Chemical Methods, Method 3540C, SW-846, Third Edition, Updates I, II, IIA, IIB, and III Revised December 1996, US EPA.

Department of Defense Quality Systems Manual for Environmental Laboratories (DOD QSM), Version 4.1, 04/22/09.

The National Environmental Laboratory Accreditation Conference (NELAC) Standards, June 2003.

LIST OF TABLES AND FIGURES

Table 1 Summary of Method Modifications
Figure 1 Example of Logbook Page

TITLE: **PREPARATION OF SEDIMENT/SOIL SAMPLES BY SOXHLET EXTRACTION USING METHOD 3540 FOR PESTICIDE/PCB ANALYSIS**

TABLE 1

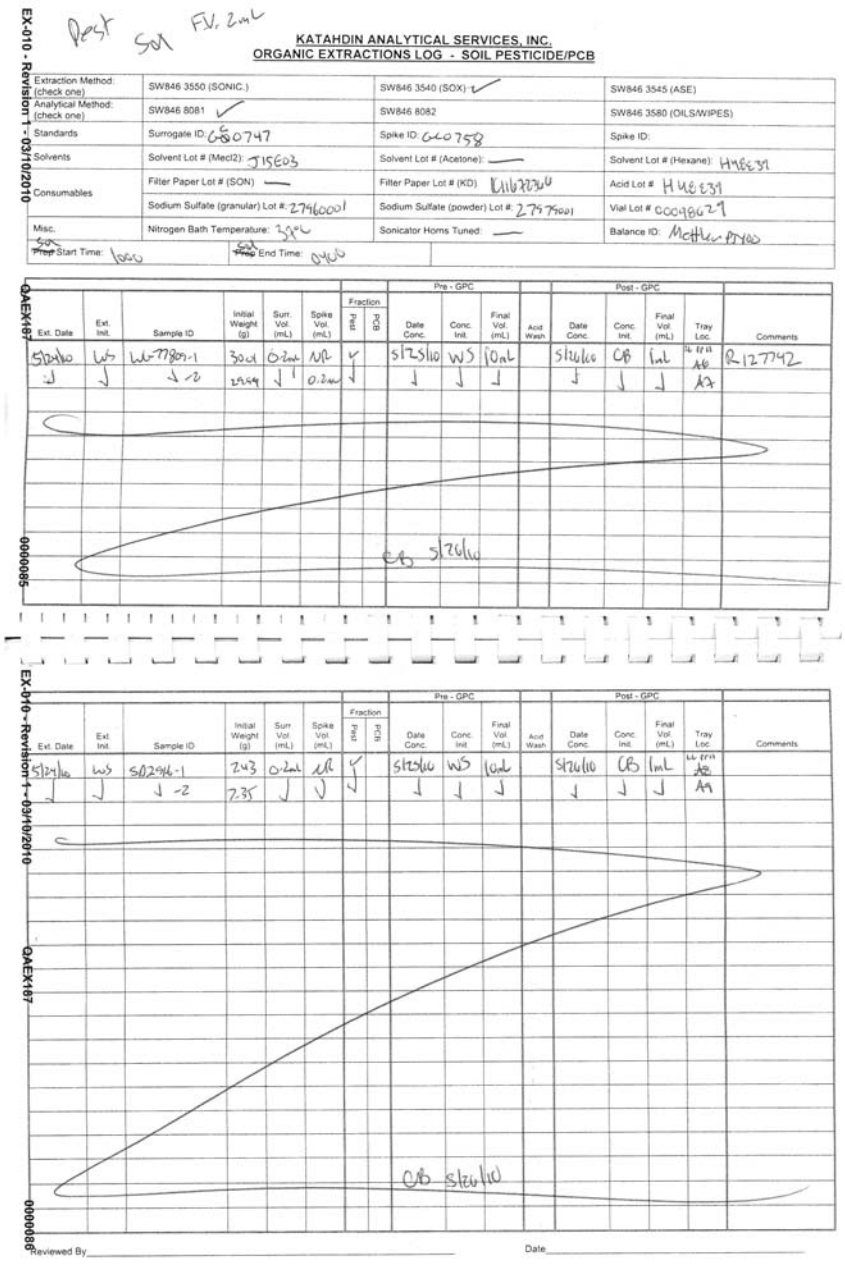
SUMMARY OF METHOD MODIFICATIONS

TOPIC	KATAHDIN SOP CA-524-07	METHOD 3540, current revision
Apparatus/Materials	1. short stem funnels	1. drying columns
Reagents		
Sample preservation/ handling		
Procedures	1. Use 30 grams of sample and 30 grams of sodium sulfate. 2. Use 250 mL of methylene chloride 3. no apparatus height specification for concentration on water bath 4. water bath at 75-85 deg C 5. sample removed from water bath when volume reaches ~6 mL 6. Solvent exchange to hexane is performed using K-D apparatus with addition of approximately 50 mL hexane at the start of concentration process	1. Use 10 grams of sample and 10 grams of sodium sulfate. 2. Use 300 mL of methylene chloride 3. partially immerse concentrator tube in water and lower apparatus to complete concentration in 10-15min 4. water bath at 80-90 deg C 5. sample removed from water bath when volume reaches 1-2 mL 6. Solvent exchange to hexane is performed using K-D apparatus with addition of approximately 50 mL hexane after concentrating methylene chloride extract to 1 mL
QC - Spikes		
QC - LCS		
QC - Accuracy/Precision		
QC - MDL		

TITLE: **PREPARATION OF SEDIMENT/SOIL SAMPLES BY SOXHLET EXTRACTION USING METHOD 3540 FOR PESTICIDE/PCB ANALYSIS**

FIGURE 1

EXAMPLE OF LOGBOOK PAGE



Pest Soil FV. 2mL

KATAHDIN ANALYTICAL SERVICES, INC.
ORGANIC EXTRACTIONS LOG - SOIL PESTICIDE/PCB

Extraction Method: (check one)	SW846 3550 (SONIC.)	SW846 3540 (SOX) ✓	SW846 3545 (ASE)
Analytical Method: (check one)	SW846 8081 ✓	SW846 8082	SW846 3580 (OILS/WIPES)
Standards	Surrogate ID: GC0747	Spike ID: GC0758	Spike ID:
Solvents	Solvent Lot # (Mecl2): J15E03	Solvent Lot # (Acetone): —	Solvent Lot # (Hexane): H46E31
Consumables	Filter Paper Lot # (SON) —	Filter Paper Lot # (KD) K1127736	Acid Lot # H46E31
	Sodium Sulfate (granular) Lot #: 2746001	Sodium Sulfate (powder) Lot #: 2747501	Vial Lot # G0048627
Misc.	Nitrogen Bath Temperature: 39°C	Sonicator Horns Tuned: —	Balance ID: McHlw-PT400
~~Prep~~ Start Time: 1000	~~Prep~~ End Time: 0400		

Ext. Date	Ext. Init.	Sample ID	Initial Weight (g)	Surr. Vol. (mL)	Spike Vol. (mL)	Fraction Pest	Fraction PCB	Pre - GPC Date Conc.	Pre - GPC Conc. Init.	Pre - GPC Final Vol. (mL)	Acid Wash	Post - GPC Date Conc.	Post - GPC Conc. Init.	Post - GPC Final Vol. (mL)	Tray Loc.	Comments
5/24/10	WS	WW-77809-1	30.01	0.2mL	NA	✓		5/25/10	WS	10mL		5/26/10	CB	1mL	~~AB~~ A8	R127742
↓	↓	↓ -2	29.99	↓	0.2mL	↓		↓	↓	↓		↓	↓	↓	A7	

CB 5/26/10

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Ext. Date	Ext. Init.	Sample ID	Initial Weight (g)	Surr. Vol. (mL)	Spike Vol. (mL)	Fraction Pest	Fraction PCB	Pre - GPC Date Conc.	Pre - GPC Conc. Init.	Pre - GPC Final Vol. (mL)	Acid Wash	Post - GPC Date Conc.	Post - GPC Conc. Init.	Post - GPC Final Vol. (mL)	Tray Loc.	Comments
5/24/10	WS	SO2946-1	7.43	0.2mL	NA	✓		5/25/10	WS	10mL		5/26/10	CB	1mL	~~AB~~ A8	
↓	↓	↓ -2	7.35	↓	↓	↓		↓	↓	↓		↓	↓	↓	A9	

CB 5/26/10

QAEX187 EX-010 - Revision 1 - 03/10/2010 0000086

Reviewed By_____ Date_____

TITLE: **PREPARATION OF SEDIMENT/SOIL SAMPLES BY SOXHLET EXTRACTION USING METHOD 3540 FOR SUBSEQUENT EXTRACTABLE SEMIVOLATILE ANALYSIS**

Prepared By: Mike Thomas Date: 7/98

Approved By:

Group Supervisor: Michael Thomas Date: 11/15/00

Operations Manager: J C Benton Date: 11/15/00

QA Officer: Deborah J. Nadeau Date: 11.16.00

General Manager: Dennis F. Hufnagel Date: 11/20/00

Revision History:

SOP Revision	Changes	Approval Initials	Approval Date	Effective Date
01	Minor changes throughout. Clarifications to procedure section.	DN	11.16.00	11/16/00
02	Definitions added to section 1.1. Wording was added or changed to clarify sections 4, 5, 6, 7, 8 + 9. Minor changes throughout. New figures.	MRC	11.09.04	11.09.04
03 LAD 6-26-06	Updated Sect. 7.0 to include SIM. Updated figures 2 and 3 to include current SVOA ~~spikes~~ compounds used. Updated Sect. 5.0 to include all compounds analyzed for. Updated logbook page. minor edits throughout.	LAD	04/06	04/06
04	Added waste generated information. Updated Spikes and Surrogates. Added SIM LCSD and MS/D requirements. Updated Table 1. Added GPC references. Added LCSD after LCS.	LAD	09/07	09/07
05	Updated logbook page. Added adipate compounds to Fig. 2. Added recording of consumable's lot #'s and recording the nitrogen water bath temp. in logbook	LAD	07/08	07/08

TITLE: PREPARATION OF SEDIMENT/SOIL SAMPLES BY SOXHLET EXTRACTION USING METHOD 3540 FOR SUBSEQUENT EXTRACTABLE SEMIVOLATILE ANALYSIS

SOP Revision	Changes	Approval Initials	Approval Date	Effective Date
06	Added balance criteria. Changed all weight criteria to +/- 0.05g. Revised section 7 to reflect current techniques. Added SOP CA-108 reference for sub-sampling. Updated logbook example	LAD	08/09	08/09
07	Removed targeting sample weights. Added to weigh out a minimum 30g sample. Removed decanting samples prior to extracting. Added putting solid waste in the "I" waste stream. Updated Logbook page.	LAD	08/10	08/10

TITLE: **PREPARATION OF SEDIMENT/SOIL SAMPLES BY SOXHLET EXTRACTION USING METHOD 3540 FOR SUBSEQUENT EXTRACTABLE SEMIVOLATILE ANALYSIS**

Please acknowledge receipt of this standard operating procedure by signing and dating both of the spaces provided. Return the bottom half of this sheet to the QA Department.

I acknowledge receipt of copy ___ of document **SOP CA-526-07**, titled **PREPARATION OF SEDIMENT/SOIL SAMPLES BY SOXHLET EXTRACTION USING METHOD 3540 FOR SUBSEQUENT EXTRACTABLE SEMIVOLATILE ANALYSIS.**

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STANDARD OPERATING PROCEDURE

I acknowledge receipt of copy ___ of document **SOP CA-526-07**, titled **PREPARATION OF SEDIMENT/SOIL SAMPLES BY SOXHLET EXTRACTION USING METHOD 3540 FOR SUBSEQUENT EXTRACTABLE SEMIVOLATILE ANALYSIS.**

Recipient: _____ Date: _____

TITLE: **PREPARATION OF SEDIMENT/SOIL SAMPLES BY SOXHLET EXTRACTION USING METHOD 3540 FOR SUBSEQUENT EXTRACTABLE SEMIVOLATILE ANALYSIS**

1.0 SCOPE AND APPLICATION

The purpose of this SOP is to describe the procedures and requirements for extracting semivolatile organic compounds from solids such as soils, sludges, and wastes using Method 3540. The Soxhlet extraction process ensures intimate contact the sample matrix with the extraction solvent.

This method is applicable to the isolation and concentration of water-insoluble and slightly water soluble organics in preparation for a variety of chromatographic procedures.

1.1 Definitions

METHOD BLANK (laboratory reagent blank): An artificial sample designed to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus. For aqueous samples, reagent water is used as a blank matrix; for soil samples, baked organic-free sand is used as a blank matrix. The blank is taken through the appropriate steps of the process.

LABORATORY CONTROL SAMPLE (LCS): A blank that has been spiked with the analyte(s) from an independent source, and is analyzed exactly like a sample. Its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements. The matrix used should be phase matched with the samples and well characterized.

MATRIX SPIKE/MATRIX SPIKE DUPLICATE (MS/MSD): Predetermined quantities of stock solutions of certain analytes are added to a sample matrix prior to sample extraction and analysis. Samples are split into duplicates, spiked and analyzed. Percent recoveries are calculated for each of the analytes detected. The relative percent difference between the samples is calculated and used to assess analytical precision.

SURROGATES: Organic compounds which are similar to analytes of interest in chemical composition, extraction and chromatography, but which are not normally found in environmental samples. These compounds are spiked into all blanks, standards, samples and spiked samples prior to analysis. Percent recoveries are calculated for each surrogate.

1.2 Responsibilities

This method is restricted to use by, or under the supervision of analysts experienced in the extraction of samples for semivolatile analysis. Each analyst must demonstrate and document their ability to generate acceptable results with this method. Refer to Katahdin SOP QA-805, current revision, “Personnel Training and Documentation of Capability”.

It is the responsibility of all Katahdin technical personnel involved in the extraction of samples for semivolatile analysis to read and understand this SOP, adhere to the procedures outlined, and to properly document their data in the appropriate lab notebook. Any deviations from the test or irregularities with the samples should also be recorded in the lab notebook and reported to the Department Manager or designated qualified data reviewer responsible for this data.

It is the responsibility of the Department Manager to oversee that the members of his/her group follow this SOP, to assure that their work is properly documented, and to indicate periodic review of the pertinent logbooks.

1.3 Safety

Users of this procedure must be cognizant of inherent laboratory hazards, proper disposal procedures for contaminated materials and appropriate segregation of hazardous wastes. The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical should be treated as a potential health hazard. A reference file of material safety data sheets is available to all personnel involved in the chemical analysis. Everyone involved with the procedure must be familiar with the MSDSs for all the materials used in this procedure.

Each qualified analyst or technician must be familiar with Katahdin Analytical Environmental Health and Safety Manual including the Katahdin Hazardous Waste Plan and must follow appropriate procedures. These include the use of appropriate personal protective equipment (PPE) such as safety glasses, gloves and lab coats when working with chemicals or near an instrument and not taking food or drink into the laboratory. Each analyst should know the location of all safety equipment. Each analyst shall receive a safety orientation from their Department Manager, or designee, appropriate for the job functions they will perform.

1.4 Waste Disposal

Wastes generated during the preparation of samples must be disposed of in accordance with the procedures described in the current revision of the Katahdin Hazardous Waste Plan and Safety Manual and SOP SD-903, “Sample Disposal,” current revision. Expired standards are lab packed, placed in the Katahdin hazardous waste storage area, and disposed of in accordance with this SOP.

Any methylene chloride solvent waste generated during the rinsing of glassware etc. should be disposed of in the “D” waste stream satellite accumulation area nearest the point of generation. Acetone and methanol are considered flammable waste, and should be disposed of in the “O” waste stream satellite accumulation area nearest the point of generation. Post-extraction soil samples, used glass wool, and sodium sulfate waste should be disposed of in the soil with organics “I” waste stream satellite

accumulation area nearest the point of generation. Please refer to the current revision of SOP CA-107 for the location of satellite waste accumulation areas.

2.0 SUMMARY OF METHOD

2.1 The solid sample is mixed with anhydrous sodium sulfate, placed in a Soxhlet extractor and extracted with methylene chloride.

2.2 The extract is then dried and concentrated for subsequent 8270 Semivolatile Organics analysis.

3.0 INTERFERENCES

Contaminants in solvents, reagents, glassware, and other sample processing hardware may cause method interferences such as discrete artifacts and/or elevated baselines in the total ion current profiles (TICPs). All of these materials routinely must be demonstrated to be free from interferences under the conditions of the analysis by running laboratory method blanks. Interferences caused by phthalate esters can pose a major problem in semivolatile organics analysis because many phthalates are also target analytes. Common flexible plastics contain varying amounts of phthalates that are easily extracted during laboratory operations, so cross-contamination of glassware frequently occurs when plastics are handled. Interferences from phthalates can best be minimized by avoiding the use of such plastics in the laboratory. At no time may gloves that have not been tested for phthalates or gloves known to contain phthalates be used or stored in the organic extraction lab. Additionally, whenever possible plastic items in this lab must be replaced with metal or Teflon or other non-phthalate plastic substitute.

Special care should be taken to ensure clean glassware and apparatus are used, pre-rinsed with the appropriate solvent prior to use. Solvents should be analyzed prior to use to demonstrate that each lot is free of contaminants that may interfere with the analysis.

Interferences coextracted from the samples will vary considerably from source to source. If analysis of an extracted sample is prevented due to interferences, further cleanup of the sample extract may be needed to minimize interferences.

4.0 APPARATUS AND MATERIALS

4.1 Soxhlet apparatus:

4.1.1 Soxhlet extractor – 45/50 top joint and 24/40 lower joint.

4.1.2 500 mL flat-bottom boiling flask

4.1.3 Allihn cooling water condenser

4.2 Powder Funnels – 100 mm top diameter, 35 mm stem

4.3 Kuderna-Danish (K-D) apparatus

4.3.1 Concentrator tube - 10-mL

4.3.2 Evaporation flask - 500-mL

4.3.3 Snyder column - Three-ball macro

4.4 Nitrogen evaporation (N-EVAP) apparatus.

4.5 Boiling stones, 12 mesh silicon carbide (carborundum) – pre-purified by Soxhlet extraction in methylene chloride

4.6 Water bath - Heated, with concentric ring cover, capable of temperature control (± 5°C). The bath should be used in a hood.

4.7 Vials - Glass, 1.8-mL capacity, with polytetrafluoroethylene (PTFE)-lined septum vials, and 12 mL with Teflon-lined caps for extracts designated for GPC cleanup.

4.8 Glass wool (fiberglass) - baked at 400°C for a minimum of 4 hours or overnight.

4.9 Heating mantles - Rheostat controlled.

4.10 Disposable glass pasteur pipets, 5 ¾” and bulbs.

4.11 Drying oven - capable of maintaining 105°C for glassware drying.

4.12 Muffle oven – capable of maintaining 400 °C for baking glass wool and organic-free sand.

4.13 Beakers, 250 or 400 mL

4.14 Top-loading balance - capable of weighing to 0.**01** g.

4.15 Spatulas, stainless-steel

4.16 Long forceps, stainless-steel

4.17 Metal clips – for securing Soxhlets to boiling flasks

4.18 Filter Paper, 18.5 cm, Fisherbrand or Whatman 114V (or equivalent)

5.0 REAGENTS

5.1 Sodium Sulfate - anhydrous powdered and granular crystals, reagent grade, certified by the manufacturer/vendor as purified heating to 400°C prior to receipt by the laboratory.

5.2 Methylene chloride, methanol, and acetone - pesticide residue analysis grade or equivalent. Methylene chloride and acetone are evaluated, by lot, prior to use, by concentration of approximately 400 mL to 1.0 mL followed by GC/MS analysis.

5.3 Organic-free sand, purified by baking at 400 °C. Method blanks serve as checks on the baked sand.

5.4 Base/Neutral and Acid (SVOA) Surrogate Spiking Solution - Surrogate standards are added to all samples and calibration solutions. Prepare a surrogate standard spiking solution that contains the following compounds at the indicated concentrations in acetone.

Compound	Conc.
phenol-$_{d6}$	100 ug/mL
2,4,6-tribromophenol	100 ug/mL
2-fluorophenol	100 ug/mL
nitrobenzene-$_{d5}$	50 ug/mL
p-terphenyl-$_{d14}$	50 ug/mL
2-fluorobiphenyl	50 ug/mL

Store the spiking solution at -10°C to -20°C in Teflon-sealed containers. These solutions must be replaced after six months, or sooner if comparison with quality control check samples indicates a problem. If reanalysis of a method blank still indicates surrogates out of criteria, a new surrogate solution must be used.

5.5 SIM Surrogate Spiking Solution- Surrogate Standards are added to all samples and calibration solutions. Prepare a surrogate solution that contains the following compounds at a concentration of 2 ug/mL in acetone.

Compound	Conc. ug/mL
Fluorene-d10	2.0 ug/mL
2-Methylnaphthalene-d10	2.0 ug/mL
Pyrene-d10.	2.0 ug/mL
2,4-Dibromophenol	2.0 ug/mL

Store the spiking solution at -10°C to -20°C in Teflon-sealed containers. These solutions must be replaced after six months, or sooner if comparison with quality control check samples indicates a problem. If reanalysis of a method blank still indicates surrogates out of criteria, a new surrogate solution must be used.

5.6 Base/Neutral and Acid (SVOA) Lab Control Sample / Matrix Spike Spiking Solution - Prepare a spiking solution in methanol that contains the following mixes listed in Figure 2 at a concentration of 50 ug/ml for the base/neutral compounds and 100 ug/ml for the acid compounds. Store the spiking solution at -10°C to -20°C in Teflon-sealed containers. These solutions must be replaced after six months, or sooner if comparison with quality control check samples indicates a problem.

5.7 Base/Neutral (SIM) Matrix Spike/ Lab Control Sample Spike Solution for SIM-SVOA. Prepare a spiking solution in methanol that contains the compounds listed in Figure 2 at a concentration of 2 ug/mL for base/neutral. Take out 1.0 mL of Base/Neutral and Acid Matrix Spike/Lab Control Spiking Solution for SVOA and dilute it to 25.0 mL in methanol. Store the solution Spiking at -10°C to -20°C in Teflon-sealed containers. These solutions must be replaced after six months, or sooner if comparison with quality control check samples indicates a problem.

5.8 Base/Neutral and Acid (SVOA) Appendix IX Lab Control Sample / Matrix Spike Spiking Solution – Prepare a spiking solution in methanol that contains the compounds listed in Figure 3 at concentrations of 100 ug/ml. Store the spiking solution at -10°C to -20°C in Teflon-sealed containers. These solutions must be replaced after six months, or sooner if comparison with quality control check samples indicates a problem.

6.0 SAMPLE COLLECTION, PRESERVATION AND HANDLING

Sediment/soil samples must be collected in a soil jar and must be maintained at 4°C (±2°C).

Holding time for extraction of sediment/soil samples for Method 3540 is 14 days from date of sample collection, although the analyst should be aware that actual holding times employed may be project/program specific.

Store all extracts at 4°C (±2°C) in the dark in labeled Teflon-sealed containers. See SOP SD-902, "Sample Receipt and Internal Control," current revision, for storage areas and temperature maintenance procedures.

TITLE: **PREPARATION OF SEDIMENT/SOIL SAMPLES BY SOXHLET EXTRACTION USING METHOD 3540 FOR SUBSEQUENT EXTRACTABLE SEMIVOLATILE ANALYSIS**

7.0 PROCEDURES

The following information must be recorded in the extraction logbook (all that are applicable).

- Extraction method
- Surrogate and spike IDs
- Lot numbers of all solvents, acids and bases, sodium sulfate, filter paper
- Nitrogen evaporation water bath temperature
- pH
- Sonicator horns tuned?
- Extraction and concentration dates
- Extraction and concentration analyst
- Separatory funnel and sonication extraction start and end times.
- CLLE and Soxhlet extraction start and end times, also the prep start and end times.
- Sample ID or QC sample ID
- Initial and final volumes or weight
- Surrogate and spike amounts
- Final extract tray location
- Any comments regarding the sample extraction (ie. Emulsion)

All solid samples need to be cleaned up to reduce matrix interferences, time permitting. The cleanup procedure employed is gel permeation chromatography (GPC).

Samples need to be “swiped” out when removing and “swiped” in when replacing samples in storage locations to maintain the internal chain of custody. Refer to Katahdin SOP, Sample Receipt and Internal Control, current revision, for the proper procedure for removal and return samples.

Fill out the sample preparation/extraction log with the necessary information before starting the extraction.

Prerinse all glassware three times with methylene chloride.

7.1 Preparing the Soxhlet Extraction Apparatus

7.1.1 Rinse the Soxhlet extractors and 500 mL flat-bottom boiling flasks three times with methylene chloride. Be sure that the solvent rinses through the large vapor tube and smaller siphon tubes of the Soxhlet. Inspect these for tiny cracks. Also rinse the 24/40 lower joint.

7.1.2 Add ~ 250 mLs of methylene chloride to the 500 mL boiling flask. Add several boiling stones. Using stainless steel forceps and working in a hood,

place a plug of the pre-baked glass wool at the bottom of the Soxhlet so that the siphon tube hole is covered. Insert the 24/40 joint of the Soxhlet extractor into the 500 mL boiling flask and secure with a metal clip. Cover the top of the Soxhlet extractor with a piece of aluminum foil until ready to begin loading the sample. Record the solvent lot number in the extraction logbook.

7.2 Sample Handling

7.2.1 Sediment/soil samples – Do not decant any water layer on a sediment sample. Mix the sample thoroughly with the stainless steel spatula. If the sample container is full to the extent that stirring the sample is impractical, try to remove the "best representative" aliquot from the jar based on color, particle size, moisture, etc. Discard any foreign objects such as sticks, leaves, and rocks.

7.2.2 Gummy, fibrous, or oily materials not amenable to mixing should be cut, shredded, or otherwise reduced in size to allow for maximum exposure of the sample surfaces to the extraction solvent. Materials such as glass, rubber, metal, etc. may not require mixing with powdered sodium sulfate to disperse the sample. Plastic materials must be tested for degradation (melting) in methylene chloride prior to Soxhlet extraction.

7.2.3 Refer to Katahdin SOP CA-108, current revision, "Basic Laboratory Technique" for more information on subsampling.

7.3 The following steps should be performed <u>rapidly</u> <u>to</u> <u>avoid</u> <u>loss</u> <u>of the</u> <u>more</u> <u>volatile</u> <u>extractables</u>. Weigh out an approximate, greater than 30 g portion of sample into a labeled 400-mL beaker. Record sample weight to the nearest 0.01 g in appropriate extraction logbook. Add between 30 g and 60 g of anhydrous powdered sodium sulfate as required to produce a "free-flowing" mixture. The amount of sodium sulfate added will depend upon the moisture content of the sample (e.g., low moisture content will require less sodium sulfate). Mix well with a spatula. Keep the spatula in the sample beaker and <u>cover</u> the beaker with aluminum foil.

7.4 A method blank must be prepared with each extraction batch, not to exceed 20 client samples. To prepare method blank, weigh out one greater than 30 g portion of purified sand in a labeled 400 mL beaker. Add 60 g sodium sulfate and mix well. Although a "free-flowing" mixture can be achieved with less than 60 g sodium sulfate, the method blank must contain 60 g in order to evaluate the sodium sulfate as a potential source of contamination.

7.5 A laboratory control sample (LCS) must be prepared with each extraction batch, not to exceed 20 client samples. To prepare LCS, weigh out one greater 30 g portion of

purified sand in a labeled 400 mL beaker. Add 30 g sodium sulfate and mix well. If combined SIM-SVOA analysis is requested, a separate LCS must be prepared for each analysis. If an MS/MSD pair is not extracted on a particular day, an LCS/LCSD pair may be required in order to meet client-specific or program-specific requirements. This information will be disseminated from the project manager or Department Manager.

7.6 A matrix spike/matrix spike duplicate (MS/MSD) set must be prepared for every 20 samples. To prepare MS/MSD, weigh out two approximate, greater than 30 portions of the sample designated for MS/MSD into each of two labeled 400 mL beakers. Record sample weights to nearest 0.01 g in appropriate extraction logbook. Add 30 - 60 g sodium sulfate to each to produce a free-flowing mixture, and mix well. If combined SIM-SVOA analysis is requested, a separate MS/MSD must be prepared for each analysis.

7.7 Once all of the QC and field samples have been weighed and mixed with sodium sulfate, begin adding each to the assembled and appropriately labeled Soxhlet extractors using the stainless steel spatulas. Carefully scrape all of the mixtures from the beaker walls so that no more than 1% remains behind in the beaker. Be careful not to have any of the solid material fall into the extract flask through the large vapor tube.

7.8 To all samples, method blank, LCS/LCSD, and MS/MSD add 1.0 mL of the appropriate base/neutral and acid surrogate spiking solution listed below using the pre-rinsed 1.0 mL gas tight syringe. Record surrogate spike volume and identification code in extraction logbook. Thoroughly rinse syringe with solvent prior to using it for another spiking solution.

7.8.1 If the request is for SVOA, use the SVOA surrogate solution (sect. 5.4)

7.8.2 If the request is for SIM, use the SIM surrogate solution (sect. 5.5).

7.8.3 If the request is for SIM-SVOA, use both the SIM and SVOA surrogate solutions. NOTE: Separate LCS/LCSD and/or MS/MSD are needed for each analysis and should be spiked with the appropriate surrogate.

7.9 To the LCS/LCSD and the MS/MSD add 1.0 mL of the appropriate base/neutral and acid (SVOA) matrix spike/LCS spiking solution listed below using a 1.0 mL gas tight syringe. Record matrix spike/LCS spiking solution volume and identification code in extraction logbook. Thoroughly rinse syringe with solvent when spiking is completed.

7.9.1 If the request is for SVOA, add 1 mL of the SVOA spiking solution (sect. 5.6).

7.9.2 If the request is for SIM, add 1 mL of the SIM Spiking solution (sect. 5.7).

7.9.3 If the request is for SVOA/SIM, add 1 mL of the SVOA spiking solution and 1 mL of the SIM Spiking solution to appropriate LCS/LCSD and/or MS/MSD. (sect's 5.6 and 5.7).

7.9.4 If the request is for SVOA Appendix IX, add 1 mL of the SVOA Appendix IX spiking solution and 1 mL of the SVOA spiking solution (sect's 5.6 and 5.8).

7.10 Place each of the Soxhlet extractors in a heating mantle and lower the Allihn cooling water condensers into the 45/50 joints of the extractors. Save the pieces of aluminum foil for covering the Soxhlets when the extraction is complete. Switch on the individual heating mantles and be sure that the Rheostat of the variable transformer is set to 55-60% of the output voltage. Once the methylene chloride begins to boil and the Soxhlet begins to cycle (solvent will immerse the sample and collect in the Soxhlet until the level reaches that of the small siphon tube and then begin to spill over into the extract flask), re-check the apparatus' for leaks. Allow the samples to extract for 18-24 hours. Be sure the chiller/recirculator temperature is set low enough to provide enough cooling capacity for the number of extractions in the batch.

7.11 When the extraction is complete, allow the extracts to cool before dismantling. Tilt each extractor slightly to cause any remaining solvent in the sample chamber to drain through the siphon tube into the extract flask. This will help to cool the extract flask and make the apparatus easier to dismantle. Remove the Allihn condenser and replace the aluminum foil on top of the extractor. Move the extractors to a hood and detach the extractor from the extract flask. Try to drain as much solvent as possible from the extractor into the flask. **This is done by rinsing a glass tube in methylene chloride and pressing on the sample slightly so that as solvent as possible is drained into the extract flask.** Cover the flask with aluminum foil and store in the interim extract storage refrigerator unless the extracts are to be concentrated the same day.

7.12 Immediately remove the extracted soil/sodium sulfate mixtures from the extractors using a square edge spatula, and dispose of in an appropriate solid waste container. It is important to do this soon after the extractors are dismantled, as the sample mixture will tend to "freeze" into a solid mass in the Soxhlet as the solvent dries. Put the solid waste in the "I" waste stream.

CONCENTRATION OF EXTRACTS

7.13 Rinse the K-D glassware (flask, concentration tube, and Snyder column, including the ground glass joints on the flask and columns) three times with methylene chloride before assembling. Add two boiling chips to the K-D. Insert 18.5 cm filter

papers into short stem powder funnels and add ~ 2 inches of sodium sulfate crystals. Rinse the sodium sulfate in the assembled funnels with ~20-30 mLs of methylene chloride. Place the assembled K-D's under the funnels. Record the filter paper and sodium sulfate lot numbers in the extraction logbook.

7.14 Transfer the extracts to the K-D concentrator setups through the sodium sulfate in the funnels. This is the drying step, which is required to remove residual water from the extracts. Any large water layers must be removed by other means, prior to pouring through the sodium sulfate. After pouring all of the extract volume through the sodium sulfate, rinse the extract flask three times with ~ 2 – 3 mLs of methylene chloride. Add the rinsings through the sodium sulfate to complete a quantitative transfer. Rinse the sodium sulfate with ~ 15 mLs of methylene chloride and allow draining.

7.15 All samples should go through GPC cleanup except if time does not permit. Refer to the current revision of Katahdin SOP CA-513, Extract Cleanup Using Gel Permeation Chromatography, for appropriate concentrating procedures.

7.16 If samples are not to be GPC'd, when time does not permit, follow Steps 7.17 through 7.22 to concentrate extracts to final volume of 1 mL.

7.17 Transfer the labels from the extract flasks to the K-Ds. Remove the funnel and attach a 3-ball macro Snyder column. Pre-wet the Snyder column with 1 mL of methylene chloride.

7.18 Place the K-D in a hot water bath (75-85°C). Gently swirl K-D in the water until boiling begins. At the proper distillation rate, the Snyder balls should chatter but the chambers should not flood with condensed solvent. The K-D should be kept in a vertical orientation while on the bath. When the apparent volume in the concentrator tube reaches ≈ 4-6 mL, remove the K-D from the water bath. **Do not allow the evaporator to go dry. If the sample extract does go dry, re-extraction must occur immediately.** Allow the K-D to cool for 10 minutes. Rinse the Snyder column lower joint with ≈ 1 mL of methylene chloride. Remove the Snyder column. Wipe off any water from the neck above the lower joint of the flask. Separate the K-D flask from the concentrator tube, rinsing the ground glass joint with ≈ 1 mL methylene chloride.

7.19 Reduce the extract in the concentrator tube to approximately 1 mL using the nitrogen blow-down apparatus. The bath temperature must be no higher than the boiling point of the solvent (39°C for methylene chloride). Turn the gas to 3 psi. Be careful not to splash the extract out of the tube. During concentration on the N-evap, the internal wall of the concentrator tube and the N-evap sparging pipet must be rinsed down at least once or twice with ≈1 mL of methylene chloride. The solvent level in the concentrator tube must be positioned below the level of the water bath

as much as possible to prevent water from condensing into the sample extract. As the extract volume is reduced, lower the N_2 sparging pipet closer to the surface of the extract to expedite the concentration. Record the temperature of the water in the nitrogen evaporation water bath in the extraction logbook, also note any problems or extract losses, if they occur.

7.20 When the apparent volume reaches slightly less than 1 mL, remove the concentrator tube and allow it to cool.

7.21 Complete the quantitative transfer of the extract to a 1.8 mL vial by using methylene chloride. Adjust the volume of the methylene chloride extract to 1.0 mL using the 1.8 mL reference vial for volume comparison.

7.22 Label the vial with lab sample number, extraction date, matrix and analysis. Store extract vials at a temperature of 4 ± 2 °C until ready for analysis. Indicate in the extractions logbook the box number and “tray location” of the individual extract vials.

8.0 QUALITY CONTROL AND ACCEPTANCE CRITERIA

A method blank must be extracted for each and every item listed below:

- Each sample matrix (soil, water)
- Each day of extraction (24 hours midnight - midnight)
- Each extraction method or level
- Every 20 samples extracted in a 24-hour period

A laboratory control sample (LCS) is required for each and every item listed below:

- Each sample matrix
- Each extraction method or level
- Every extraction batch of twenty or fewer samples

Refer to the current revision of the applicable Katahdin SOP for analysis of extractable semivolatile organics for quality control acceptance criteria.

Each extractions analyst must demonstrate proficiency in performing the extractions that prepare samples for analysis. Demonstration consists of preparation (extraction), by the analyst, of at least four aliquots which are then analyzed according to the analytical method in question. These QC samples must meet all quality control acceptance limits. Demonstration must be documented by use of a form which summarizes the results of the analysis of these aliquots, calculated percent recoveries, and standard deviation. Demonstration of proficiency must be done one time per analyst initially and then annually thereafter. Refer to SOPs QA-805 and QA-807, current revision.

If, upon analysis of the extracted samples, it is discovered that quality control acceptance criteria have not been met, all associated samples must be evaluated against all the QC. In some cases data may be reported, perhaps with narration, while in other cases, other corrective action may be taken. The corrective actions may include re-extraction of the samples associated with the quality control sample that did not meet acceptance criteria, or may include making new reagents and standards if the standardization is suspect. These decisions are based on holding time considerations, client and project specific Data Quality Objectives and on review of chromatograms. The supervisor, Operations Manager, and/or Quality Assurance Officer may be consulted to evaluate data. Some samples may not be able to be reanalyzed within hold time. In these cases "qualified" data with narration may be advisable after consultation with the client.

Much of the work performed at the lab is analyzed in accordance with specific QC requirements spelled out in a project specific Quality Assurance Project Plan (QAPP) or in a program specific Quality Systems Manual (QSM). The reporting limits, acceptance criteria and/or corrective actions may be different than those specified in this SOP. In these cases the appropriate information will be communicated to the Department Manager and/or senior chemists before initiation of the analyses so that specific product codes can be produced for the project. In addition, the work order notes for each project will describe the specific QAPP or QSM to be followed.

9.0 METHOD PERFORMANCE

The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. The MDLs are determined per type of instrument and filed with the Organic Department Manager and with the QAO. Refer to the current revision of Katahdin SOP QA-806, Method Detection Limit, Instrument Detection Limit and Reporting Limit Studies and Verifications, for procedures on determining the MDL.

Refer to the applicable analytical SOP for other method performance parameters and requirements.

10.0 APPLICABLE DOCUMENTS/REFERENCES

Test Methods for Evaluating Solid Waste-Physical/Chemical Methods, Method 3540C, SW-846, Third Edition, Updates I, II, IIA, IIB, and III Revised December 1996, US EPA.

Department of Defense Quality Systems Manual for Environmental Laboratories (DOD QSM), Version 4.1, 04/22/09.

TITLE: **PREPARATION OF SEDIMENT/SOIL SAMPLES BY SOXHLET EXTRACTION USING METHOD 3540 FOR SUBSEQUENT EXTRACTABLE SEMIVOLATILE ANALYSIS**

The National Environmental Laboratory Accreditation Conference (NELAC) Standards, June 2003.

Katahdin SOP QA-806, Method Detection Limit, Instrument Detection Limit and Reporting Limit Studies and Verifications, current revision.

LIST OF TABLES AND FIGURES

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Figure 2 LCS/Matrix Spike Component List
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TITLE: **PREPARATION OF SEDIMENT/SOIL SAMPLES BY SOXHLET EXTRACTION USING METHOD 3540 FOR SUBSEQUENT EXTRACTABLE SEMIVOLATILE ANALYSIS**

TABLE 1

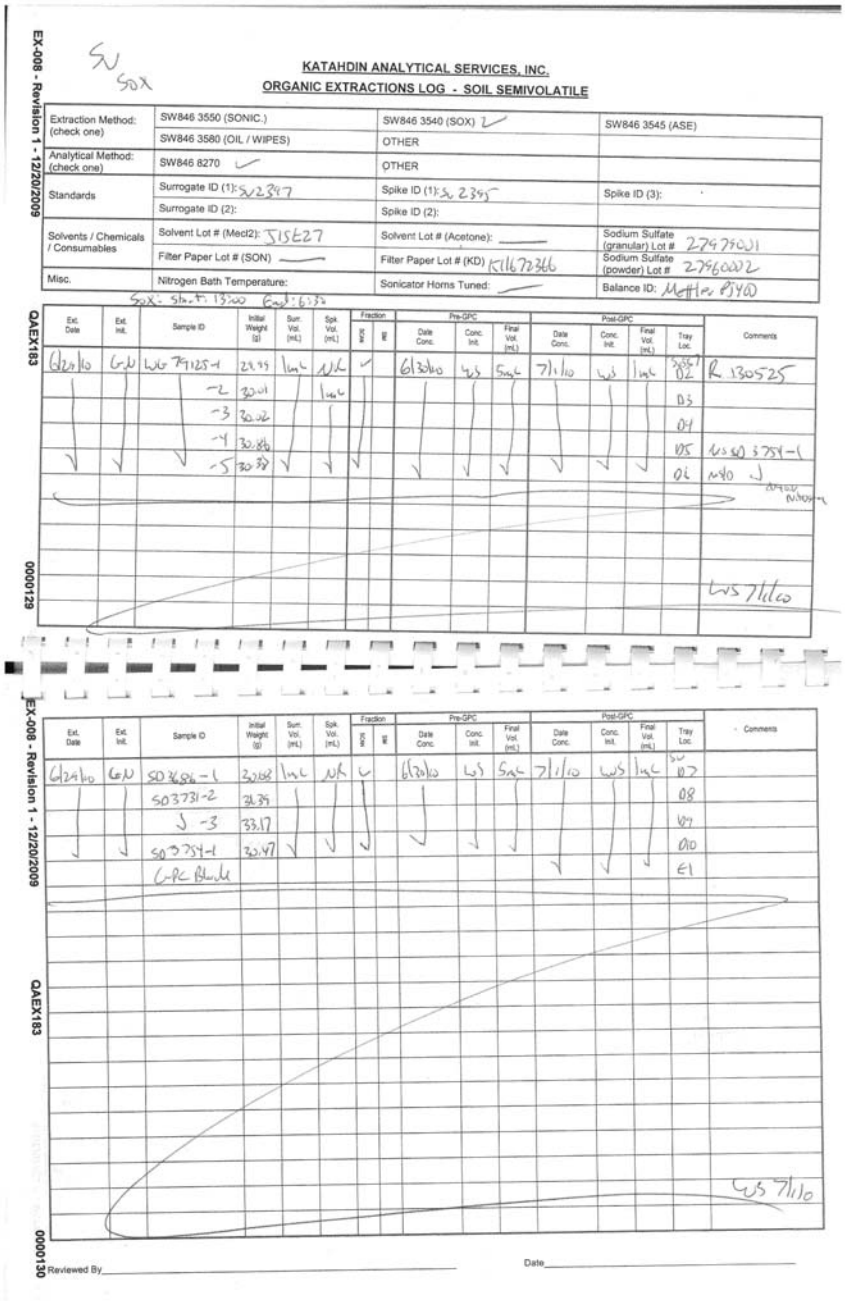
SUMMARY OF METHOD MODIFICATIONS

TOPIC	KATAHDIN SOP CA-526-07	METHOD 3540, current revision
Apparatus/Materials	1. short stem funnels	2. drying columns
Reagents		
Sample preservation/ handling		
Procedures	1. Use 30 grams of sample and 30 grams of sodium sulfate 2. Place a plug of glass wool in soxhlet then add sample 3. Use 250 mL of methylene chloride for extraction 4. Extract the sample for 18 - 24 hours 5. Extract dried using Na_2SO_4 in short stem funnels 6. Rinse the extract flask three times with ~ 2 – 3 mLs of methylene chloride then rinse the sodium sulfate with ~ 15 mLs of methylene chloride to complete a quantitative transfer 7. no apparatus height specification for concentration on water bath 8. Water bath at 75-85 deg C 9. Sample removed from water bath when volume reaches ~6 mL	1. Use 10 grams of sample and 10 grams of sodium sulfate. 2. Place sample between 2 plugs of glass wool 3. Use 300 mL of methylene chloride for extraction 4. Extract the sample for 16 - 24 hours at 4 - 6 cycles/hour 5. Extract dried using Na_2SO_4 in drying columns 6. Wash the extractor flask and sodium sulfate column with 100 to 125 mL of extraction solvent to complete the quantitative transfer 7. partially immerse concentrator tube in water and lower apparatus to complete concentration in 10-20min 8. Water bath at 15-20 deg C above solvent boiling point 9. Sample removed from water bath when volume reaches 1-2 mL
QC - Spikes	1. Acid surrogate and spike components at 100 ug/mL; base/neutral surrogate and spike components at 50 ug/mL	1. Acid surrogate and spike components at 200 ug/mL; base/neutral surrogate and spike components at 100 ug/mL
QC - LCS	1. Acid surrogate and spike components at 100 ug/mL; base/neutral surrogate and spike components at 50 ug/mL	1. Acid surrogate and spike components at 200 ug/mL; base/neutral surrogate and spike components at 100 ug/mL
QC - Accuracy/Precision		
QC – MDL		

TITLE: **PREPARATION OF SEDIMENT/SOIL SAMPLES BY SOXHLET EXTRACTION USING METHOD 3540 FOR SUBSEQUENT EXTRACTABLE SEMIVOLATILE ANALYSIS**

FIGURE 1

EXAMPLE OF LOGBOOK PAGE



EX-008 - Revision 1 - 12/20/2009

SV
SOX

KATAHDIN ANALYTICAL SERVICES, INC.
ORGANIC EXTRACTIONS LOG - SOIL SEMIVOLATILE

Extraction Method: (check one)	SW846 3550 (SONIC.)	SW846 3540 (SOX) ✓	SW846 3545 (ASE)
	SW846 3580 (OIL / WIPES)	OTHER	
Analytical Method: (check one)	SW846 8270 ✓	OTHER	
Standards	Surrogate ID (1): SV2397	Spike ID (1): SV 2395	Spike ID (3):
	Surrogate ID (2):	Spike ID (2):	
Solvents / Chemicals / Consumables	Solvent Lot # (MeCl2): J15E27	Solvent Lot # (Acetone): ___	Sodium Sulfate (granular) Lot # 27975001
	Filter Paper Lot # (SON) ___	Filter Paper Lot # (KD) K1167366	Sodium Sulfate (powder) Lot # 27960002
Misc.	Nitrogen Bath Temperature:	Sonicator Horns Tuned: ___	Balance ID: Mettler B340

SOX: Start: 1300 End: 6:30

Ext. Date	Ext. Init.	Sample ID	Initial Weight (g)	Surr. Vol. (mL)	Spk. Vol. (mL)	Fraction SON	Fraction WE	Pre-GPC Date Conc.	Pre-GPC Conc. Init.	Pre-GPC Final Vol. (mL)	Post-GPC Date Conc.	Post-GPC Conc. Init.	Post-GPC Final Vol. (mL)	Tray Loc.	Comments
6/29/10	GN	LW 791251-1	29.99	1mL	N/A	✓		6/30/10	LWS	5mL	7/1/10	LWS	1mL	SV 02	R 130525
		-2	30.01		1mL									03	
		-3	30.02											04	
		-4	30.06											05	LWS 0 3754-1
		-5	30.07											06	MB ✓
															07/01/10
															LWS 7/1/10

0000129

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Ext. Date	Ext. Init.	Sample ID	Initial Weight (g)	Surr. Vol. (mL)	Spk. Vol. (mL)	Fraction SON	Fraction WE	Pre-GPC Date Conc.	Pre-GPC Conc. Init.	Pre-GPC Final Vol. (mL)	Post-GPC Date Conc.	Post-GPC Conc. Init.	Post-GPC Final Vol. (mL)	Tray Loc.	Comments
6/29/10	GN	SO 3686-1	30.08	1mL	N/A	✓		6/30/10	LWS	5mL	7/1/10	LWS	1mL	SV 07	
		SO 3731-2	32.39											08	
		✓ -3	33.17											09	
		SO 3754-1	30.47	✓	✓	✓		✓	✓	✓	✓	✓	✓	010	
		GPC Blank												011	
															LWS 7/1/10

QAEX183

0000130

Reviewed By_____ Date_____

TITLE: **PREPARATION OF SEDIMENT/SOIL SAMPLES BY SOXHLET EXTRACTION USING METHOD 3540 FOR SUBSEQUENT EXTRACTABLE SEMIVOLATILE ANALYSIS**

FIGURE 2

LCS/MATRIX SPIKE COMPONENT LIST

BASE/NEUTRALS	
1-Methylnaphthalene	Bis (2-chloroethoxy) methane
1,1-Biphenyl	Bis (2-chloroethyl) ether
1,2,4-Trichlorobenzene	Bis (2-Chloroisopropyl) ether)
1,2-Dichlorobenzene	Bis (2-ethylhexyl) adipate
1,3-Dichlorobenzene	Bis (2-ethylhexyl) phthalate
1,4-Dichlorobenzene	Butylbenzyl phthalate
1,4-Dioxane	Caprolactam
2,4-Dinitrotoluene	Carbazole
2,6-Dinitrotoluene	Chrysene
2-Chloronaphthalene	Dibenz (a, h) anthracene
2-Methylnaphthalene	Dibenzofuran
2-Nitroaniline	Diethyl adipate
3,3'-Dichlorobenzidine	Diethyl phthalate
3-Nitroaniline	Dimethyl phthalate
4-Bromophenylphenyl ether	Di-n-butylphthalate
4-Chloroaniline	Di-n-octyl phthalate
4-Chlorophenylphenyl ether	Fluoranthene
4-Nitroaniline	Fluorene
Acenaphthene	Hexachlorobenzene
Acenaphthylene	Hexachlorobutadiene
Acetophenone	Hexachlorocyclopentadiene
Aniline	Hexachloroethane
Anthracene	Indeno (1,2,3-cd) pyrene
Atrazine	Isophorone
Azobenzene	Naphthalene
Benzaldehyde	Nitrobenzene
Benzidine	N-Nitrosodimethylamine
Benzo (a) Anthracene	N-Nitroso-di-n-propylamine
Benzo (a) pyrene	N-Nitrosodiphenylamine
Benzo (b) fluoranthene	Phenanthrene
Benzo (ghi) perylene	p-toluidine
Benzo (k) fluoranthene	Pyrene
Benzyl alcohol	Pyridine

ACIDS		
2, 3, 4, 6-Tetrachlorophenol	2-Chlorophenol	Benzoic acid
2,4,5-Trichlorophenol	2-Methylphenol	Ethyl methanesulfonate
2,4,6-Trichlorophenol	2-Nitrophenol	Methyl methanesulfonate
2,4-Dichlorophenol	4,6-Dinitro-2-methylphenol	Pentachlorophenol
2,4-Dimethylphenol	4-Chloro-3-methylphenol	Phenol
2,4-Dinitrophenol	4-Methylphenol	
2,6-Dichlorophenol	4-Nitrophenol	

TITLE: **PREPARATION OF SEDIMENT/SOIL SAMPLES BY SOXHLET EXTRACTION USING METHOD 3540 FOR SUBSEQUENT EXTRACTABLE SEMIVOLATILE ANALYSIS**

FIGURE 3

APPENDIX IX LCS/MATRIX SPIKE COMPONENT LIST

1,2,4,5-Tetrachlorobenzene	Hexachloropropene
1,3,5-Trinitrobenzene	Isodrin
1,4-Naphthoquinone	Isosafrole
1-Chloronaphthalene	Kepone
1-Naphthylamine	m-Dinitrobenzene
2,4-D	Methapyrilene
2-Acetyl aminofluorene	Methyl parathion
2-Naphthylamine	n-Nitrosodiethylamine
2-Picoline	n-Nitrosodi-n-butylamine
3,3-Dimethylbenzidine	n-Nitrosomethylethylamine
3-Methylcholanthrene	n-Nitrosomorpholine
4-Aminobiphenyl	n-Nitrosopyrrolidine
4-Nitroquinoline-1-oxide	n-Nitrotrosopiperidine
5-Nitro-o-toluidine	O,O,O-Triethyl phosphorothioate
7,12-Dimethylbenz(a)anthracene	o-Toluidine
a,a-Dimethylphenethylamine	Parathion
Acetophenone	p-Dimethylaminoazobenzene
Aramite	Pentachlorobenzene
Chlorobenzilate	Pentachloronitriobenzene
Diallate	Phenacetin
Dibenz(a,j)acridine	Phorate
Dimethoate	p-Phenylenediamine
Dinoseb	Pronamide
Diphenylamine	Safrole
Disulfoton	Silvex (2,4,5-TP)
Famphur	Sulfotep
Hexachlorophene	Thionazin

TITLE: **PREPARATION OF SEDIMENT/SOIL AND TISSUE SAMPLES BY ACCELERATED SOLVENT EXTRACTION USING METHOD 3545 FOR SUBSEQUENT EXTRACTABLE PESTICIDE and PCB ANALYSIS**

Prepared By: Galen Nickerson Date: 6-23-06

Approved By:

Department Manager: [signature] Date: 6-23-06

Operations Manager: Deborah J. Radeau Date: 6-23-06

QA Officer: Leslie Dimond Date: 6-23-06

Revision History:

SOP Revision	Changes	Approval Initials	Approval Date	Effective Date
01	Sect. 1.4 - Added solvent and acid waste streams. Changed solvent in sect. 7.4.2 from hexane to MeCl2. Updated logbook example. Added recording of solvent, Na2SO4, hydromix, filterpaper Lot #'s as well as the temperature of the Na waterbath in the logbook.	LAD	07/08	07/08
02	Updated section 4 with current materials. Updated section 7 with current techniques. Changed when Hexane is added during the solvent exchange process. Changed all weights to record to 0.05g. Updated logbook example. Added CA-108 reference for subsampling.	LAD	08/09	08/09

TITLE: **PREPARATION OF SEDIMENT/SOIL AND TISSUE SAMPLES BY ACCELERATED SOLVENT EXTRACTION USING METHOD 3545 FOR SUBSEQUENT EXTRACTABLE PESTICIDE and PCB ANALYSIS**

Please acknowledge receipt of this standard operating procedure by signing and dating both of the spaces provided. Return the bottom half of this sheet to the QA Department.

I acknowledge receipt of copy _____ of document **SOP CA-537-02,** titled **Preparation of Sediment/Soil and Tissue Samples by Accelerated Solvent Extraction Using Method 3545 for Subsequent Extractable Pesticide and PCB Analysis**.

Recipient: _____ Date: _____

KATAHDIN ANALYTICAL SERVICES, INC.
STANDARD OPERATING PROCEDURE

I acknowledge receipt of copy _____ of document **SOP CA-537-02,** titled **Preparation of Sediment/Soil and Tissue Samples by Accelerated Solvent Extraction Using Method 3545 for Subsequent Extractable Pesticide and PCB Analysis**.

Recipient: _____ Date: _____

TITLE: **PREPARATION OF SEDIMENT/SOIL AND TISSUE SAMPLES BY ACCELERATED SOLVENT EXTRACTION USING METHOD 3545 FOR SUBSEQUENT EXTRACTABLE PESTICIDE and PCB ANALYSIS**

1.0 SCOPE AND APPLICATION

Method 3545 is a procedure for extracting water insoluble or slightly water soluble semivolatile organic compounds from soils, clays, sediments, sludges, waste solids and tissues samples. This Pressurized Fluid Extraction (PFE) method uses elevated temperature (100°C or 175°C) and pressure (1500 - 2000 psi) to achieve analyte recoveries equivalent to those from Soxhlet extraction, using less solvent and taking significantly less time than the Soxhlet procedure.

This method is applicable to the extraction of organochlorine pesticides and PCBs. Organochlorine pesticides and PCBs may then be analyzed by a variety of chromatographic procedures.

1.1 Definitions

ANALYTICAL BATCH: 20 or fewer samples which are analyzed together with the same method sequence and the same lots of reagents and with the manipulations common to each sample within the same time period or in continuous sequential time periods.

METHOD BLANK (laboratory reagent blank): An artificial sample designed to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus. For aqueous samples, reagent water is used as a blank matrix; for soil samples, baked organic-free sand is used as a blank matrix. The blank is taken through the appropriate steps of the process.

LABORATORY CONTROL SAMPLE (LCS): A blank that has been spiked with the analyte(s) from an independent source, and is analyzed exactly like a sample. Its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements. The matrix used should be phase matched with the samples and well characterized.

MATRIX SPIKE/MATRIX SPIKE DUPLICATE (MS/MSD): Predetermined quantities of stock solutions of certain analytes are added to a sample matrix prior to sample extraction and analysis. Samples are split into duplicates, spiked and analyzed. Percent recoveries are calculated for each of the analytes detected. The relative percent difference between the samples is calculated and used to assess analytical precision.

SURROGATES: Organic compounds which are similar to analytes of interest in chemical composition, extraction and chromatography, but which are not normally found in environmental samples. These compounds are spiked into all blanks,

standards, samples and spiked samples prior to analysis. Percent recoveries are calculated for each surrogate.

1.2 Responsibilities

This method is restricted to use by, or under the supervision of analysts experienced in the extraction of samples for pesticide and PCB analysis. Each analyst must demonstrate and document their ability to generate acceptable results with this method. Refer to Katahdin SOP QA-805, current revision, "Personnel Training".

It is the responsibility of all Katahdin technical personnel involved in the extraction of samples for pesticide and PCB analysis to read and understand this SOP, adhere to the procedures outlined, and to properly document their data in the appropriate lab notebook. Any deviations from the test or irregularities with the samples should also be recorded in the lab notebook and reported to the Department Manager or designated qualified data reviewer responsible for this data.

It is the responsibility of the Department Manager to oversee that the members of his/her group follow this SOP, to assure that their work is properly documented, and to indicate periodic review of the pertinent logbooks.

1.3 Safety

Users of this procedure must be cognizant of inherent laboratory hazards, proper disposal procedures for contaminated materials and appropriate segregation of hazardous wastes. The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical should be treated as a potential health hazard. A reference file of material safety data sheets is available to all personnel involved in the chemical analysis. Everyone involved with the procedure must be familiar with the MSDSs for all the materials used in this procedure.

Each qualified analyst or technician must be familiar with Katahdin Analytical Environmental Health and Safety Manual including the Katahdin Hazardous Waste Management Plan and must follow appropriate procedures. These include the use of appropriate personal protective equipment (PPE) such as safety glasses, gloves, and lab coats when working with chemicals or near an instrument and not taking food or drink into the laboratory. Each analyst should know the location of all safety equipment. Each analyst shall receive a safety orientation from their department manager, or designee, appropriate for the job functions they will perform.

1.4 Waste Disposal

Wastes generated during the preparation of samples must be disposed of in accordance with the procedures described in the current revision of the Katahdin Hazardous Waste Plan and Safety Manual and SOP SD-903, "Sample Disposal," current revision. Expired standards are lab packed, placed in the Katahdin hazardous waste storage area, and disposed of in accordance with this SOP.

Any methylene chloride solvent waste generated during the rinsing of glassware etc. should be disposed of in the "D" waste stream satellite accumulation area nearest the point of generation. Acetone and hexane are considered flammable waste, and should be disposed of in the "O" waste stream satellite accumulation area nearest the point of generation. Post-extraction soil samples, used glass wool, and sodium sulfate waste should be disposed of in the soil with organics "I" waste stream satellite accumulation area nearest the point of generation. Acid waste generated during the cleanup of PCB samples should be disposed of in the "K" satellite accumulation area nearest the point of generation. Please refer to the current revision of SOP CA-107 for the location of satellite waste accumulation areas.

2.0 SUMMARY OF METHOD

Samples are prepared for extraction by weighing out a specific quantity of sample and mixing said quantity with pelletized diatomaceous earth (Hydromatrix) to remove moisture. The sample is then loaded into an extraction cell and placed on the Accelerated Solvent Extractor (ASE).

The extraction cell containing the sample is heated to the analyte-specific extraction temperature (see section 7.0), pressurized with hexane and extracted for a period of time outlined in section 7.0.

The solvent is collected from the extraction cells into 60 mL vials and allowed to cool. The solvent is then concentrated and, as needed, exchanged into solvent compatible with the cleanup or determinative step being employed.

3.0 INTERFERENCES

Contaminants in solvents, reagents, glassware, and other sample processing hardware may cause method interferences such as discrete artifacts and/or elevated baselines in the total ion current profiles (TICPs). All of these materials routinely must be demonstrated to be free

from interferences under the conditions of the analysis by running laboratory method blanks. Interferences caused by phthalate esters can pose a major problem in semivolatile organics analysis because many phthalates are also target analytes. Common flexible plastics contain varying amounts of phthalates that are easily extracted during laboratory operations, so cross-contamination of glassware frequently occurs when plastics are handled. Interferences from phthalates can best be minimized by avoiding the use of such plastics in the laboratory. At no time may gloves that have not been tested for phthalates or gloves known to contain phthalates be used or stored in the organic extraction lab. Additionally, whenever possible plastic items in this lab must be replaced with metal or Teflon or other non-phthalate plastic substitute.

Special care should be taken to ensure clean glassware and apparatus are used, pre-rinsed with the appropriate solvent prior to use. Solvents should be analyzed prior to use to demonstrate that each lot is free of contaminants that may interfere with the analysis. Interferences coextracted from the samples will vary considerably from source to source. If analysis of an extracted sample is prevented due to interferences, further cleanup of the sample extract may be needed to minimize interferences.

4.0 APPARATUS AND MATERIALS

4.1. Pressurized fluid extraction device: Dionex Accelerated Solvent Extractor, Model number ASE 200 with appropriately sized extraction cells. The cells will accommodate 15 g of sample and are made of stainless steel which is capable of withstanding the pressure requirements necessary for this procedure.

4.2. Analytical Balance: Mettler PJ4000 balance capable of weighing to 0.01 g

4.3. Vials for the collection of extracts: Dionex 60 ml pre-cleaned, open to screw cap with PTFE-lined silicone septum.

4.4. Filter disk for extraction vessels: Dionex 1.91 cm, Type D28.

4.5. 400 ml beakers

4.6 Ottawa Sand (Fisher P/N 523-3)

4.7 Kuderna-Danish (K-D) apparatus

4.7.1 Concentrator tube - 10-mL

4.7.2 Evaporation flask - 500-mL

4.7.3 Snyder column - Three-ball macro

4.8 Nitrogen evaporation (N-EVAP) apparatus.

4.9 Stainless steel spatula.

4.10 Porcelain mortar and pestle.

4.11 Boiling stones, 12 mesh silicon carbide (carborundum) – pre-purified by Soxhlet extraction in methylene chloride.

4.12 Vials - Glass, 12 mL and 4 mL capacity

4.13 500 ul syringes

4.14 Funnel powder, glass.

4.15 Filter paper, 18.5 cm, Fisherbrand or Whatman 114V (or equivalent)

4.16 Water bath or steam bath capable of maintaining a temperature of at least 85°C.

5.0 REAGENTS

5.1 Aluminum oxide (Alumina, acid), Brockman activity I, 60-325 mesh

5.2 Drying agents

5.2.1 Pelletized diatomaceous earth (Hydromatrix) - Fisher P/N.

5.2.2 Sodium sulfate crystals, Na_2SO_4.

5.3 Extraction solvents

5.3.2 Methylene Chloride - Pesticide grade or equivalent. Lot must be verified by concentrating ≈ 300 mL to 1 mL and evaluating by both GC/MS and GC/FID analyses.

5.3.3 Hexane - Pesticide grade or equivalent. Lot must be verified by concentrating 200-300 mLs to 1 mL followed by GC/ECD analysis.

5.3.4 Acetone – Pesticide grade or equivalent. Lot must be verified by concentrating ≈ 300 mL to 1 mL followed by GC/MS, GC/ECD, and GC/FID analyses.

5.3.5 Organochlorine pesticides and PCBs may be extracted with acetone/methylene chloride (1:1,v/v) or hexane (100%).

5.3.6 Other solvent systems may be employed, provided that the analyst can demonstrate adequate performance for the analytes of interest in the sample matrix

CAUTION: For best results with very wet samples (e.g., ≥ 30% moisture), reduce or eliminate the quantity of hydrophilic solvent used.

5.4 Pre-purified nitrogen is used to purge and/or pressurize the extraction cell.

5.5 Spiking Solutions

5.5.1 Pesticide/PCB surrogate spiking solution - Prepare a solution of decachlorbiphenyl (DCB) and tetrachloro-meta-xylene (TCMX) at a concentration of 1 ug/mL in acetone. Store the solution at –10 to -20 °in a Teflon sealed container. Solution must be verified by GC/ECD prior to use, and must be replaced every 6 months or sooner if degradation is evident.

5.5.2 Pesticide/PCB matrix spike/Lab control sample spiking solution - Prepare separate spiking solutions for Pesticides and one for PCBs in pesticide grade methanol and acetone, respectively, that contain all target analytes listed below:

Pesticide Spiking Solution

Analyte	ug/mL	Analyte	ug/mL
4,4'-DDD	0.5	Endosulfan I	0.5
4,4'-DDE	0.5	Endosulfan II	0.5
4,4'-DDT	0.5	Endosulfan Sulfate	0.5
Aldrin	0.5	Endrin	0.5
alpha-BHC	0.5	Endrin Aldehyde	0.5
beta-BHC	0.5	Endrin Ketone	0.5
delta-BHC	0.5	gamma-BHC (Lindane)	0.5
Dieldrin	0.5	Heptachlor	0.5
alpha-Chlordane	0.5	Heptachlor Epoxide	0.5
gamma-Chlordane	0.5	Methoxychlor	0.5

PCB Spiking Solution

Analyte	ug/mL
Aroclors 1016/1260	5.0

Store the solution at –10 to -20 °C in a Teflon sealed container. The solution must be verified by GC/ECD prior to use, and must be replaced every 6 months or sooner if degradation is evident.

6.0 SAMPLE COLLECTION, PRESERVATION AND HANDLING

Holding time for extraction of sediment/soil and tissue samples for Method 3545 is 14 days from date of sample collection, although the analyst should be aware that actual holding times employed may be project/program specific.

Store all extracts at 4°C (± 2°C) in the dark in labeled Teflon-sealed containers. See SOP SD-902, "Sample Receipt and Internal Control," current revision, for storage areas and temperature maintenance procedures.

7.0 PROCEDURES

7.1 Preparing the Accelerated Solvent Extractor

7.1.1 Before extractions can begin, the system must first go through its daily maintenance checks. To begin, turn on the system and nitrogen gas tank. Check the system pressure to ensure that the solvent pressure is at 10 psi, air is at 50 psi, and compression is at 130 psi. Next, check the solvent bottle and fill with the appropriate solvent if necessary. At this time the rinse and waste vials should be emptied and four 60 ml vials need to be placed in the rinse positions of the sample collection carousel. Record the solvent lot number in the extraction logbook.

7.1.2 The system must now be rinsed before the analysis can begin. Press the rinse button on the touch pad. The system will immediately begin its rinse cycle. This rinse procedure should be repeated at least three times before any samples are extracted to ensure that all contaminants are removed from the system.

7.1.3 To prepare extraction cells, disassemble the ASE extractor cells and clean each piece with soapy water. Next rinse each piece with acetone to ensure that all water is removed. Next, rinse the body and two screw caps three times with methylene chloride. Be sure you are using a solvent whose lot has been checked. Inspect each screw cap to ensure that the o-rings are not crushed and in need of replacement. O-rings should be replaced after approximately 50 extractions to ensure proper fit. Cell bodies should also be

checked for nicks and dings at each end. If any dings are present the cell should be placed out of rotation until it can be repaired. If any instrument maintenance is necessary record the maintenance performed in the instrument maintenance logbook.

7.1.4 Once the extraction cells have been rinsed replace the bottom cell screw cap. The bottom of the cell body is the end that is imprinted with Dionex. Next, place 2 19.8 mm filter disks into the top of the cell body and push it to the bottom of the cell with the plunger that was supplied with the system. Record the lot numbers of the filter disks in the extraction logbook.

If extracting pesticides/PCBs from tissue samples weigh out 5.00 ±1.00 g of aluminum oxide (alumina, acid) into cell and place a second filter on the top of alumina. Avoiding matrix affect interference for tissue sample, the aluminum oxide is used to remove lipid. Record the lot numbers of the aluminum oxide and filters in the extraction logbook.

7.1.5 Label each extraction cell and clean, rinsed, 60 ml collection vial with the appropriate sample ID with a black marker.

7.2 Sample preparation

7.2.1 Sediment/soil samples - Decant and discard any water layer on a sediment sample. Mix the sample thoroughly with the stainless steel spatula. If the sample container is full to the extent that stirring the sample is impractical, try to remove the "best representative" aliquot from the jar based on color, particle size, moisture, etc. Discard any foreign objects such as sticks, leaves, and rocks.

7.2.2 Gummy, fibrous, or oily materials not amenable to grinding should be cut, shredded, or otherwise reduced in size to allow mixing and maximum exposure of the sample surfaces for the extraction. Materials such as glass, rubber, metal, etc. may not require mixing with Hydromatrix to disperse the sample. Plastic materials must be tested for degradation (melting) in methylene chloride prior to ASE extraction.

7.2.3 Tissue samples are blended prior to handling in extraction laboratory.

7.2.4 Refer to Katahdin Analytical Services SOP CA-108, current revision, "Basic Laboratory Technique" for more information regarding subsampling.

7.3 Sample Handling

The following steps should be performed rapidly to avoid loss of the more volatile extractables.

7.3.1 Weigh out 15.00 ± 0.05g portion of sample into a 400 ml beaker. For tissue sample, weigh out a 5.00 ± 0.05g portion of sample into a 400 ml beaker. Record sample weight to the nearest 0.05g in the appropriate extraction logbook.

7.3.2 Add enough Hydromatrix to the sample to produce a "free-flowing" mixture, around 5g. For tissue sample, pulverize the mixture (sample-hydromatrix) using the porcelain mortar-pestle apparatus. At this point don't add an excessive amount because more Hydromatrix can be added later in the procedure. This ensures that the sample will properly fit in the extraction cell. The amount of Hydromatrix will depend upon the moisture content of the sample (e.g., low moisture content will require less Hydromatrix). Mix well with a spatula. Keep the spatula in the sample beaker and cover the beaker with aluminum foil. Record the Hydromatrix lot number in the extraction logbook.

7.3.3 A method blank must be prepared with each extraction batch, not to exceed 20 client samples. To prepare a method blank, weigh out a 5.00 ± 0. 05g portion of Ottawa sand for tissue sample batch or 15.00 ± 0.05g portion for sediment/soil sample batch into a 400 ml beaker. Record the weight to the nearest 0.05 g in the appropriate extraction logbook. Add enough Hydromatrix to the sand to produce a "free-flowing" mixture. At this point don't add an excessive amount because more Hydromatrix can be added later in the procedure. This ensures that the sample will properly fit in the extraction cell. Mix well with a spatula. Keep the spatula in the sample beaker and cover the beaker with aluminum foil.

7.3.4 A laboratory control sample (LCS) must be prepared with each extraction batch, not to exceed 20 client samples. If no MS/MSD is to be prepared a laboratory control sample duplicate must be prepared. To prepare an LCS (and LCSD), weigh out a 15.00 ± 0.05g portion of Ottawa sand into a 400 ml beaker; for tissue sample, weigh out a 5.00 ± 0. 05 g of Ottawa sand into a 400 mL beaker. Record the weight to the nearest 0. 05 g in the appropriate extraction logbook. Add enough Hydromatrix, approximately 5g to the sand to produce a "free-flowing" mixture. At this point don't add an excessive amount because more Hydromatrix can be added later in the procedure. This ensures that the sample will properly fit in the extraction cell. Mix well with a spatula. Keep the spatula in the sample beaker and cover the beaker

with aluminum foil. **If extracting both pesticide and PCB separate LCS/D and MS/D need to be prepared.**

7.3.5 A matrix spike/matrix spike duplicate (MS/MSD) set must be prepared for every 20 samples. To prepare MS/MSD, weigh out a 15.00 ± 0.05g portion of designee sample into a 400 ml beaker. For tissue sample, weigh out a 5.0 ± 0.05g portion of designee sample into a 400 mL beaker. Record the weight to the nearest 0.05g in the appropriate extraction logbook. Add enough Hydromatrix approximately 5g to the sand to produce a "free-flowing" mixture. At this point don't add an excessive amount because more Hydromatrix can be added later in the procedure. This ensures that the sample will properly fit in the extraction cell. Mix well with a spatula. Keep the spatula in the sample beaker and cover the beaker with aluminum foil.

7.3.6 Once all the QC and field samples have been weighed and mixed with a portion of Hydromatrix, find the appropriately labeled extraction cell and place the cell funnel, rinsed three times in methylene chloride, on the open end. This funnel was supplied with the system. Pour the contents of the beaker into the extraction cell. Carefully scrape all the mixtures from the beaker walls so that no more than 1% remains behind in the beaker. If there is head space remaining in the extraction cell fill the remaining space with more Hydromatrix by pouring the sample back into the beaker and mixing the new Hydromatrix into the sample. This will minimize the amount of solvent used. Again, pour the sample back into the same extraction cell and cover with a screw cap. Rinse the cell funnel with extraction solvent between each sample.

7.3.7 To all tissue samples, method blank, LCS, and MS/MSD add 0.2 mL of Pest/PCB Surrogate spiking solution using a pre-rinsed 500 uL gas tight syringe. To all sediment/soil samples and QC being extracted add 0.5 mL of Pest/PCB surrogate spiking solution using a pre-rinsed 0.5 mL gas-tight syringe. Record surrogate spike volume and identification code in extraction logbook. Thoroughly rinse syringe with solvent when spiking is complete. To LCS and MS add 0.5 mL of appropriate spike solution to each.

7.3.8 Replace all screw caps and ensure that each is properly tightened. Place each extraction cell into the ASE sample carousel. Place the corresponding collection vial into the appropriate location on the sample collection carousel. Be certain that the cell and vial are in the same number position of the carousel. In order to avoid a possible carryover, samples should be placed in order of their cleanness.

7.3.9 Press the menu button on the ASE touch pad. Choose option number one and press enter. Select method number one for Pesticide and PCB analysis, press enter. Press start on the
touch pad. The extraction process will begin and takes approximately 14 minutes per sample to complete.

NOTE: Recommended extraction conditions:

<u>For Pest/PCB (saved in the instrument as method one)</u>
Oven temperature: 100°C
Pressure: 1500 - 2000 psi
Static time: 5 min (after 5 min pre-heat equilibration)
Flush volume: 60% of the cell volume
Nitrogen purge: 90 sec at 150 psi (purge time may be extended for larger cells)
Static Cycles: 1

Optimize the conditions, as needed, according to the manufacturer's instructions. In general, the pressure is not a critical parameter, as the purpose of pressurizing the extraction cell is to prevent the solvent from boiling at the extraction temperature and to ensure that the solvent remains in intimate contact with the sample. Any pressure in the range of 1500 - 2000 psi should suffice.

Once established, the same pressure should be used for all samples extracted for the same analysis type.

As stated above, the recommended conditions have been saved as methods on the instrument. If it becomes necessary to re-program conditions, follow the above guidelines.

7.3.10 Once the extraction process is complete and the instrument is idle remove the sample extracts and label with appropriate sticker. They are now ready to be stored in the interim extract storage refrigerator unless the samples are to be concentrated the same day.

7.3.11 Remove the extraction cells from the ASE and empty their contents into the appropriate solid waste container.

7.3.12 The extract is now ready for concentration, cleanup, or analysis, depending on the extent of interferents and the determinative method to be employed. Certain cleanup and/or determinative methods may require a solvent exchange prior to cleanup and/or sample analysis.

7.4 Concentration of Extracts

7.4.1 If samples are to be GPC'd, refer to the current revision of Katahdin SOP CA-513, Extract Cleanup Using Gel Permeation Chromatography, for appropriate concentrating procedures.

7.4.2 If samples are not to be GPC'd follow steps 7.4.3 through 7.4.9 to concentrate extracts to final volume of 5.0 mLs for soil/sediment samples and 2.0 mL for tissue samples

7.4.3 Before assembling, rinse the K-D glassware (flask, concentration tube, and Snyder column, including the ground glass joints on the flask and columns) three times with hexane if using 100 % hexane for Pesticide/PCB extraction, if not rinse three times with methylene chloride. Add two boiling chips to the K-D. Insert 18.5 cm filter papers into short stem powder funnels and add ≈ 2 inches of sodium sulfate crystals. Rinse the sodium sulfate in the assembled funnels with ≈20-30 mLs of methylene chloride. Place the assembled K-D's under the funnels. Visually examine each 60mL vial of sample. If there is excessive moisture in the sample, biphasic layering will be seen. If this occurs, add approximately 1 inch of sodium sulfate crystals to the vial. This should remove most of the moisture. Record the lot number of the sodium sulfate in the extraction logbook.

7.4.4 For a solvent exchange, no GPC, add approximately 50 mL Hexane to funnel and let drain through. Since methylene chloride has a lower boiling point than Hexane, this will result in a final extract in hexane only. Record the lot number of the solvent in the extraction logbook.

7.4.5 Transfer the extracts to the K-D concentrator setups through the sodium sulfate in the funnels. This is the drying step, which is required to remove residual water from the extracts. After pouring all of the extract volume through the sodium sulfate, rinse the extract vial three times with methylene chloride. Add the rinsings through the sodium sulfate to complete a quantitative transfer. Rinse the sodium sulfate with ≈ 15 mLs of methylene chloride and allow draining.

7.4.6 Transfer the labels from the extract flasks to the K-Ds. Remove the funnel, add one or two clean boiling stones to the K-D evaporative flask and attach a 3-ball macro Snyder column. Pre-wet the Snyder column with 1 mL of hexane.

7.4.7 Place the K-D in a hot water bath (85-90°C). Gently swirl K-D in the water until boiling begins. At the proper distillation rate, the Snyder balls should chatter but the chambers should not flood with condensed solvent. The K-D should be kept in a vertical orientation while on the bath. When the apparent volume in the concentrator tube reaches ≈ 6 mL, remove the K-D from the water bath. Allow the K-D to cool for 10 minutes. Rinse the Snyder column lower joint with ≈ 1 mL of hexane. Remove the Snyder column. Wipe off any water from the neck above the lower joint of the flask. Separate the K-D flask from the concentrator tube, rinsing the ground glass joint with ≈ 1 mL hexane.

7.4.8 Reduce the extract in the concentrator tube to approximately 1 mL using the nitrogen blow-down apparatus. The bath temperature must be no higher than the boiling point of the solvent (39°C for methylene chloride). Turn the gas to 3 psi. Be careful not to splash the extract out of the tube. During concentration on the N-evap, the internal wall of the concentrator tube and the N-evap sparging pipet must be rinsed down at least once or twice with ≈1 mL of hexane. The solvent level in the concentrator tube must be positioned below the level of the water bath as much as possible to prevent water from condensing into the sample extract. As the extract volume is reduced, lower the N_2 sparging pipet closer to the surface of the extract to expedite the concentration. Record the temperature of the water in the nitrogen evaporation water bath in the extraction logbook, also note any problems or extract losses, if they occur.

7.4.9 Complete quantitative transfer of the extract to a vial by using hexane. Adjust the volume of the hexane extract to 5 mL in a 12mL vial using the appropriate "reference vial" for volume comparison. For Pesticides/PCB from tissue samples, adjust the volume of hexane extract to 2.0 mL in a 4.0 mL vial using the appropriate "reference vial" for volume comparison.

7.4.10 Label the vial with lab sample number, extraction date, matrix and analysis. Store extract vials at a temperature of 4 ± 2 °C until ready for analysis. Indicate in the extractions logbook the box number and "tray location" of the individual extract vials.

7.4.11 All sample extracts for 8082 PCB analysis must undergo a sulfuric acid wash (cleanup) prior to analysis. Sample extracts for 8081 pesticide do not undergo further cleanup unless requested by the client. All soil/sediment sample extracts for combined 8081/8082 analyses must be split. One portion must be acid cleaned for 8082 analysis. The associated method

blank must be split and acid-cleaned in the same fashion. PCB LCSs and matrix spikes are acid cleaned also. Pesticide LCSs and matrix spike samples are not subjected to further cleanup. Please refer to Katahdin SOP CA525 (current revision), Extract Cleanup Using Sulfuric Acid, for further instructions.

8.0 QUALITY CONTROL AND ACCEPTANCE CRITERIA

A method blank must be extracted for each and every item listed below:

- Each sample matrix (soil, water)
- Each day of extraction (24 hours midnight - midnight)
- Each extraction method or level
- Every 20 samples extracted in a 24-hour period

A laboratory control sample (LCS) is required for each and every item listed below:

- Each sample matrix
- Each extraction method or level
- Every extraction batch of twenty or fewer samples

Refer to the current revision of the applicable Katahdin SOP for analysis of Pesticides and PCBs for quality control acceptance criteria.

9.0 METHOD PERFORMANCE

The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. The MDLs are determined annually per type of instrument and filed with the Organic Department Manager and with the QAO. Refer to the current revision of Katahdin SOP QA-806, Method Detection Limit, Instrument Detection Limit and Reporting Limit Studies and Verifications, for procedures on determining the MDL.

Refer to the applicable analytical SOP for other method performance parameters and requirements.

TITLE: **PREPARATION OF SEDIMENT/SOIL AND TISSUE SAMPLES BY ACCELERATED SOLVENT EXTRACTION USING METHOD 3545 FOR SUBSEQUENT EXTRACTABLE PESTICIDE and PCB ANALYSIS**

10.0 APPLICABLE DOCUMENTS/REFERENCES

Test Methods for Evaluating Solid Waste-Physical/Chemical Methods, Method 3545A, SW-846, Third Edition, Updates I, II, IIA, IIB, III, IIIA, IIIB and IV, Revised February 2007, US EPA.

Department of Defense Quality Systems Manual for Environmental Laboratories (DOD QSM), Version 4.1, 04/22/09.

The National Environmental Laboratory Accreditation Conference (NELAC) Standards, June 2003.

LIST OF TABLES AND FIGURES

Table 1 Summary of Method Modifications
Figure 1 Example of Logbook Page

TITLE: **PREPARATION OF SEDIMENT/SOIL AND TISSUE SAMPLES BY ACCELERATED SOLVENT EXTRACTION USING METHOD 3545 FOR SUBSEQUENT EXTRACTABLE PESTICIDE and PCB ANALYSIS**

TABLE 1

SUMMARY OF METHOD MODIFICATIONS

TOPIC	KATAHDIN SOP CA-537-02	METHOD 3545, current revision
Apparatus/Materials		
Reagents	Katahdin receives a certificate with each lot indicating sodium sulfate crystals were dried by the manufacturer at prescribed conditions.	Section 5.3.3 Drying agents should be purified by heating at 400 °C for 4 hours…
Sample preservation/ handling	Samples are not ground prior to mixing with the drying agent.	Section 7.3 Grind a sufficient weight of the dried sample…
Procedures	Section 7.3.9 Nitrogen purge for Pesticide/PCB and DRO: 90 sec at 150 psi Oven temperature for DRO: 175°C	Section 7.8 Recommended extraction conditions for all extractions: Nitrogen purge: 60 sec at 150 psi. Oven temperature: 100 °C
QC - Spikes		
QC - LCS		
QC - Accuracy/Precision		
QC - MDL		

TITLE: **PREPARATION OF SEDIMENT/SOIL AND TISSUE SAMPLES BY ACCELERATED SOLVENT EXTRACTION USING METHOD 3545 FOR SUBSEQUENT EXTRACTABLE PESTICIDE and PCB ANALYSIS**

FIGURE 1

EXAMPLE OF LOGBOOK PAGE

PCB
ASE

KATAHDIN ANALYTICAL SERVICES, INC.
ORGANIC EXTRACTIONS LOG - SOIL PESTICIDE/PCB

Extraction Method: (check one)	SW846 3550 (SONIC.)	SW846 3540 (SOX)	SW846 3545 (ASE) X
Analytical Method: (check one)	SW846 8081	SW846 8082 X	SW846 3580 (OILS/WIPES)
Standards	Surrogate ID: GC0612	Spike ID: GC0608	Spike ID:
Solvents	Solvent Lot # (Mecl2): —	Solvent Lot # (Acetone): G51E06	Solvent Lot # (Hexane): G46E07
Consumables	Filter Paper Lot # (SON) —	Filter Paper Lot # (KD) J1S5884	Acid Lot # H04032
	Sodium Sulfate Lot #: 279 69 002		
Misc.	Nitrogen Bath Temperature: 35°C	Sonicator Horns Tuned: —	Balance ID: Mettler PJ400

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						Fraction		Pre - GPC				Post - GPC				
Ext. Date	Ext. Init.	Sample ID	Initial Weight (g)	Surr. Vol. (mL)	Spike Vol. (mL)	Pest	PCB	Date Conc.	Conc. Init.	Final Vol. (mL)	Acid Wash	Date Conc.	Conc. Init.	Final Vol. (mL)	Tray Loc.	Comments
6-16-09	AC	WG65085-1	14.96	0.5mL	NR		X	—			✓	6-16-09	KF	5mL	KF 6-23 C2	R102347
		-2	14.98		0.5mL		X								C3	
		-3	15.00				X				✓	6-17-09	AC		C12	
								KF 6-16-09								

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						Fraction		Pre - GPC				Post - GPC				
Ext. Date	Ext. Init.	Sample ID	Initial Weight (g)	Surr. Vol. (mL)	Spike Vol. (mL)	Pest	PCB	Date Conc.	Conc. Init.	Final Vol. (mL)	Acid Wash	Date Conc.	Conc. Init.	Final Vol. (mL)	Tray Loc.	Comments
6-16-09	AC	SC3169-1	14.97	0.5mL	NR		X	—			✓	6-16-09	KF	5mL	KF 6-23 C4	
		-3	14.97												C5	
		-5	15.02												C6	
		-7	14.99												C7	
		-9	14.99												C8	
		-11	15.04									6-17-09	AC		C9	
		-13	15.02												C10	
		-15	15.03												C11	
								KF 6-16-09								

QAEX162

0000076

Reviewed By_____ Date_____

TITLE: **ACID DIGESTION OF AQUEOUS SAMPLES BY EPA METHOD 3010 FOR ICP AND ICP-MS ANALYSIS OF TOTAL OR DISSOLVED METALS**

Prepared By: George Brewer Date: 11/97

Approved By:

Group Supervisor: George Brewer Date: 01/19/01

Operations Manager: John C. Burton Date: 1/22/01

QA Officer: Deborah J. Nadeau Date: 1·22·01

General Manager: Dennis F. Keegan Date: 1/22/01

Revision History:

SOP Revision	Changes	Approval Initials	Approval Date	Effective Date
01 3010A	Format changes, added pollution prevention, block digester; revised database references; revised and added tables.	DN	1·22·01	1/22/01
02 3010A	Added wording allowing use of digestates for ICP-MS analysis. Added use of block digester as primary heating source & adjusted volumes. Revised standard solution names & concs. in Figures 3 & 4.	DN	8·29·02	8·29·02
03	Added Uranium to spiking solutions for LCS & MS/D. Removed the Internal Custody Record for Metals Digestates figure and reference.	LAD	04/06	04/06
04	Minor changes to Section 7 to reflect current practices. Updated Figure 1 - Sample Prep Logbook. Updated Figure 2 and 3 - Spike amounts.	LAD	05/09	05/09
05	Added references. Updated Figure 2 and 3 with correct spike information. Added CA-108 reference for subsampling information.	LAD	04/10	04/10

TITLE: **ACID DIGESTION OF AQUEOUS SAMPLES BY EPA METHOD 3010 FOR ICP AND ICP-MS ANALYSIS OF TOTAL OR DISSOLVED METALS**

Please acknowledge receipt of this standard operating procedure by signing and dating both of the spaces provided. Return the bottom half of this sheet to the QA Department.

I acknowledge receipt of copy ____ of document **SOP CA-604-05**, titled **ACID DIGESTION OF AQUEOUS SAMPLES BY EPA METHOD 3010 FOR ICP AND ICP-MS ANALYSIS OF TOTAL OR DISSOLVED METALS**.

Recipient: _____ Date: _____

KATAHDIN ANALYTICAL SERVICES, INC.
STANDARD OPERATING PROCEDURE

I acknowledge receipt of copy ____ of document **SOP CA-604-05**, titled **ACID DIGESTION OF AQUEOUS SAMPLES BY EPA METHOD 3010 FOR ICP AND ICP-MS ANALYSIS OF TOTAL OR DISSOLVED METALS**.

Recipient: _____ Date: _____

TITLE: **ACID DIGESTION OF AQUEOUS SAMPLES BY EPA METHOD 3010 FOR ICP AND ICP-MS ANALYSIS OF TOTAL OR DISSOLVED METALS**

1.0 SCOPE AND APPLICATION

The purpose of this SOP is to describe the procedure utilized by Katahdin Analytical Services, Inc. personnel to solubilize metals in aqueous samples, wastes that contain suspended solids, and mobility-procedure extracts prior to analysis by inductively coupled plasma atomic emission spectroscopy (ICP) and inductively coupled plasma mass spectrometry (ICP-MS). This SOP applies to samples prepared by EPA Method 3010, with the method modifications mentioned in Table 2.

1.1 Definitions - none.

1.2 Responsibilities

This method is restricted to use by, or under the supervision of analysts experienced in the acid digestion of aqueous samples by EPA Method 3010. Each analyst must demonstrate and document their ability to generate acceptable results with this method. Refer to Katahdin SOP QA-805, current revision, "Personnel Training & Documentation of Capability".

It is the responsibility of all Katahdin technical personnel involved in the acid digestion of aqueous samples using EPA Method 3010 to read and understand this SOP, to adhere to the procedures outlined, and to properly document their work in the appropriate lab notebook. Any deviations from the method or irregularities with the samples should also be recorded in the lab notebook and reported to the Supervisor or designated qualified data reviewer responsible for these data.

It is the responsibility of the Supervisor to ensure that technical personnel perform acid digestions in accordance with this SOP and to confirm that their work is properly documented through periodic review of the associated logbooks.

1.3 Safety

The acids used in this procedure are highly corrosive and reactive, and spiking standards contain toxic metals. The toxicity and reactivity of client samples are usually unknown, so samples should always be assumed to present a contact hazard. To reduce or eliminate exposure to potentially harmful chemicals, lab coats, gloves, and safety glasses or goggles must be worn whenever handling samples or reagents. Additional safety apparel, including face shields, rubber aprons, dust masks, and rubber shoe protectors, is available in the metals prep lab and should be worn whenever circumstances warrant.

Acids should be added to samples slowly and carefully while watching for reactions. This should be done under a hood, in case harmful fumes are evolved.

Hood sashes should be lowered as far as possible whenever beakers are being heated in the hood. Use caution when handling hot beakers.

Each qualified analyst or technician must be familiar with Katahdin Analytical Health and Safety Manual including the Katahdin Hazardous Waste Management Plan and must follow appropriate procedures. These include the use of appropriate personal protective equipment (PPE) such as safety glasses, gloves and lab coats when working with chemicals or near an instrument and not taking food or drink into the laboratory. Each analyst should know the location of all safety equipment. Each analyst shall receive a safety orientation from their supervisor, or designee, appropriate for the job functions they will perform.

1.4 Pollution Prevention/Waste Disposal

Whenever possible, laboratory personnel should use pollution prevention techniques to address their waste generation. Refer to the current revision of the Katahdin Hazardous Waste Management Program for further details on pollution prevention techniques.

Excess spiking solutions must be emptied into the corrosive waste carboy located in the metals prep lab for subsequent appropriate disposal in accordance with the Chemical Hygiene Plan and Safety Manual.

Sample digestates should be stored for a minimum of 60 days after digestion to allow for analysis, and reanalysis if necessary. Digestates older than 60 days may be emptied into the corrosive waste carboy in the metals prep lab for subsequent appropriate disposal in accordance with the Chemical Hygiene Plan and Safety Manual.

Any other wastes generated during the preparation of samples must be disposed of in accordance with the Katahdin Chemical Hygiene Plan and Safety Manual and SOP SD-903, "Sample Disposal," current revision.

2.0 SUMMARY OF METHOD

The aqueous sample is refluxed with nitric acid in a covered digestion vessel. Additional nitric acid is added until the color of the digestate has stabilized. After the digestate has been evaporated to a low volume, it is refluxed with hydrochloric acid and diluted to the appropriate final volume with reagent water.

Samples may be concentrated (i.e. final digestate volume less than initial sample volume) during digestion if lower detection limits are required. Volumes of reagents and spiking standards must be added in proportion to the final volume of the digestate. Because concentration of samples during digestion increases the concentrations of dissolved solids

and may exacerbate analytical interferences, concentration factors greater than 5 are not recommended.

3.0 INTERFERENCES

Interferences are discussed in the applicable analytical SOPs.

4.0 APPARATUS AND MATERIALS

4.1. 250 mL and 400 mL pre-cleaned Griffin beakers (cleaned according to the current revision of SOP CA-100, "Labware Cleaning") for digestion using a hot plate. If digestion will be performed using a block digester, 70ml graduated, polyethylene block digester tubes (with attached snap caps) will be used instead of glass beakers.

4.2 Ribbed watch glasses. If digestion is performed using a hot plate, 75 mm diameter and 100 mm diameter glass watch glasses (pre-cleaned as above) are used. If digestion is performed using a block digester, 40mm diameter disposable polyethylene watch glasses are used.

4.3 Adjustable volume automatic pipets covering the range from 10 uL to 1000 uL and disposable pipet tips; calibrated Finn pipets or Eppendorf pipets are acceptable.

4.4 Disposable graduated polystyrene specimen containers with pouring lips, 200 mL capacity.

4.5 Hot plate, block digester, or other heating source - adjustable and capable of maintaining a temperature of 90-95°C. Hot plates must be numbered for easy identification.

4.6 Device for measuring hot plate temperature. This may consist of a heat-resistant 100ml beaker containing reagent water in which a thermometer is immersed. When using a block digester, a digestion tube containing reagent water in which a thermometer is immersed may be used. The temperature of one hot plate is measured each day, on a rotating basis. The hot plate identification number and the measured temperature are recorded on the sample preparation logbook sheet.

4.7 Plastic funnels, pre-cleaned as in Section 4.1.

4.8 Filter funnel holders, capable of suspending plastic funnels above disposable specimen containers.

4.9 Polyethylene wash bottles for dispensing reagent water and 5% HNO_3.

4.10 Filter paper, Whatman No. 41 or equivalent. Filters are acid-washed immediately prior to use as follows. Place a pre-cleaned funnel in the funnel holder and put a disposable plastic specimen container under the funnel to collect the rinsates. Place a folded filter in the funnel and rinse three times with approximate 10 mL volumes of 5% HNO_3, making sure the entire surface of the filter is wetted each time and allowing each rinse to drain completely before continuing. Then rinse three times with approximate 25 mL volumes of reagent water. Discard the rinsates into the appropriate waste container. The acid-washed filter is now ready for use.

4.11 Polyethylene sample containers with screw caps or graduated polyethylene sample containers with attached snap lids, 125 mL capacity. These are not necessary when using the block digester since the final digestates are stored in the digestion tubes.

4.12 Repipetters (adjustable repeating pipetters with reservoirs) for dispensing concentrated nitric acid and 1:1 HCl.

5.0 REAGENTS

5.1 Concentrated nitric acid, HNO_3 – trace metals grade.

5.2 Concentrated hydrochloric acid, HCl – trace metals grade.

5.3 Reagent water - water that meets the performance specifications of ASTM Type II water (ASTM D1193).

5.4 Hydrochloric acid, 1:1. Add a volume of concentrated hydrochloric acid to an equivalent volume of reagent water and swirl gently to mix.

5.5 Nitric acid, 5% v/v. Add 25 mL concentrated HNO_3 to 475 mL reagent water in a 500 mL wash bottle. Cap, point the dispensing tip into a sink, and shake gently to mix.

5.6 Multi-element spiking solutions (as listed in Figure 3).

6.0 SAMPLE COLLECTION, PRESERVATION AND HANDLING

Samples to be analyzed for dissolved metals should be filtered through a 0.45 um membrane filter and preserved as soon as possible after collection. Samples to be analyzed for total metals should be preserved, unfiltered, as soon as possible after collection. Aqueous samples are preserved by acidification with nitric acid to a pH of <2.

TITLE: **ACID DIGESTION OF AQUEOUS SAMPLES BY EPA METHOD 3010 FOR ICP AND ICP-MS ANALYSIS OF TOTAL OR DISSOLVED METALS**

Please refer to Katahdin Analytical Services SOP CA-108, "Basic Laboratory Technique", current revision, for information on subsampling.

7.0 PROCEDURES

7.1 Prior to performing the digestion, make a list of the samples that are to be digested. Enter digestion information (Katahdin Sample Numbers, QC Batch ID, preparation date, analyst initials, etc.) into the ACCESS computer spreadsheet. Print out a copy of the spreadsheet. With a permamament marker, make sample labels and attach to the polyethylene sample containers that will contain the digestates.

7.2 If using glass beakers as the digestion vessels, submerge previously cleaned beakers three times into a 10% nitric acid bath, then rinse three times with reagent water. The polyethylene digestion tubes used in conjunction with the block digester do not require acid rinsing or precleaning. Label the digestion vessels with sample numbers.

7.3 If digestion is performed using a block digester, the sample aliquot may be measured in the digestion vessel using the graduations on the digestion tubes. Measure 50 ml of well-mixed sample into a 70 ml block digestion tube. A larger sample aliquot may be used (up to 250 mL) if concentration of the sample during digestion is desired. Sample volumes larger than 50 mL may be digested in 250 mL beakers. Measure aliquot of well-mixed sample into a graduated specimen cup and transfer into a properly cleaned 250 mL beaker. Sample volumes of more than 50ml may not be digested using the 70ml block digester tubes. The volumes of reagents and spiking solutions used must be adjusted in proportion to the final digestate volume. The reagent and spiking solution volumes listed below are based on a final volume of 50 mL.

7.4 Add spike solutions to matrix spike samples and laboratory control samples (refer to Figure 3 for spiking instructions).

7.5 Use a repipetter to add 1.5 mL of concentrated HNO_3 (per 50 mL final volume) to the sample. Cover with a ribbed watch glass and place on heatsource. Heat cautiously, without boiling the sample, and evaporate to a low volume (10 - 15 mL).

<u>NOTE</u>: Do not allow any portion of the bottom of the digestion vessel to go dry during any part of the digestion. If a sample is allowed to go to dryness, low recoveries may result. Should this occur, discard the digestate and re-prepare the sample.

7.6 Cool the sample and add another 1.5 mL aliquot (per 50 mL final volume) of concentrated HNO_3. Cover and resume heating, increasing the temperature until a gentle reflux action occurs.

7.7 Continue heating, adding additional acid as necessary, until the digestate is light in color or does not change in appearance with continued refluxing.

7.8 Evaporate digestate to a low volume (10 - 15 mL).

7.9 Cool the sample and use a repipetter to add 5 mL (per 50 mL final volume) of 1:1 HCl. Cover the sample and resume heating, refluxing for an additional 15 minutes to dissolve any precipitate or residue resulting from evaporation.

7.10 Allow the sample to cool.

7.11 If the digestate contains visible particulate material, it must be filtered. Use a pre-cleaned funnel and acid-rinsed filter paper to filter the digestate into a clean graduated plastic specimen container or block digester digestion tube. Using a wash bottle, rinse the digestion vessel with reagent water and add the rinsates to the filter apparatus. After all of the liquid in the filter has drained into the specimen container or digestion tube, thoroughly rinse the filter three times with small (5-10 mL) volumes of reagent water, allowing the liquid to drain completely after each rinse.

If the digestion was performed using hot plates and the digestate does not contain particulate material, simply decant the digestate into a clean graduated specimen container (or graduated sample container with attached snap lid), rinse the beaker with reagent water, and add the rinsates to the container.

If the digestion was performed using a block digester and the digestate contains no visible particulate material, the digestate may be brought to final volume and stored in the digestion tube without decanting or rinsing.

7.12 Using the graduations on the specimen container, snap-lid container or digestion tube, dilute to the required final volume with reagent water. If a specimen container has been used, transfer the contents to the corresponding labeled polyethylene sample bottle, cap the bottle, and discard the empty specimen container. If a snap-lid container or digestion tube has been used, close and secure the snap-lid. Shake the container gently to mix. The digestate is now ready for analysis.

7.13 Review the ACCESS computer spreadsheet for accuracy. If any information is incorrect, make the necessary changes to the computer spreadsheet and print out a corrected copy. Do not discard the original copy of the spreadsheet. Record (hand write) the sample bottle ID, reagent lot numbers, spiking information, initial and final volumes, hot plate ID and hot plate temperature in the appropriate spaces on the spreadsheet. Record any method deviations, irregularities with the samples, or other pertinent observations at the bottom of the page, and sign and date the spreadsheet. Bind all copies of the spreadsheet in the sample preparation log. An

example sample preparation logbook page (ACCESS spreadsheet) is included as Figure 1.

7.14 Place each batch of digestates in a box labeled with the QC Batch ID, and put the box of digestates in the metals digestates storage area.

7.15 A condensation of the procedure described above is included in this SOP as Table 3. A controlled copy of this table may be posted in the metals preparation laboratory for reference by the analyst.

8.0 QUALITY CONTROL AND ACCEPTANCE CRITERIA

8.1 At least one preparation blank for waters (PBW) is processed concurrently with each digestion batch of 20 or fewer samples, and is used to assess contamination resulting from the digestion procedure. The PBW consists of an aliquot of reagent water that is digested using the same reagents as those used to digest associated samples. The initial and final volumes of the PBW must be identical to those of the associated samples (i.e., if the associated samples were concentrated during digestion, the PBW must also be concentrated). Refer to the appropriate analytical SOP for PBW acceptance criteria and corrective actions.

8.2 At least one laboratory control sample for waters (LCSW) is processed concurrently with each digestion batch of 20 or fewer samples. The LCSW consists of an aliquot of reagent water that is spiked to contain all analytes of interest at known concentrations, and is digested using the same reagents as those used to digest associated samples. The initial and final volumes of the LCSW must be identical to those of the associated samples (i.e., if the associated samples were concentrated during digestion, the LCSW must also be concentrated). Directions for spiking the LCSW are contained in Figures 3 and 4. The measured analyte recoveries for the LCSW are used to assess digestion method performance. Refer to the appropriate analytical SOP for LCSW recovery acceptance criteria and corrective actions.

8.3 Matrix spiked samples are processed concurrently with each digestion batch at a minimum frequency of one per digestion batch. A matrix spike sample consists of an aliquot of a sample that is spiked with known amounts of all analytes of interest. Matrix spike recoveries are used to assess the effects of sample matrix on digestion and analysis performance. Directions for spiking matrix spike samples are contained in Figures 3 and 4. Refer to the appropriate analytical SOP for matrix spike recovery acceptance criteria and corrective actions.

8.4 Matrix spiked duplicate samples are processed concurrently with each digestion batch at a minimum frequency of one per digestion batch. Matrix spiked duplicate samples are used to assess the precision of the digestion and analysis methods.

Refer to the appropriate analytical SOP for matrix spike duplicate precision acceptance criteria and corrective actions.

NOTE: Clients may choose specific samples for matrix spike and matrix spike duplicate analysis; otherwise, the choice is left to the person performing the digestion. The sample volumes available may restrict the choice of samples used for matrix spike and duplicate digestion. Field blank samples should not be chosen for matrix spike and matrix spike duplicate analysis.

8.5 The quality control measures and frequencies described above are minimum requirements. They are summarized for reference in Table 1. Individual clients and analytical programs may impose additional QC requirements.

9.0 METHOD PERFORMANCE

Refer to the applicable analytical SOPs for method performance information.

10.0 APPLICABLE DOCUMENTS/REFERENCES

Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, USEPA SW846, 3rd Edition, Final Updates I, II, IIA, IIB, III, IIIA, IIIB and IV, February 2007, Method 3010A.

Department of Defense Quality Systems Manual for Environmental Laboratories (DOD QSM), Version 4.1, 04/22/09.

The National Environmental Laboratory Accreditation Conference (NELAC) Standards, June 2003.

Katahdin SOP CA-101, Equipment Maintenance and Troubleshooting, current revision.

Katahdin SOP QA-806, Method Detection Limit, Instrument Detection Limit and Reporting Limit Studies and Verifications, current revision.

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TITLE: **ACID DIGESTION OF AQUEOUS SAMPLES BY EPA METHOD 3010 FOR ICP AND ICP-MS ANALYSIS OF TOTAL OR DISSOLVED METALS**

TABLE 1

QC REQUIREMENTS

Analytical Method	QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action
3010	Preparation Blank for Waters (PBW)	One per prep batch of 20 or fewer samples	Refer to analytical method	Refer to analytical method
	Laboratory Control Sample for Waters (LCSW)	One per prep batch of 20 or fewer samples	Refer to analytical method	Refer to analytical method
	Matrix Spike Sample	One per prep batch	Refer to analytical method	Refer to analytical method
	Matrix Spike Duplicate Sample	One per prep batch	Refer to analytical method	Refer to analytical method
	Demonstration of analyst proficiency; accuracy and precision	One time demonstration by each analyst performing the method	Must pass all applicable QC for method	Repeat analysis until able to perform passing QC; document successful performance in personal training file

TITLE: **ACID DIGESTION OF AQUEOUS SAMPLES BY EPA METHOD 3010 FOR ICP AND ICP-MS ANALYSIS OF TOTAL OR DISSOLVED METALS**

TABLE 2

SUMMARY OF METHOD MODIFICATIONS

TOPIC	KATAHDIN SOP CA-604-05	EPA METHOD 3010, current revision
Apparatus/Materials	1) Disposable plastic specimen cup used to measure sample volume. 2) Digestion performed in 250 mL, 400 mL Griffin beaker, or 70ml digestion tube to facilitate evaporation. 3) Ribbed watch glass used throughout digestion to reduce contamination.	1) Graduated cylinder used to measure sample volume. 2) Digestion performed in 150 mL Griffin beaker. 3) Ribbed and non-ribbed watch glasses alternated in digestion.
Procedures	1) Digestate may be analyzed for antimony and silver. 2) Sample aliquots larger or smaller than 100 mL may be used. 3) Sample evaporated to 10 - 15 mL.	1) Digestate may not be analyzed for antimony and silver. 2) Requires sample aliquot of 100 mL. 3) Sample evaporated to 5 mL.

TITLE: **ACID DIGESTION OF AQUEOUS SAMPLES BY EPA METHOD 3010 FOR ICP AND ICP-MS ANALYSIS OF TOTAL OR DISSOLVED METALS**

TABLE 3

PROCEDURE CONDENSATION: EPA METHOD 3010

1. If performing digestion on a hot plate, rinse glass beakers and ribbed watch glasses 3 times in acid bath. Then rinse beakers and watch glasses 3 times with reagent water. If performing digestion with block digester, polyethylene digestion tubes do not require precleaning.
2. Label digestion vessels with sample numbers.
3. Mix sample well, measure 50 mL (or smaller or larger aliquot) into a polyethylene digestion tube. If using glass beakers, measure aliquot into graduated specimen container, and transfer to appropriate digestion vessel.
4. Add spike solutions to matrix spike samples and LCSW (refer to Figure 3 of this SOP).
5. Add 1.5 mL (per 50 mL final volume) concentrated HNO_3 to sample.
6. Cover with a ribbed watch glass.
7. Place on heating device (hotplate or block digester) and evaporate to 10 - 15 mL.
8. Cool sample and add another 1.5 mL (per 50 mL final volume) concentrated HNO_3.
9. Resume heating until gentle reflux action occurs.
10. Continue heating, adding additional HNO_3 as necessary until digestion is complete.
11. Evaporate to 10 - 15 mL.
12. Cool sample and add 5 mL (per 50 mL final volume) 1:1 HCl. Resume heating and reflux gently for 15 minutes.
13. Cool sample and filter (if necessary) or decant into a graduated polyetheyne digestion tube. Rinse beaker with reagent water and filter or decant rinsate into specimen container.
14. Dilute to appropriate final volume with reagent water.
15. Cap sample container and shake gently to mix.

TITLE: **ACID DIGESTION OF AQUEOUS SAMPLES BY EPA METHOD 3010 FOR ICP AND ICP-MS ANALYSIS OF TOTAL OR DISSOLVED METALS**

FIGURE 1

EXAMPLE PAGE FROM METALS SAMPLE PREPARATION LOGBOOK

Katahdin Analytical Services, Inc. — **Metals Preparation Benchsheet**

Reagent Information:
JT Baker HNO3: H11034 JT Baker HCL: H39027 KMG H2O2: N/A Method: 3010

LCS / Spike — LCS/Spiking Information:
- ☑ ☑ I.V. CLPP-SPK-1 (ID/Vol): MS1404 / 0.05 mL
- ☑ ☑ CLPP-SPK-INT1 (ID/Vol): MU1002I / 0.5 mL
- ☑ ☑ CLPP-SPK-INT2 (ID/Vol): MU1009 / 0.5 mL
- ☑ ☑ Uranium Spike (ID/Vol): MS1594 / 0.005 mL
- ☐ ☐ CLPP-SPK-4 (ID/Vol): N/A / mL

Hot Plate/Block ID: A
Start Time/Temp.: 930 / 95 °C
End Time/Temp.: 1500 / 95 °C
Thermometer ID/Pos.: ALC 8 / 1.4

Fisher Filter Paper: 411672325.2

Sample ID	Batch ID	Initial Wt/Vol	Initial Units	Final Vol	Final Units	MX	Meth	Anal.	Date	Initial Color	Initial Clarity	Final Color	Final Clarity	Artifacts	Bottle
LCSWAB01ICW0	AB01ICW0	0.05	L	0.05	L	AQ	IC	AJB	02/01/2010	N/A	N/A	N/A	N/A		
PBWAB01ICW0	AB01ICW0		L		L	AQ	IC	AJB	02/01/2010	N/A	N/A	N/A	N/A		
SD0405-001	AB01ICW0		L		L	AQ	IC	AJB	02/01/2010						A
SD0405-001P	AB01ICW0		L		L	AQ	IC	AJB	02/01/2010						
SD0405-001S	AB01ICW0		L		L	AQ	IC	AJB	02/01/2010						
SD0405-002	AB01ICW0		L		L	AQ	IC	AJB	02/01/2010						
SD0405-003	AB01ICW0		L		L	AQ	IC	AJB	02/01/2010						
SD0405-004	AB01ICW0		L		L	AQ	IC	AJB	02/01/2010						
SD0405-005	AB01ICW0		L		L	AQ	IC	AJB	02/01/2010						
SD0422-001	AB01ICW0		L		L	AQ	IC	AJB	02/01/2010						B
SD0423-001	AB01ICW0		L		L	AQ	IC	AJB	02/01/2010						A
SD0429-001	AB01ICW0		L		L	AQ	IC	AJB	02/01/2010						B
SD0429-002	AB01ICW0		L		L	AQ	IC	AJB	02/01/2010						
SD0455-001	AB01ICW0		L		L	AQ	IC	AJB	02/01/2010						
SD0455-002	AB01ICW0		L		L	AQ	IC	AJB	02/01/2010						
SD0455-003	AB01ICW0		L		L	AQ	IC	AJB	02/01/2010						
SD0455-004	AB01ICW0		L		L	AQ	IC	AJB	02/01/2010						

AJB 2-1-10

Digestion performed by: AJB On: 2-1-10

Page: AB003 Revision: 00

TITLE: **ACID DIGESTION OF AQUEOUS SAMPLES BY EPA METHOD 3010 FOR ICP AND ICP-MS ANALYSIS OF TOTAL OR DISSOLVED METALS**

FIGURE 2

PREPARATION OF MATRIX SPIKES, LABORATORY CONTROL SAMPLES, AND SPIKING SOLUTIONS FOR DIGESTION OF AQUEOUS SAMPLES BY METHOD 3010

Sample or Solution Name	Component Solution Name	Source of Component	Amount of Component Added per 50 mL Final Volume (mL)
Laboratory Control Sample (LCSW) and Matrix Spike	CLPP-SPK-1	Inorganic Ventures	0.050
	CLPP-SPK-INT1	Lab Prepared (see below)	0.50
	CLPP-SPK-INT2	Lab Prepared (see below)	0.50
	1000 mg/L Uranium Standard	Inorganic Ventures	0.005

Sample or Solution Name	Component Solution Name	Source of Component	Amount of Component Added per 100 mL Final Volume (mL)
CLPP-SPK-INT1	1000 mg/L Se	High Purity Standards	1.0
	1000 mg/L As	High Purity Standards	1.0
	1000 mg/L Pb	High Purity Standards	1.0
	1000 mg/L Cd	High Purity Standards	2.5
	1000 mg/L Sb	High Purity Standards	1.0
	10000 mg/L K	High Purity Standards	10.0
	10000 mg/L Na	High Purity Standards	7.5
	10000 mg/L Mg	High Purity Standards	5.0
	10000 mg/L Ca	High Purity Standards	2.5
CLPP-SPK-INT2	2007ICS-1	Inorganic Ventures	10.0
	1000 mg/L Sr	High Purity Standards	5.0
	1000 mg/L Sn	High Purity Standards	5.0
	10000 mg/L Si	High Purity Standards	5.0

TITLE: **ACID DIGESTION OF AQUEOUS SAMPLES BY EPA METHOD 3010 FOR ICP AND ICP-MS ANALYSIS OF TOTAL OR DISSOLVED METALS**

FIGURE 3

ELEMENT CONCENTRATIONS IN MATRIX SPIKES, LABORATORY CONTROL SAMPLES, AND THEIR COMPONENT SPIKING SOLUTIONS FOR DIGESTION OF AQUEOUS SAMPLES BY METHOD 3010

Element	CONCENTRATION IN SOLUTION, mg/L							
	Matrix Spike	LCSW	CLPP-SPK-1	CLPP-SPK-4	CLPP-SPK-INT1	CLPP-SPK-INT2	2007 ICS-1	1000 mg/L U
Aluminum	2.000	2.000	2000					
Antimony	0.500	0.500		100	100			
Arsenic	0.500	0.500		4	10			
Barium	2.000	2.000	2000					
Beryllium	0.050	0.050	50					
Boron	0.500	0.500		50		50	500	
Cadmium	0.250	0.250		5	25			
Calcium	2.500	2.500			250			
Chromium	0.200	0.200	200					
Cobalt	0.500	0.500	500					
Copper	0.250	0.250	250					
Iron	1.000	1.000	1000					
Lead	0.500	0.500		2	10			
Magnesium	5.000	5.000			500			
Manganese	0.500	0.500	500					
Molybdenum	0.300	0.300		30		30	300	
Nickel	0.500	0.500	500					
Potassium	10.000	10.000			1000			
Selenium	0.500	0.500		5	50			
Silicon	5.230	5.230				523	230	
Silver	0.050	0.050	50					
Sodium	7.500	7.500			750			
Strontium	0.500	0.500		50		50		
Thallium	0.500	0.500		5	10			
Tin	0.500	0.500		50		50		
Titanium	1.000	1.000		100		100	1000	
Uranium	0.100	0.100						1000
Vanadium	0.500	0.500	500					
Zinc	0.500	0.500	500					

TITLE: ACID DIGESTION OF SOLID SAMPLES BY USEPA METHOD 3050 FOR METALS ANALYSIS BY ICP-AES AND GFAA

Prepared By: George Brewer Date: 3/98

Approved By:

Group Supervisor: George Brewer Date: 01/24/01

Operations Manager: [illegible] C. Burto Date: 1/24/01

QA Officer: Deborah J. Nadeau Date: 1.24.01

General Manager: [illegible] Date: 1/25/01

Revision History:

SOP Revision	Changes	Approval Initials	Approval Date	Effective Date
01 3050B	Format changes, added pollution prevention, added MSD, added spiking instruction tables.	DN	1.24.01	1/24/01
02 3050B	Removed all references/procedures devoted to GFAA. Added use of digestates for ICP-MS analysis. Revised standard solution names + concs. in Tables 3 + 4 to reflect current practice.	DN	8.29.02	8.29.02
03 3050B	New Title to include ILMO5.3. Use of digestion block and polyethylene digestion tubes added to sections 4.0, 7.0 and Table 1. PBS changed from 1.0g water to 1.0g boiling chips. H_2O_2 addition from 3.0ml then 7.0mls to 2.0ml, 2.0ml then 7.0ml. Figures and Tables updated to reflect current practices.	LAD	03/08	03/08
04	Updated Tables 3 and 4 with current spike concentrations and volumes added. Updated logbook page. Added CA-108 reference for subsampling information.	LAD	08/09	08/09
05	Updated Tables 3 and 4 to reflect current spiking procedures.	LAD	09/10	09/10

TITLE: ACID DIGESTION OF SOLID SAMPLES BY USEPA METHOD 3050 FOR METALS ANALYSIS BY ICP-AES, ICP-MS

Please acknowledge receipt of this standard operating procedure by signing and dating both of the spaces provided. Return the bottom half of this sheet to the QA Department.

I acknowledge receipt of copy ___ of document **SOP CA-605-05**, titled **ACID DIGESTION OF SOLID SAMPLES BY USEPA METHOD 3050 FOR METALS ANALYSIS BY ICP-AES, ICP-MS AND ILM05.3.**

Recipient: _____Date:_____

KATAHDIN ANALYTICAL SERVICES, INC.
STANDARD OPERATING PROCEDURE

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Recipient: _____Date:_____

TITLE: ACID DIGESTION OF SOLID SAMPLES BY USEPA METHOD 3050 FOR METALS ANALYSIS BY ICP-AES, ICP-MS

1.0 SCOPE AND APPLICATION

The purpose of this SOP is to describe the Katahdin Analytical Services, Inc. procedure utilized to dissolve solid matrices and solubilize metals from solid samples prior to analysis for metals by ICP-AES and ICP-MS. This SOP applies to samples prepared by EPA Method 3050, with method modifications as summarized in Table 2.

This procedure applies to all solid sample (e.g. sediments, sludges, soils, and ashes) preparations for ICP-AES and ICP-MS analyses. This method is not a total digestion technique for most samples. It is a very strong acid digestion that will dissolve almost all elements that could become "environmentally available". By design, elements bound in silicate structures are not normally dissolved by this procedure as they are not usually mobile in the environment.

1.1 Definitions

ICP-AES – Inductively Coupled Plasma Atomic Emission Spectroscopy.

ICP-MS – Inductively Coupled Plasma Mass Spectrometry.

LCSS – Laboratory Control Sample for Solids – A standard or solid reference material that has been brought through the sample preparation process.

Matrix Spike – An aliquot of a sample to which a known amount of analyte has been added before digestion.

PBS – Preparation Blank for Solids – An aliquot of reagent water that has been brought through the sample preparation process.

1.2 Responsibilities

This method is restricted to use by, or under the supervision of analysts experienced in the acid digestion of solid samples by USEPA Method 3050 for metals analysis. Each analyst must demonstrate the ability to generate acceptable results with this method. Refer to Katahdin SOP QA-805, current revision, "Personnel Training & Documentation of Training".

It is the responsibility of all Katahdin technical personnel involved in the acid digestion of solid samples by USEPA Method 3050 to read and understand this SOP, to adhere to the procedures outlined, and to properly document their data in the appropriate lab notebook. Any deviations from the procedure or irregularities with the samples should also be recorded in the lab notebook and reported to the responsible Department Manager or designated qualified data reviewer.

It is the responsibility of the Department Manager to ensure that technical personnel perform acid digestions in accordance with this SOP and to confirm that their work is properly documented through periodic review of the associated logbooks.

1.3 Safety

The acids used in this procedure are highly corrosive and reactive, and spiking standards contain toxic metals. The toxicity and reactivity of client samples are usually unknown, so samples should always be assumed to present a contact hazard. To reduce or eliminate exposure to potentially harmful chemicals, lab coats, gloves, and safety glasses or goggles must be worn whenever handling samples or reagents. Additional safety apparel, including face shields, aprons, dust masks, and shoe protectors, is available in the Metals prep lab and should be worn whenever circumstances warrant.

Acids should be added to samples slowly and carefully, while watching for reactions. This should be done under a hood, in case harmful fumes are evolved.

Hood sashes should be lowered as far as possible whenever beakers are being heated on a hot plate. Use caution when handling hot beakers.

Personnel are required to read the Katahdin Hazrdous Waste Management Plan and Safety Manual before performing this procedure, and must be familiar with the general rules for laboratory safety, personal hygiene, housekeeping, and use of protective clothing and equipment.

1.4 Pollution Prevention/Waste Disposal

Whenever possible, laboratory personnel should use pollution prevention techniques to address their waste generation. Refer to the current revision of the Katahdin Hazardous Waste Management Program for further details on pollution prevention techniques.

Excess spiking solutions must be emptied into the corrosive waste carboy located in the Metals prep lab for subsequent appropriate disposal in accordance with the Katahdin Hazardous Waste Management Plan and Safety Manual.

Sample digestates should be stored for a minimum of 60 days after digestion to allow for analysis, and reanalysis if necessary. Digestates older than 60 days may be emptied into the corrosive waste carboy in the Metals prep lab for subsequent appropriate disposal in accordance with the Katahdin Hazardous Waste Mnagement Plan and Safety Manual.

TITLE: ACID DIGESTION OF SOLID SAMPLES BY USEPA METHOD 3050 FOR METALS ANALYSIS BY ICP-AES, ICP-MS

2.0 SUMMARY OF METHOD

A representative 1 to 2 g (wet weight) sample is digested with repeated additions of nitric acid and hydrogen peroxide. Hydrochloric acid is added to the initial digestate and the sample is refluxed. The digestate is then filtered and diluted to a final volume of 100 mL.

3.0 INTERFERENCES

Interferences are discussed in the applicable analytical SOPs.

4.0 APPARATUS AND MATERIALS

4.1 Digestion vessels. If digestion is performed using a hot plate, the appropriate digestion vessels are 100 mL pre-cleaned Griffin beakers (cleaned according to the current revision of SOP CA-100, "Labware Cleaning" and CA-602, “Glassware Preparation and Sample Preservation for Trace Element Analyses”). If digestion is performed using a block digester, the appropriate digestion vessels are new 70 mL disposable graduated polyethylene digestion tubes with attached snap lids.

4.2 Ribbed watch glasses. If digestion is performed using a hot plate, 75 mm diameter glass watch glasses (pre-cleaned as above) are used. If digestion is performed using a block digester, 40 mm diameter disposable polyethylene watch glasses are used.

4.3 Adjustable volume automatic pipets covering the range from 10 uL to 1000 uL and disposable pipet tips; calibrated Finn pipets or Eppendorf pipets are acceptable.

4.4 Disposable graduated polystyrene specimen containers with pouring lips, 200 mL capacity.

4.5 Hot plate or block digester, griddle, or other heating source - adjustable and capable of maintaining a temperature of $95^{o}C \pm 5^{o}C$. Heating sources must be numbered for easy identification.

4.6 Device for measuring hot plate temperature, consisting of a flask or digestion vessel in which the bulb of a thermometer is immersed in sand or water. The temperature of each hot plate used is measured and recordedeach day. The hot plate identification number and the measured temperature are recorded on the sample preparation logbook sheet.

4.7 Plastic funnels, pre-cleaned as in Section 4.1.

4.8 Filter funnel holders, capable of suspending plastic funnels above disposable specimen containers.

4.9 Polyethylene wash bottles for dispensing reagent water and 5% HNO_3.

4.10 Filter paper, Whatman No. 41 or equivalent. Filters are acid-washed immediately prior to use as follows. Place a pre-cleaned funnel in the funnel holder and put a disposable plastic specimen container under the funnel to collect the rinsates. Place a folded filter in the funnel and rinse three times with approximate 10 mL volumes of 5% HNO_3, making sure the entire surface of the filter is wetted each time and allowing each rinse to drain completely before continuing. Then rinse three times with approximate 25 mL volumes of reagent water, again allowing each rinse to drain completely. Discard the rinsates into the appropriate waste container. The acid-washed filter is now ready for use.

4.11 Polyethylene sample containers with screw caps or graduated polyethylene sample containers with attached snap lids, 125 mL capacity.

4.12 Repipetters (adjustable repeating pipetters with reservoirs) for dispensing concentrated nitric acid, 1:1 HNO_3, and concentrated HCl.

4.13 Analytical balance capable of reading to 0.01 gram.

4.14 Spatulas, scoops, or spoons; plastic or stainless steel, rinsed with 5% HNO_3 and reagent water. Disposable tongue depressors may be used and do not requrire to be rinsed.

5.0 REAGENTS

5.1 Concentrated nitric acid, HNO_3 – trace metals grade.

5.2 Concentrated hydrochloric acid, HCl – trace metals grade.

5.3 Reagent water - water that meets the performance specifications of ASTM Type II water (ASTM D1193).

5.4 Nitric acid, 1:1. Add a volume of concentrated HNO_3 to an equivalent volume of reagent water and swirl gently to mix.

5.5 Nitric acid, 5% v/v. Add 25 mL concentrated HNO_3 to 475 mL reagent water in a 500 mL wash bottle. Cap, point the dispensing tip into a sink, and shake gently to mix.

5.6 30% hydrogen peroxide (H_2O_2) - spectrometric grade.

5.7 Multielement spiking solutions (see Table 3 for a list of required spiking solutions).

5.8 Solid reference material – a soil containing all the elements of interest, with empirically established method-specific recoveries and acceptance limits for all analytes. Solid reference materials are purchased with documentation of analysis provided by the vendor. See Figure 4 for an example certificate of analysis for a solid reference material.

6.0 SAMPLE COLLECTION, PRESERVATION AND HANDLING

Samples should be collected in clean plastic or glass containers. Samples must be refrigerated (4°C ±2°C) upon receipt by the laboratory. The holding time for solid samples is 6 months from the date of sample collection.

7.0 PROCEDURE

The procedure described below is condensed for quick reference in Table 3.

SAMPLE PREPARATION

7.1 Prior to performing the digestion, make a list of the samples that are to be digested. Enter digestion information (Katahdin Sample Numbers, QC Batch ID, preparation date, analyst initials, etc.) into the ACCESS computer spreadsheet. Print out a copy of the spreadsheet (see Figure 2 for an example). Hand label the digestate vessels

7.2 If using glass beakers as the digestion vessels, submerge previously cleaned beakers and watch glasses three times into a 10% nitric acid bath, then rinse three times with reagent water. The polyethylene digestion tubes used in conjunction with the block digeter do not require acid rinsing or precleaning. Label the digestion vessels with sample numbers.

7.3 Weigh 1 to 2 g of well-mixed sample into a properly cleaned, labeled, and tared Griffin beaker or polyethylene digestion tube. Record (hand write) the weight of each sample on the printout of the digestion spreadsheet. Refer to Katahdin Analytical Services SOP CA-108, current revision “Basic Laboratory Technique” for more information on subsampling.

7.4 Weigh an appropriate amount of solid reference material to a clean, labeled, and tared Griffin beaker or polyethylene digestion tube to serve as a laboratory control sample.

7.5 Add spike solutions to matrix spike samples (refer to Tables 3 and 4 for spiking instructions).

7.6 Using repipetters, add 10 mL of 1:1 HNO_3, mix the slurry. Cover with a ribbed watch glass and place on heat source. Gently heat the sample to 95^oC ± 5 ^oC and reflux for 10 to 15 minutes without boiling. Remove the digestion vessel from the heat source and cool the sample.

7.7 Add 5 mL of concentrated HNO_3 to the sample, replace the watch glass, and reflux for 30 minutes. If brown fumes are generated, indicating oxidation of the sample by HNO_3, repeat this step (addition of 5 mL of concentrated HNO_3) until no brown fumes are given off by the sample, indicating complete reaction by HNO_3.

7.8 Continue heating the sample at 95^oC ± 5^oC without boiling until the digestate has evaporated to approximately 5 to 10 mL or until two hours have elapsed, whichever occurs first. Do not allow the sample to go to dryness. Remove the digestion vessel from the heat source and cool the sample.

7.9 Add 2 mL of reagent water and 2 mL of 30% H_2O_2 to the sample, replace the watch glass, and heat gently on the heat source to start the peroxide reaction. Continue heating until effervescence subsides.

7.10 Add an additional 2 mL of 30% H_2O_2 to the sample, replace the watch glass, and heat gently on the heat source to start the peroxide reaction. Continue heating until effervescence subsides.

7.11 Add an additional 6 mL of 30% H_2O_2 in 1-mL aliquots with warming until the effervescence is minimal or until the general sample appearance is unchanged.

7.12 Continue heating the sample at 95^oC ± 5^oC without boiling until the digestate has evaporated to approximately 5 to 10 mL or until two hours have elapsed, whichever occurs first. Do not allow the sample to go to dryness. Remove the sample from the heat source and cool.

7.13 Add 10 mL of concentrated HCl to the digest from 7.12, replace the watch glass, and reflux at 95^oC ± 5^oC for 15 minutes. Remove the sample from the heat source and cool.

7.14 Use a pre-cleaned funnel and acid-rinsed filter paper to filter the digestate into a clean graduated polystyrene specimen container or graduated polyethylene sample container with attached snap lid. Using a wash bottle, rinse the digestion vessel with reagent water and add the rinsates to the filter apparatus. After all of the liquid in the filter has drained into the specimen container, thoroughly rinse the filter three times with small (5-10 mL) volumes of reagent water, allowing the liquid to drain completely after each rinse. Using the graduations on the specimen container or snap-lid container, dilute to 100 mL with reagent water. If a specimen container has been used, transfer the contents to the corresponding labeled polyethylene sample bottle, cap the bottle, and discard the empty specimen container. If a snap-lid

container has been used, close and secure the snap-lid. Shake the container gently to mix. The digestate is now ready for ICP-AES or ICP-MS analysis.

7.15 Review the ACCESS computer spreadsheet for accuracy. If any information is incorrect, make the necessary changes to the computer spreadsheet and print out a corrected copy. Do not discard the original copy of the spreadsheet. Record (hand write) reagent lot numbers, spiking information, and heat source temperature in the appropriate spaces on the spreadsheet. Record any method deviations, irregularities with the samples, or other pertinent observations at the bottom of the page, and sign and date the spreadsheet. Bind all copies of the spreadsheet in the sample preparation log. An example sample preparation logbook page (ACCESS spreadsheet) is included as Figure 2.

7.15 Reopen the electronic ACCESS spreadsheet for the digestion and transcribe the sample weights from the handwritten, bound copy into the electronic copy. The information in this electronic spreadsheet will later be imported into the ACCESS metals database and used to calculate sample concentrations on a weight basis.

7.16 Place each batch of digestates in a box labeled with the QC Batch ID, and put the box of digestates in the metals digestates storage area.

CALCULATIONS

7.17 Analytical results for solid samples are reported on a dry weight basis. Total solids are determined by the Wet Chemistry Group, and are recorded in spreadsheets that are electronically imported into the Access metals database. Final dry weight concentrations are calculated by the Access database as follows:

$$\text{Concentration (mg/kg dry weight)} = (C \times V) / (W \times S)$$

where: C = Measured concentration (mg/L)
V = Digestate final volume (L)
W = Sample wet weight (kg)
S = % Solids/100

8.0 QUALITY CONTROL AND ACCEPTANCE CRITERIA

USEPA Method 3050 requires the laboratory to perform specific quality control checks to assess laboratory performance and data quality. Minimum frequencies, acceptance criteria, and corrective actions for these control checks are tabulated in Table 1 and are described below. Table 1 criteria are intended to be guidelines for analysts. The table does not cover all possible situations. If any of the QC requirements are outside the recovery ranges listed in Table 1, all associated samples must be evaluated against all the QC. In some cases data may be reported, but may be reanalyzed in other cases. Making new reagents and

standards may be necessary if the standardization is suspect. The corrective actions listed in Table 1 may rely on analyst experience to make sound scientific judgements. These decisions are based on holding time considerations and client and project specific Data Quality Objectives. The Depatment Manager, Operations Manager, and/or Quality Assurance Officer may be consulted to evaluate data. Some samples may not be able to be reanalyzed within hold time. In these cases "qualified" data with narration may be advisable after consultation with the client.

8.1 At least one preparation blank for soils (PBS) is processed concurrently with each digestion batch of 20 or fewer samples, and is used to assess contamination resulting from the digestion procedure. The PBS consists of a 1.0 g of boiling stones that is digested using the same reagents as those used to digest associated samples. Refer to the appropriate analytical SOP for PBS acceptance criteria and corrective actions.

8.2 At least one laboratory control sample for soils (LCSS) is processed concurrently with each digestion batch of 20 or fewer samples. The LCSS consists of an aliquot of a solid reference material for which the concentrations of the analytes of interest have been empirically established (solid-matrix LCSS), or an aliquot of reagent water that is spiked to contain all analytes of interest at known concentrations (aqueous-matrix LCSS). The solid reference material should normally be used as the LCSS, unless a particular client or analytical program requires that spiked reagent water be used. The LCSS is digested using the same reagents as those used to digest associated samples. Directions for spiking the aqueous-matrix LCSS are contained in Table 3. The measured analyte recoveries for the LCSS are used to assess digestion method performance. Refer to the appropriate analytical SOP for LCSS recovery acceptance criteria and corrective actions.

8.3 Matrix spike samples are processed along with each digestion batch at a minimum frequency of one per digestion batch. A matrix spike sample consists of an aliquot of a sample that is fortified with known amounts of all analytes of interest prior to digestion. Matrix spike recoveries are used to assess the biasing effects of sample matrix on digestion and analysis performance. Directions for spiking matrix spike samples are contained in Figure 2. Refer to the appropriate analytical SOP for matrix spike recovery acceptance criteria and corrective actions.

8.4 Matrix spiked duplicate samples are processed concurrently with each digestion batch at a minimum frequency of one per digestion batch. Matrix spiked duplicate samples are used to assess the precision of the digestion and analysis methods. Refer to the appropriate analytical SOP for matrix spike duplicate precision acceptance criteria and corrective actions.

<u>NOTE</u>: Clients may choose specific samples for matrix spike and duplicate analysis; otherwise, the choice is left to the person performing the digestion.

8.5 The quality control measures and frequencies described above are minimum requirements. Individual clients and analytical programs may impose additional QC requirements.

9.0 METHOD PERFORMANCE

Refer to the applicable instrumental analysis SOP for method performance information.

10.0 APPLICABLE DOCUMENTS/REFERENCES

"Test Methods for the Evaluation of Solid Waste," United States Environmental Protection Agency, SW-846, Third Edition, Final Update III, 12/96, Method 3050B.

Department of Defense Quality Systems Manual for Environmental Laboratories (DOD QSM), Version 4.1, 04/22/09.

The National Environmental Laboratory Accreditation Conference (NELAC) Standards, June 2003.

LIST OF TABLES AND FIGURES

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Table 2 Summary of Method Modifications – Method 3050
Table 3 Preparation of Matrix Spikes and Spiking Solutions
Table 4 Element Concentrations in ICP-AES Matrix Spikes and Their Component Spiking Solutions
Figure 1 Procedure Condensation – Method 3050
Figure 2 Example Page from Metals Sample Preparation Logbook
Figure 3 Example Certificate of Analysis for Solid Reference Material

TABLE 1

QC REQUIREMENTS – METHOD 3050

Method	QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action
3050	Preparation Blank for Solids (PBS)	One per prep batch of 20 or fewer samples.	Refer to analytical method.	Refer to analytical method.
	Laboratory Control Sample for Solids (LCSS)	One per prep batch of 20 or fewer samples.	Refer to analytical method.	Refer to analytical method.
	Matrix Spike Sample	One per prep batch.	Refer to analytical method.	Refer to analytical method.
	Matrix Spike Duplicate Sample	One per prep batch.	Refer to analytical method.	Refer to analytical method.
	Demonstration of analyst proficiency	One-time demonstration by each analyst performing the method.	Must pass all applicable QC for method.	Repeat analysis until able to perform passing QC; document successful performance in personal training file.

TITLE: ACID DIGESTION OF SOLID SAMPLES BY USEPA METHOD 3050 FOR METALS ANALYSIS BY ICP-AES, ICP-MS

TABLE 2

SUMMARY OF METHOD MODIFICATIONS – METHOD 3050

Topic	Katahdin SOP CA-605-02	Method 3050, current revision
Apparatus /Materials	1) Digestion performed in 100 mL Griffin beaker or 70 mL polyethylene tube. 2) Graduated disposable plastic cup or 120 mL polyethylene tube used to bring digestate to final volume.	1) Digestion performed in 250 mL Griffin beaker. 2) Volumetric flask used to bring digestate to final volume.
Procedure	1) Digestate volume reduced to 5 to 10 mL prior to filtering. 2) After filtration, the filters are rinsed three times with reagent water. 3) 30% H_2O_2 is added in two 2 mL aliquots and then six 1 mL aliquots.	1) Digestate volume reduced to 5 mL prior to filtering. 2) After filtration, the filters are rinsed twice with reagent water. 3) 30% H_2O_2 is added in one 3 mL aliquot and then seven 1 mL aliquots.

TABLE 3

PREPARATION OF MATRIX SPIKES AND SPIKING SOLUTIONS FOR DIGESTION OF SOLID SAMPLES BY USEPA METHOD 3050

Sample or Solution Name	Component Solution Name	Source of Component	Amount of Component Added per 100 mL Final Volume (mL)
Matrix Spike for ICP-AES	CLPP-SPK-1	Inorganic Ventures(IV)	0.10
	CLPP-SPK-INT1	Lab Prepared (see below)	1.00
	CLPP-SPK-INT2	Lab Prepared (see below)	1.00
	1000 mg/L Uranium Std.	IV or High Purity Standards	0.01

Sample or Solution Name	Component Solution Name	Source of Component	Amount of Component Added per 100 mL Final Volume (mL)
CLPP-SPK-INT1	1000 mg/L As,Pb,Sb,Se,Tl	High Purity Standards	1.0 each
	1000 mg/L Cd	High Purity Standards	2.5
	10000 mg/L K	High Purity Standards	10.0
	10000 mg/L Na	High Purity Standards	7.5
	10000 mg/L Mg	High Purity Standards	5.0
	10000 mg/L Ca	High Purity Standards	2.5
CLPP-SPK-INT2	1000 mg/L Mo	IV or High Purity Standards	3.0
	1000 mg/L B,Li,Sn,Sr,Ti	IV or High Purity Standards	5.0 each
	10000 mg/L Si	High Purity Standards	5.0

TITLE: ACID DIGESTION OF SOLID SAMPLES BY USEPA METHOD 3050 FOR METALS ANALYSIS BY ICP-AES, ICP-MS

TABLE 4

ELEMENT CONCENTRATIONS IN ICP-AES MATRIX SPIKES AND THEIR COMPONENT SPIKING SOLUTIONS FOR DIGESTION OF SOLID SAMPLES BY METHOD 3050

	CONCENTRATION IN SOLUTION, mg/L							
Element	**Matrix Spike**	**CLPP-SPK-1**	**CLPP-SPK-4**	**CLPP-SPK-INT1**	**CLPP-SPK-INT2**			**1000 mg/L U**
Aluminum	2.000	2000						
Antimony	0.100		100	10				
Arsenic	0.100		4	10				
Barium	2.000	2000						
Beryllium	0.050	50						
Boron	0.500				50			
Cadmium	0.250		5	25				
Calcium	2.500			250				
Chromium	0.200	200						
Cobalt	0.500	500						
Copper	0.250	250						
Iron	1.000	1000						
Lead	0.100		2	10				
Lithium	0.500				50			
Magnesium	5.000			500				
Manganese	0.500	500						
Molybdenum	0.300				30			
Nickel	0.500	500						
Potassium	10.000			1000				
Selenium	0.100		5	10				
Silicon	5.000				500			
Silver	0.050	50						
Sodium	7.500			750				
Strontium	0.500				50			
Thallium	0.100		5	10				
Tin	0.500				50			
Titanium	0.500				50			
Uranium	0.100							1000
Vanadium	0.500	500						
Zinc	0.500	500						

TITLE: ACID DIGESTION OF SOLID SAMPLES BY USEPA METHOD 3050 FOR METALS ANALYSIS BY ICP-AES, ICP-MS

FIGURE 1

PROCEDURE CONDENSATION – METHOD 3050

1. Prepare and print out ACCESS spreadsheet.
2. If performing digestion on a hot plate, rinse 250 mL Griffin beakers and ribbed watch glasses 3 times in acid bath. Then rinse beakers and watch glasses 3 times with laboratory reagent grade water. If perfoming digestion with block digester, polyethylene digestion tubes do not require precleaning.
3. Label digestion vessels (beakers or polyethylene sample tubes) with sample numbers.
4. Weigh 1 to 2 g of well-mixed sample into tared digestion vessels. Record sample weights.
5. Add spike solutions to matrix spike samples.
6. Add 10 mL 1:1 HNO_3 to samples and cover with watch glasses.
7. Reflux for 10 to 15 minutes at $95^o \pm 5^o$ C. without boiling. Cool samples.
8. Add 5 mL conc. HNO_3, cover beakers, and reflux for 30 minutes.
9. Repeat Step 8 as necessary until digestion is complete.
10. Reduce sample volumes to 5 to 10 mL or heat for 2 hours, whichever occurs first.
11. Cool sample and add 2 mL reagent water and 2 mL 30% H_2O_2. Heat gently until effervescence subsides.
12. Cool sample and add 2 mL 30% H_2O_2. Heat gently until effervescence subsides.
13. Cool samples and add 6 mL of 30% H_2O_2 in 1 mL aliquots. Heat gently until effervescence subsides.
14. Reduce sample volumes to 5 to 10 mL or heat for 2 hours, whichever occurs first.
15. Add 10 mL conc. HCl and reflux for 10 to 15 minutes at $95^o \pm 5^o$ C.
16. Cool sample and filter into graduated specimen container. Bring to volume with reagent water and transfer to labeled polyethylene bottle.
17. Enter sample weights into ACCESS spreadsheet.

TITLE: ACID DIGESTION OF SOLID SAMPLES BY USEPA METHOD 3050 FOR METALS ANALYSIS BY ICP-AES, ICP-MS

FIGURE 2

EXAMPLE PAGE FROM METALS SAMPLE PREPARATION LOGBOOK

Katahdin Analytical Services, Inc. — Metals Preparation Benchsheet

Reagent Information:
JT Baker HNO3: M12022 JT Baker HCL: H64040 KMG H2O2: 6[illegible]022 Method: 3050H

LCS / Spike — LCS/Spiking Information:
- ☐ ☑ I.V. CLPP-SPK-1 (ID/Vol): MS1569 / 0.1 mL
- ☐ ☑ CLPP-SPK-INT1 (ID/Vol): MW11904 / 1.0 mL
- ☐ ☑ CLPP-SPK-INT2 (ID/Vol): MW11864 / 1.0 mL
- ☐ ☑ Uranium Spike (ID/Vol): MS1594 / ~~0.02~~ 0.01 mL ASD 7/31/09
- ☐ ☐ CLPP-SPK-4 (ID/Vol): N/A / mL

Hot Plate/Block ID: B
Start Temp.: 95 °C
End Temp.: 95 °C
Thermometer ID/Pos.: ALC 8 / 1.4
Fisher Filter Paper: K1147223B
LCSS: MS1578 Balance ID: Ohaus Galaxy 400 / Mettler AE200

REVIEWED
EM 073109
KATAHDIN ANALYTICAL METALS SECTION

Sample ID	Batch ID	Initial Wt/Vol	Initial Units	Final Vol	Final Units	MX	Meth	Anal.	Date	Initial Color	Initial Texture	Final Color	Final Clarity	Artifacts	Bottle
LC2SZG311CS0	ZG311CS0	0.5074	g	0.10	L	SL	IC	AJB	07/31/2009	N/A	N/A	N/A	N/A	N/A	N/A
LCSSZG311CS0	ZG311CS0	0.5034	g		L	SL	IC	AJB	07/31/2009	N/A	N/A	N/A	N/A		
PBSZG311CS0	ZG311CS0	1.00	g		L	SL	IC	AJB	07/31/2009	N/A	N/A	N/A	N/A		
SC4328-001	ZG311CS0	1.79	g		L	SL	IC	AJB	07/31/2009						A
SC4328-001P	ZG311CS0	1.05	g		L	SL	IC	AJB	07/31/2009						
SC4328-001S	ZG311CS0	1.04	g		L	SL	IC	AJB	07/31/2009						
SC4348-001	ZG311CS0	1.35	g		L	SL	IC	AJB	07/31/2009						
SC4348-002	ZG311CS0	1.24	g		L	SL	IC	AJB	07/31/2009						
SC4348-003 7/31/09	ZG311CS0	1.11	g		L	SL	IC	AJB	07/31/2009						
SC4357-001 ASD	ZG311CS0	1.40	g		L	SL	IC	AJB	07/31/2009						
SC4357-~~002~~ 002	ZG311CS0	1.17	g		L	SL	IC	AJB	07/31/2009						
SC4357-~~003~~ 003	ZG311CS0	1.52	g	0.10	L	SL	IC	AJB	07/31/2009						A

ASD 7/31/09

Digestion performed by: ASD Date: 7/31/09 Page: ZG104 Revision: 00

TITLE: ACID DIGESTION OF SOLID SAMPLES BY USEPA METHOD 3050 FOR METALS ANALYSIS BY ICP-AES, ICP-MS

FIGURE 3

EXAMPLE CERTIFICATE OF ANALYSIS FOR SOLID REFERENCE MATERIAL

ENVIRONMENTAL RESOURCE ASSOCIATES®
The Industry Standard™

M51475

DataPacK™
Lot No. D051-540

Trace Metals in Soil
Catalog No. 540

Certification

Method 3050 HNO3, H2O2, HCl Parameter	Total Concentration [1] (mg/Kg)	Certified Value [2] (mg/Kg)	Performance Acceptance Limits™ [3] (mg/Kg)
aluminum	55600*	7870	4630 - 11100
antimony	160	70.5	D.L. - 149
arsenic	316	289	234 - 344
barium	869	211	174 - 247
beryllium	60.9	54.4	45.2 - 63.6
boron	129	91.3	58.8 - 124
cadmium	114	101	82.9 - 119
calcium	9750*	3680	2970 - 4390
chromium	249	224	180 - 268
cobalt	113	101	82.7 - 119
copper	94.9	88.0	73.3 - 103
iron	24400*	15700	6610 - 24900
lead	184	158	129 - 187
magnesium	3780*	2260	1760 - 2750
manganese	703	420	343 - 497
mercury	5.32	5.18	3.42 - 6.87
molybdenum	80.2	69.6	55.5 - 83.7
nickel	137	120	99.1 - 141
potassium	33000*	3000	2200 - 3800
selenium	146	130	101 - 159
silver	127	104	68.9 - 139
sodium	15600*	1080	692 - 1470
strontium	326	113	90.5 - 135
thallium	106	94.0	72.8 - 115
tin	175	149	104 - 194
titanium	3100*	284	116 - 453
vanadium	151	111	85.1 - 137
zinc	311	272	215 - 329

Method 3050 HNO3, H2O2 Parameter	Total Concentration [1] mg/Kg	Certified Value [2] mg/Kg	Performance Acceptance Limits™ [3] mg/Kg
aluminum	55600*	7380	4440 - 10300
antimony	160	75.2	D.L. - 198
arsenic	316	284	225 - 343
barium	869	217	177 - 257
beryllium	60.9	53.6	42.7 - 64.5
boron	129	89.5	58.9 - 120
cadmium	114	103	83.6 - 122
calcium	9750*	3540	2800 - 4270
chromium	249	224	172 - 275
cobalt	113	101	82.0 - 120
copper	94.9	85.5	70.4 - 100
iron	24400*	12500	5480 - 19500
lead	184	162	132 - 192
magnesium	3780*	2160	1650 - 2670
manganese	703	415	330 - 500
mercury	5.32	5.18	3.42 - 6.87
molybdenum	80.2	68.8	52.7 - 84.9
nickel	137	119	98.5 - 140
potassium	33000*	2840	2160 - 3520
selenium	146	135	104 - 166
silver	127	107	49.8 - 164
sodium	15600*	1010	709 - 1310
strontium	326	111	89.0 - 133
thallium	106	99.3	76.8 - 122
tin	175	148	70.6 - 225
titanium	3100*	283	104 - 463
vanadium	151	104	70.5 - 138
zinc	311	275	222 - 328

KATAHDIN ANALYTICAL SERVICES, INC.
STANDARD OPERATING PROCEDURE

SOP Number: CA-611
Revision History
Cover Page
Page 1

TITLE: DIGESTION AND ANALYSIS OF SOLID SAMPLES FOR MERCURY BY USEPA METHOD 7471

Prepared By: George Brewer Date: 12/97

Approved By:

Group Supervisor: George Brewer Date: 01/29/01

Operations Manager: John C. Burton Date: 1/29/01

QA Officer: Deborah J. Nadeau Date: 1.29.01

General Manager: Dennis F. Hufnah Date: 1/29/01

Revision History:

SOP Revision	Changes	Approval Initials	Approval Date	Effective Date
02 7471A	Format changes, added pollution prevention, other minor changes to sections 7,8 and QA Table.	DN	1.29.01	1/29/01
03 7471A	Changed Leeman PS200 Automated Mercury Analyzer to Cetac MA100 Mercury analyzer. Revised Sect. 10 to show correct reference material. Removed fig. 2 Revised sect. 4.8, 5.7 and 8.9 to reflect current practises. minor changes through out	LAD	021605	021605
04 7471A	Sect. 5.9 and 5.10 - changed preparation of intermediate mercury standards from daily to monthly. Sect. 7.8 - removed calibration blanks (LCB/CCB). They are prepared in sect. 7.6. Added weighing of boiling chips for the prep blanks. Sect. 8.3 - Removed intermediate standards	LAD	03/08	03/08
05	Revised Sections 8 and 10, and Tables 1 and 2 to update compliance from method 7471A to method 7471B.	LAD	02/09	02/09
06	Added LOD definition. Updated sections 8, 9, 10 and Table 1 for DoD QSM version 4.1 compliance.	DN	08/09	08/09

TITLE: DIGESTION AND ANALYSIS OF SOLID SAMPLES FOR MERCURY BY USEPA METHOD 7471

Revision History:

SOP Revision	Changes	Approval Initials	Approval Date	Effective Date
07	Added Table 2 with DoD QSM Version 4.1 QC Requirements	LAD	04/10	04/10
08	Sect. 4.6 - Changed thermometer type. Added LCSO - A LCS prepped using aqueous mercury LCS spike. Updated type of marker used to label digestion bottles. Updated corrective action for failing PQL standard.	LAD	12/10	12/10

TITLE: DIGESTION AND ANALYSIS OF SOLID SAMPLES FOR MERCURY BY USEPA METHOD 7471

Please acknowledge receipt of this standard operating procedure by signing and dating both of the spaces provided. Return the bottom half of this sheet to the QA Department.

I acknowledge receipt of copy ___ of document SOP CA-611-08, Titled Digestion and Analysis of Solid Samples for Mercury by USEPA Method 7471.

Recipient: _____Date:_____

KATAHDIN ANALYTICAL SERVICES, INC.
STANDARD OPERATING PROCEDURE

I acknowledge receipt of copy ___ of document SOP CA-611-08, Titled Digestion and Analysis of Solid Samples for Mercury by USEPA Method 7471.

.

Recipient: _____Date:_____

TITLE: DIGESTION AND ANALYSIS OF SOLID SAMPLES FOR MERCURY BY USEPA METHOD 7471

1.0 SCOPE AND APPLICATION

The purpose of this SOP is to describe the procedure used by Katahdin Analytical Services, Inc. personnel for the digestion and analysis solid samples for mercury using cold vapor atomic absorption spectrophotometry.

This method is applicable to the determination of mercury in soils, sediments, bottom deposits, and sludges under USEPA Method 7471 (Test Method for Evaluating Solid Wastes, USEPA SW 846, Third Edition).

1.1 Definitions

CCB - Continuing Calibration Blank - An analyte-free solution consisting of acidified laboratory reagent grade water used to verify calibration accuracy periodically during analysis.

CCV - Continuing Calibration Verification - A midrange standard used to verify calibration accuracy periodically during analysis.

Duplicate - A second aliquot of a sample that is prepared and analyzed in the same way as the original sample in order to determine the precision of the method.

ICB - Initial Calibration Blank - An analyte-free solution consisting of acidified laboratory reagent grade water used to verify calibration accuracy.

ICV - Initial Calibration Verification - A standard made from a source independent from the calibration standards and with analyte concentrations different from those in the CCV; used to verify the accuracy of the instrument calibration.

IDL - Instrument Detection Limit - The lowest concentration of an analyte that can be determined with 95% confidence by the instrument.

LCS - Laboratory Control Sample - A standard or solid reference material that has been brought through the sample preparation process. LCSS utilizes the standard reference material. LCSO is spiked with aqueous mercury LCS spike.

LOD – Limit of Detection – An estimate of the minimum amount of a substance that an analytical process can reliably detect. An LOD is analyte and matrix-specific and is used for DoD QSM acceptance criteria.

PB - Preparation Blank - Laboratory reagent grade water that has been brought through the sample preparation process.

PQL - Practical Quantitation Limit - The lowest concentration of an analyte that is routinely reported by the laboratory; nominally three to five times the IDL.

Matrix Spike - An aliquot of a sample to which a known amount of analyte has been added before digestion.

MDL - Method Detection Limit - The minimum concentration of an analyte that can be identified, measured, and reported with 99% confidence that the analyte concentration is greater than zero.

1.2 Responsibilities

This method is restricted to use by, or under the supervision of analysts experienced in the analysis of mercury by USEPA Method 7471. Each analyst must demonstrate and document their ability to generate acceptable results with this method. Refer to Katahdin SOP QA-805, current revision, “Personnel Training & Documentation of Capability”.

It is the responsibility of all Katahdin technical personnel involved in analysis of mercury by USEPA Method 7471 to read and understand this SOP, to adhere to the procedures outlined, and to properly document their data in the appropriate lab notebook. Any deviations from the test or irregularities with the samples should also be recorded in the lab notebook and reported to the Department Manager or designated qualified data reviewer responsible for this data.

It is the responsibility of the Department Manager to ensure that members of their group follow this SOP, to ensure that their work is properly documented, and to initiate periodic review of the associated logbooks.

1.3 Safety

Many of the samples and reagents used in cold vapor atomic absorption are toxic or corrosive. Gloves, safety glasses, lab coats, and other protective clothing should be worn whenever these materials are handled. Because of the toxic nature of mercury vapor, care must be taken to avoid its inhalation. The instrument exhaust fan must be in operation whenever the mercury analyzer is in use (the fan should never be shut off).

Users of this procedure must be cognizant of inherent laboratory hazards, proper disposal procedures for contaminated materials and appropriate segregation of hazardous wastes. The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical should be treated as a potential health hazard. A reference file of material safety data sheets is available to all personnel involved in the chemical analysis. Everyone involved with the procedure must be familiar with the MSDSs for all the materials used in this procedure.

Each qualified analyst or technician must be familiar with Katahdin Analytical Environmental Health and Safety Manual including the Katahdin Hazardous Waste Plan and must follow appropriate procedures. These include the use of appropriate personal protective equipment (PPE) such as safety glasses, gloves and lab coats when working with chemicals or near an instrument and not taking food or drink into the laboratory. Each analyst should know the location of all safety equipment. Each analyst shall receive a safety orientation from their Department Manager, or designee, appropriate for the job functions they will perform.

1.4 Pollution Prevention/Waste Disposal

Whenever possible, laboratory personnel should use pollution prevention techniques to address there waste generation. Refer to the current revision of the Katahdin Hazardous Waste Management Plan for further details on pollution prevention techniques.

Samples, sample digestates, standards, and other reagents used in cold vapor atomic absorption may contain high concentrations of acids, mercury, and other toxic metals. They should be disposed of in a manner appropriate to the types of hazards they present. All digested mercury samples and standards and excess reagents and standards should be disposed of in the satellite waste container for corrosive wastes (labeled “Waste Stream A”) that is located in the Metals Prep lab. Further information regarding waste classification and disposal may be obtained by consulting the laboratory's Katahdin Analytical Environmental Health and Safety Manual and the Department Manager.

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. It relies on the volatility of elemental mercury at room temperature. During preparation, organic mercurials are oxidized and elemental mercury is ionized to Hg^{3+}. During instrumental analysis, mercuric ions are reduced to elemental mercury by the addition of stannous chloride. Elemental mercury is then aerated from solution and passes through a cell positioned in the path of a mercury spectrophotometer, where absorbance (peak height) is measured as a function of mercury concentration and recorded by the associated computer. The mercury vapor is then swept out of the instrument into an exhaust hood, where it is evacuated from the laboratory.

3.0 INTERFERENCES

In addition to inorganic forms of mercury, organic mercurials may be present in environmental samples. These organo-mercury compounds will not respond to the cold

vapor atomic absorption technique unless they are first broken down and converted to mercuric ions. The presence of undigested organo-mercurials in samples will result in a low bias for analytical results. Certain volatile organic materials will also non-specifically absorb radiation at the 253.7 nm analytical wavelength. The presence of such compounds may result in a high bias for analytical results. For these reasons, complete digestion using potassium permanganate is required for all environmental samples. Complete digestion is indicated by the persistence of the purple permanganate color (indicating the presence of excess permanganate) following digestion.

Samples that are high in chlorides may require additional permanganate to maintain a persistent purple color following digestion. During the oxidation step, chlorides are converted to free chlorine, which will absorb radiation at the 253.7 nm analytical wavelength. Any free chlorine thus generated will be present in the headspace of the digestion vessel following digestion. Because samples are poured into autosampler tubes prior to analysis by the mercury analyzer, any free chlorine present in the headspace of the digestion vessels is not sampled by the instrument and the analysis is free of chlorine interference.

4.0 APPARATUS AND MATERIALS

4.1 250 mL Pyrex media bottles with plastic screw caps, for use as digestion vessels.

4.2 Water bath capable of maintaining a constant temperature of 95° C.

4.3 Analytical balance capable of weighing to 0.01 g.

4.4 Adjustable volume automatic pipettes - 2 to 20 uL, 10 to 100 uL, 100 to 1000 uL. Calibrated Eppendorf Reference pipets and Finn digital pipets are appropriate.

4.5 Repipetters (adjustable repeating pipetters with reservoirs) for dispensing concentrated nitric acid, concentrated sulfuric acid, and other reagents.

4.6 Battery powered Traceable Pocket-Size Thermometer from Fisher Scientific, NIST-traceable, covering the range from -50° to 750° C, for monitoring the temperature of the water bath. Mercury-filled thermometers are not acceptable for use in the metals laboratory, due to the possibility of breakage and consequent contamination.

4.7 Disposable graduated polystyrene sample cups, 200 mL capacity.

4.8 CETAC M6100 Mercury Analyzer and associated peripherals and parts.

Refer to Katahdin SOP CA-629, current revision, “Operation and Maintenance of the CETAC M6100 Mercury Analyzer” for additional required materials.

TITLE: DIGESTION AND ANALYSIS OF SOLID SAMPLES FOR MERCURY BY USEPA METHOD 7471

5.0 REAGENTS

5.1 Laboratory reagent grade water – mercury-free water.

5.2 Concentrated nitric acid (HNO_3), trace metal grade

5.3 Concentrated hydrochloric acid (HCl), trace metal grade

5.4 Aqua regia: Prepare an appropriate amount immediately before use by carefully adding three volumes of concentrated HCl to one volume of concentrated HNO_3 in a heat-proof beaker or flask. Preparation of aqua regia must be performed in a fume hood.

5.5 Potassium permanganate solution, 5% w/v: Dissolve 50 g of potassium permanganate in 1 L laboratory reagent grade water. The source reagent should be labeled as suitable for use in mercury determination.

5.6 Sodium chloride – hydroxylamine hydrochloride solution: Dissolve 120 g sodium chloride and 120 g hydroxylamine hydrochloride in laboratory reagent grade water and dilute to a final volume of 1 L.

5.7 Stannous chloride solution: Add 70 mL concentrated hydrochloric acid to 500 mL of laboratory reagent grade water. Add 100 g stannous chloride and bring to a final volume of 1 L. Mix to dissolve. Reagent should be labeled as suitable for use in mercury determination.

5.8 Mercury Stock Standards: Two 10.0 mg/L mercury stock standards, obtained from separate sources, are required. The mercury concentrations of these standards must be certified by the manufacturers as traceable to NIST reference standards.

5.9 Intermediate Mercury Standard A: Appropriately dilute a mercury stock standard to obtain a solution containing 1000 ug of mercury per liter in 2% nitric acid. This intermediate standard is used to prepare calibration standards, matrix spikes, CCVs, and laboratory control samples (refer to Section 8). The identity of the stock standard currently used to prepare this intermediate standard and instructions for its dilution may be obtained by consulting the Standards Preparation Logbook maintained in the Section. Intermediate Mercury Standard A must be prepared monthly, and disposed of appropriately after use. (Note: the concentrations of all stock standards must be certified by the vendors as traceable to NIST reference materials).

5.10 Intermediate Mercury Standard B: Appropriately dilute a mercury stock standard to obtain a solution containing 1000 ug of mercury per liter in 2% nitric acid. The source of the stock standard used to prepare Intermediate Mercury Standard B must be distinct from that used to prepare Intermediate Mercury Standard A (i.e. obtained

from a separate vendor). Intermediate Mercury Standard B is used to prepare the ICV (refer to Section 8.0). The identity of the stock standard currently used to prepare this intermediate standard and instructions for its dilution may be obtained by consulting the Standards Preparation Logbook maintained in the Section. Intermediate Mercury Standard B must be prepared monthly, and disposed of appropriately after use.

5.11 Solid Reference Material: A soil with a known or empirically-established mercury concentration for use in preparing the laboratory control sample for soils. Solid reference materials should be purchased with certificates listing reference values and quality control acceptance limits. See Figure 3 for an example certificate of analysis for a solid reference material.

6.0 SAMPLE COLLECTION, PRESERVATION AND HANDLING

Soil samples to be analyzed for mercury should be collected and preserved as described in the following table.

Matrix	Container[1]	Collection Volume/ Weight	Preservation/ Treatment	Holding Time
Solid	P, G	40 g	Cool to $4^{o}C \pm 2^{o}$	28 days

[1] P = polyethylene, G = glass

7.0 PROCEDURES

BOTTLE PREPARATION

7.1 Mercury digestion bottles are reused, and must be cleaned between uses. After the previous contents of the bottles have been discarded, bottles are segregated according to whether the measured mercury concentrations of the previous contents were above the PQL (contaminated bottles) or below the PQL (uncontaminated bottles). Labels are removed from the bottles by wiping with a paper towel saturated with toluene. Both contaminated and uncontaminated bottles are then cleaned with Liquinox and water, if necessary, to remove visible grime, and rinsed thoroughly with tap water.

7.2 Uncontaminated bottles are then triple-rinsed with laboratory reagent grade water, and are ready for reuse.

7.3 Contaminated bottles are placed in a bath containing 10% HCl for at least 12 hours. After acid-leaching, these bottles are triple rinsed with laboratory reagent grade water, and are then ready for reuse.

PREPARATION OF STANDARDS, QC SAMPLES, AND BLANKS

7.4 Prior to performing the digestion, make a list of the samples that are to be digested. Enter digestion information (Katahdin Sample Numbers, Bottle IDs, QC Batch ID, preparation date, analyst initials, etc.) into the ACCESS computer database and print out a copy of the benchsheet. All necessary details of sample preparation (standards preparation information, digestion times, digestion temps, initial weights and final volumes, pertinent observations, etc.) must be recorded on this benchsheet, which will be bound in the Mercury Preparation Logbook. Refer to Figure 1 for an example page from the Mercury Preparation Logbook.

7.5 Using an industrial marker with super permanent ink, label clean digestion bottles with the appropriate sample numbers and standard identifications for each sample and standard to be digested.

7.6 Using calibrated adjustable pipettes, prepare calibration standards by adding 0 uL, 20 uL, 50 uL, 100 uL, 500 uL, and 1000 uL of Intermediate Mercury Standard A to separate appropriately-labeled digestion bottles. The mercury concentrations of these calibration standards will be, respectively, 0 ug/L (calibration blank), 0.2 ug/L, 0.5 ug/L, 1.0 ug/L, 5.0 ug/L, and 10.0 ug/L. The 0 ug/L, 0.2 ug/L and 0.5 ug/L standards are analyzed during analysis as the CCB, PQL standard and the CCV (refer to Section 8.0), respectively, as well as being used in the creation of the calibration curve.

7.7 Using a calibrated adjustable pipette, prepare the initial calibration verification (ICV) standard (refer to Section 8) by adding 600 uL of Intermediate Mercury Standard B to an appropriately labeled digestion bottle. The mercury concentration of the ICV will be 6.0 ug/L.

7.8 Prepare an appropriate number of preparation blanks (PBS) by adding 1.0 g of Teflon boiling chips to labeled digestion bottles.

7.9 Prepare an appropriate number of laboratory control samples (LCSS or LCSO) by weighing appropriate masses of solid reference material or by adding 500 uL of Intermediate Mercury Standard A respectively into labeled digestion bottles. The mercury concentration of the LCSS will depend on the solid reference material used, and the mass of each aliquot. Refer to Figure 3 for an example certificate of analysis for a solid reference material. The mercury concentration of the LCSO will be 5.0 ug/L.

7.10 Matrix spikes are prepared by adding 100 uL of Intermediate Mercury Std A to each matrix spike sample. The amount of mercury added to each matrix spike increases the final digestate concentration by 1.0 ug/L.

7.11 All calibration standards, QC samples, and blanks are digested in the same manner as client samples. Refer to Sample Preparation and Digestion, Steps 7.12 through 7.16 of this SOP.

SAMPLE PREPARATION AND DIGESTION

7.12 Weigh three approximate 0.2 g portions (a total of approximately 0.6 g) of untreated sample from different parts of the sample container and place them in the bottom of a labeled digestion bottle. The purpose of using three portions is to obtain a representative sample from the sample container.

7.13 Add 5 mL of laboratory reagent grade water and 5 mL of aqua regia to each sample, standard, and QC sample. Place bottles in a water bath located in a fume hood and heat for 2 minutes at 95° C. Remove the bottles from the water bath and allow them to cool in a fume hood.

7.14 Add 50 mL of laboratory reagent grade water and 15 mL of potassium permanganate solution to each digestion bottle, swirl to mix, and allow to stand for at least 15 minutes. Samples that contain large amounts of oxidizable organic matter may require additional 15 mL aliquots of potassium permanganate solution. This is indicated by the failure of the purple permanganate color to persist for the entire 15 minute waiting period. Add additional 15 mL aliquots to samples as necessary until the purple color persists for 15 minutes. If any of the samples requires these additional aliquots of permanganate, note that fact on the mercury preparation benchsheet and accordingly adjust the final volumes recorded on the benchsheet for those samples.

When a persistent purple color has been obtained for all samples, place the digestion bottles in the water bath and heat for 30 minutes at 95° C. Record initial and final time and temperatures on the mercury preparation benchsheet.

7.15 Remove the bottles from water bath and allow them to cool in a fume hood. If any of the samples have become colorless during heating, add additional 15 mL aliquots of potassium permanganate solution as necessary to obtain a persistent purple color and heat for an additional 30 minutes at 95° C. Record any information regarding additional permanganate aliquots on the mercury preparation benchsheet and accordingly adjust the final volumes recorded on the benchsheet for the samples affected.

7.16 Add 6 mL of sodium chloride – hydroxylamine hydrochloride solution to each digestion bottle and swirl to mix. Perform this addition in a fume hood, as chlorine gas may be evolved. This will reduce the excess permanganate, and the sample will change from purple to colorless. Add 50 mL of laboratory reagent grade water to each bottle. Wait at least 30 seconds before proceeding with analysis.

INSTRUMENTAL ANALYSIS

7.17 Digested mercury samples are analyzed using the CETAC M6100 Mercury Analyzer. Analysis is automated and is controlled by the QuickTrace software running on a dedicated PC. Detailed instructions for setting up the instrument and running samples are given Katahdin SOP CA-629, "Operation and Maintenance of the CETAC M6100 Mercury Analyzer". The following information specifically pertains to analysis of digested samples in accordance with USEPA Method 7471, and should be used in conjunction with the instructions given in Katahdin SOP CA-629.

7.18 Instrument operating conditions and quality control acceptance limits are specified in the instrument software in "templates". The template that is used to analyze digested samples in accordance with USEPA Method 7471 is named "SW846-7470-7471".

7.19 Prior to analysis, digested samples, standards, and QC samples are decanted into autosampler tubes which are placed in racks on the instrument's autosampler. The "standards" autosampler rack has 10 positions for 25 x 100 mm autosampler tubes (50 mL capacity). Tubes containing the calibration standards, the ICV, the CCV, the ICB/CCB, and the PQL standard are placed in the appropriately labeled positions in this autosampler rack.

7.20 Client samples, batch QC samples (preparation blanks and laboratory control samples), and matrix QC samples (duplicates and matrix spikes) are decanted into 17 x 100 mm autosampler tubes (15 mL capacity), which are placed in the one of the "samples" autosampler racks. The "samples" autosampler racks have 60 positions for 17 x 100 mm autosampler tubes. Instructions for filling the "samples" autosampler racks, including recording the rack position of each sample, are contained in Katahdin SOP CA-629, "Operation and Maintenance of the CETAC M6100 Mercury Analyzer".

METHOD OF STANDARD ADDITIONS

7.21 The standard addition technique involves adding known amounts of standard to one or more aliquots of the processed sample solution. This technique compensates for a sample constituent that enhances or depresses the analyte signal, thus producing a different slope from that of the calibration standards. It will not correct for additive interferences that cause a baseline shift. The method of standard additions shall be used for analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

7.21.1 The simplest version of this technique is the single-addition method, in which two identical aliquots of the sample solution, each of volume V_x, are taken. To the first (labeled A) is added a known volume V_S of a standard

analyte solution of concentration C_S. To the second aliquot (labeled B) is added the same volume V_S of the solvent. The analytical signals of A and B are measured and corrected for nonanalyte signals. The unknown sample concentration C_x is calculated:

$$C_X = \frac{S_B V_S C_S}{(S_A - S_B) V_X}$$

where S_A and S_B are the analytical signals (corrected for the blank) of solutions A and B, respectively. V_s and C_s should be chosen so that S_A is roughly twice S_B on the average, avoiding excess dilution of the sample. If a separation or concentration step is used, the additions are best made first and carried through the entire procedure.

7.21.2 Improved results can be obtained by employing a series of standard additions. To equal volumes of the sample are added a series of standard solutions containing different known quantities of the analyte, and all solutions are diluted to the same final volume. For example, addition 1 should be prepared so that the resulting concentration is approximately 50 percent of the expected absorbance from the endogenous analyte in the sample. Additions 2 and 3 should be prepared so that the concentrations are approximately 100 and 150 percent of the expected endogenous sample absorbance. The absorbance of each solution is determined and then plotted on the vertical axis of a graph, with the concentrations of the known standards plotted on the horizontal axis. When the resulting line is extrapolated to zero absorbance, the point of interception of the abscissa is the endogenous concentration of the analyte in the sample. The abscissa on the left of the ordinate is scaled the same as on the right side, but in the opposite direction from the ordinate. An example of a plot so obtained is shown in Figure 2. A linear regression program may be used to obtain the intercept concentration.

7.21.3 For the results of this MSA technique to be valid, the following limitations must be taken into consideration:

- The apparent concentrations from the calibration curve must be linear over the concentration range of concern. For the best results, the slope of the MSA plot should be nearly the same as the slope of the standard curve. If the slope is significantly different (greater than 20%), caution should be exercised.

- The effect of the interference should not vary as the ratio of analyte concentration to sample matrix changes, and the standard addition should respond in a similar manner as the analyte.

- The determination must be free of spectral interference and corrected for nonspecific background interference.

DATA REDUCTION AND REPORTING

7.22 Results are obtained in units of ug/L in the digestate. Results that exceed the calibration range of the instrument may not be reported - the sample must be appropriately diluted and reanalyzed. Results for diluted samples must be multiplied by the dilution factor prior to reporting. If additional aliquots of potassium permanganate were added during digestion, the change in digestate final volume must be taken into account in calculating the final result. Mercury results for solid samples are reported in units of ug/g, calculated on a dry weight basis. Calculation of mercury results for solid samples is performed automatically by the Metals reporting database, as follows:

$$\text{Mercury Concentration in Solid (mg/kg dry wt.)} = \frac{(C) \times (DF) \times (FV) \times 100}{(W) \times (TS)}$$

where C = Measured digestate concentration (ug/L)
DF = Instrument dilution factor
FV = Digestate final volume (L)
W = Digested wet sample weight (g)
TS = Total Solids (%)

7.23 Results are reported down to the laboratory's practical quantitation level (PQL), unless otherwise requested. Results below the PQL should be reported as "<PQL".

8.0 QUALITY CONTROL AND ACCEPTANCE CRITERIA

USEPA Method 7471 requires the laboratory to perform specific quality control checks to assess laboratory performance and data quality. Minimum frequencies, acceptance criteria, and corrective actions for these control checks are tabulated in Table 1 and are described below. Preparation instructions and the resulting mercury concentrations for calibration standards, QC standards, and matrix spikes are detailed in Sections 7.6 through 7.10 of this SOP. Table 1 criteria are intended to be guidelines for analysts. The table does not cover all possible situations. If any of the QC requirements are outside the recovery ranges listed in Table 1, all associated samples must be evaluated against all the QC. In some cases data may be reported, but may be reanalyzed in other cases. Making new reagents and standards may be necessary if the standardization is suspect. The corrective actions listed in Table 1 may rely on analyst experience to make sound scientific judgments. These decisions are based on holding time considerations and client and project specific Data Quality Objectives. The supervisor, Operations Manager, General Manager and/or Quality Assurance Officer may be consulted to evaluate data. Some samples

may not be able to be reanalyzed within hold time. In these cases "qualified" data with narration may be advisable after consultation with the client.

Much of the work performed at the lab is analyzed in accordance with specific QC requirements spelled out in a project specific Quality Assurance Project Plan (QAPP) or in a program specific Quality Systems Manual (QSM). The reporting limits, acceptance criteria and/or corrective actions may be different than those specified in this SOP. In these cases the appropriate information will be communicated to the Department Manager and/or senior chemists before initiation of the analyses so that specific product codes can be produced for the project. In addition, the work order notes for each project will describe the specific QAPP or QSM to be followed.

INITIAL DEMONSTRATION OF PERFORMANCE

8.1 Instrument detection limits (IDL) are determined quarterly for each analyte analyzed on each instrument by each method. This determination requires seven replicate analyses of laboratory reagent grade water spiked, performed on three non-consecutive days. The standard deviation of the 21 analyses is multiplied by three to obtain the IDL. For more information on performing IDL determinations, refer to the current revision of Katahdin SOP QA-806.

8.2 Method detection limits (MDL) are determined annually for each analyte analyzed on each instrument. This determination requires at least seven replicate digestions and analyses of laboratory reagent grade water spiked at 3-5 times the anticipated MDL for each analyte. MDLs differ from IDLs in that the replicates are digested prior to analysis, and they may be analyzed on a single day. The standard deviation of the 7 (or more) replicate analyses is multiplied by the Student's t-value to obtain the MDL. For more information on performing MDL determinations, refer to the current revision of Katahdin SOP QA-806.

8.3 Limits of Detection (LOD) are used when evaluating data using DoD QSM. The LOD is established by spiking a quality system matrix at 2-3 times the detection limit for a single analyte standard and 1-4 times the detection limit for a multi-analyte standard. The LOD must be verified quarterly. For more information on performing LOD determinations, refer to the current revision of Katahdin SOP QA-806.

ANALYTICAL RUN QC

8.4 Instrument calibration - The instrument must be calibrated each time it is set up, and calibration standards must be digested each day that samples are digested. Calibration includes analysis of a calibration blank and five calibration standards with graduated concentrations in the appropriate range. The concentration of one of the calibration standards must be at the Practical Quantitation Level (PQL). The correlation coefficient for the calibration curve must be at least 0.995. If the

calibration curve does not pass this test, analysis must be halted, the problem corrected, and the instrument recalibrated.

8.5 An Initial Calibration Verification (ICV) solution is analyzed after the initial calibration to check calibration accuracy. The ICV solution is prepared from a standard source different than that of the calibration standard and at a concentration within the working range of the instrument. The result of the ICV must fall within 90% to 110% of the expected value. If the ICV fails, results may not be reported from the run until the problem is corrected and a passing ICV has been analyzed.

8.6 The Continuing Calibration Verification (CCV) solution is analyzed after the initial calibration, after every ten samples, and at the end of the analytical run. The CCV solution is prepared using the same standard used for calibration at a concentration near the mid-point of the calibration curve. Results of the CCVs must fall within 90% to 110% of the expected value. If a CCV fails, associated sample results may not be reported from the run until the problem is corrected and a passing CCV has been analyzed. Also, all samples analyzed after the last passing CCV must be reanalyzed. For DoD QSM acceptance criteria, samples that are below the reporting limit may be reported if the CCV reads greater than 120%.

8.7 A calibration blank is analyzed after each ICV and CCV. A calibration blank that is analyzed after the ICV is called an Initial Calibration Blank (ICB). A calibration blank that is analyzed after a CCV is called a Continuing Calibration Blank (CCB). The absolute values of results of ICBs and CCBs must be less than the Practical Quantitation Level (PQL) for each element. If samples are being run using DoD QSM criteria, the absolute values of ICBs and CCBs must be less than the Limit of Detection (LOD). If an ICB or a CCB fails, results for the failing elements may not be reported from the run until the problem is corrected and a passing ICB or CCB has been analyzed. Also, all samples analyzed after the last passing CCB must be reanalyzed.

8.8 A standard with a mercury concentration that is at the Practical Quantitation Limit (PQL) is analyzed at the beginning of the run to determine calibration accuracy at the reporting limit. Result of the PQL standard should fall within 70% to 130% of the expected values. If the PQL fails, results may not be reported from the run until the problem is corrected and a passing PQL has been analyzed.

PREPARATION BATCH QC SAMPLES

8.9 Preparation blank (PBW or PBS), consisting of reagent water carried through the same process as associated samples, is prepared with each digestion batch of twenty or fewer samples. The results of preparation blanks must be less than the Practical Quantitation Level (PQL) for each element. For DoD QSM acceptance criteria the results must be less than ½ the PQL except for common contaminants which must be less than the PQL. If a preparation blank fails, results for the failing

elements may not be reported from the digestion batch, and all associated samples must be redigested, with the following exception. If the result for a preparation blank is greater than the PQL (greater than ½ PQL for DoD), associated sample results that are less than the PQL (less than ½ PQL for DoD) or greater than or equal to ten times the measured preparation blank concentration may be reported.

8.10 A laboratory control sample (LCSS or LCSO), consisting of solid reference material or 500 uL of Intermediate Standard A carried through the same process as associated samples, is prepared with each digestion batch of twenty or fewer samples. If a laboratory control sample fails, results may not be reported from the digestion batch, and all associated samples must be redigested. The laboratory uses a reference value and statistical acceptance limits for laboratory control samples that are supplied by the vendor of the solid reference material. The results of the LCSO must fall with in 80% - 120% of it's true value which is 5.0 ug/L. If samples are being prepared using DoD QSM acceptance criteria, the results of the LCSS or LCSO must be within 80% - 120%.

SAMPLE MATRIX QC SAMPLES

8.11 Matrix spiked duplicate samples are prepared at a minimum frequency of one per digestion batch. Matrix spike recoveries for these samples are calculated as follows:

$$\text{Recovery (\%)} = \frac{(P - S)}{A} \times 100\%$$

where: P = Spiked sample value
S = Original sample value
A = Spike amount

The recovery for each element in a spiked sample or spiked duplicate sample must fall within 75% to 125% of the actual value if the result for the unspiked sample is less than four times the amount of spike added. If one or both spike recoveries fail, a matrix interference should be suspected and the associated sample result should be flagged on the report of analysis. If DoD QSM acceptance criteria are being used, recoveries must be the same as stated for laboratory control samples.

The relative percent difference between matrix spiked duplicate sample results is calculated as follows:

$$\text{RPD (\%)} = \frac{|D_1 - D_2|}{(|D_1 + D_2|)/2} \times 100$$

where: D_1 = Spike sample result
D_2= Spike duplicate sample result

A control limit of 20% RPD is applied to matrix spike duplicate analysis. If the matrix spike duplicate analysis fails, the associated sample result should be flagged on the report of analysis.

9.0 METHOD PERFORMANCE

The method detection limit (MDL) and the limit of detection (LOD) are defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. The MDLs and LODs are determined prior to sample analysis per type of instrument and filed with the Inorganic Department Manager and with the QAO. Refer to the current revision of Katahdin SOP QA-806, Method Detection Limit, Instrument Detection Limit and Reporting Limit Studies and Verifications, for procedures on determining the MDL.

Refer to the current revision of Method 7471 for other method performance parameters and requirements.

10.0 APPLICABLE DOCUMENTS/REFERENCES

Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, USEPA SW846, 3rd Edition, Final Updates I, II, IIA, IIB, III, IIIA, IIIB and IV, February 2007, Method 7471B.

Department of Defense Quality Systems Manual for Environmental Laboratories (DOD QSM), Version 4.1, 04/22/09.

The National Environmental Laboratory Accreditation Conference (NELAC) Standards, June 2003.

Katahdin SOP CA-101, Equipment Maintenance and Troubleshooting, current revision.

Katahdin SOP QA-806, Method Detection Limit, Instrument Detection Limit and Reporting Limit Studies and Verifications, current revision.

QuickTrace M6100 Mercury Analyzer Operator Manual Version 1.0.1, CETAC Technologies

QuickTrace Mercury Analyzer Software Manual, CETAC Technologies.

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TABLE 1

QC REQUIREMENTS

Parameter/ Method	QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action
Mercury/ USEPA Method 7471B	Initial Calibration, 5 points plus a calibration blank.	Daily prior to sample analysis.	Correlation coefficient ≥ 0.995.	Correct problem and repeat calibration.
	Initial Calibration Verification (ICV), prepared from a second source.	Before beginning a sample run.	Recovery within ± 10% of true value.	Correct problem and repeat calibration.
	Initial Calibration Blank (ICB)	Before beginning a sample run.	Less than PQL.	Correct problem and repeat calibration.
	Practical Quantitation Level Standard (PQL)	Before beginning a sample run.	Recovery within ± 30% of true value.	Correct problem and repeat calibration.
	Continuing Calibration Verification (CCV)	At beginning or run, after every 10 samples, and at end of the run	Recovery within ± 10% of true value	Repeat calibration and reanalyze all samples analyzed since the last successful CCV.
	Continuing Calibration Blank (CCB)	At beginning or run, after every 10 samples, and at end of the run	Less than PQL.	Repeat calibration and reanalyze all samples analyzed since the last successful CCB.
	Preparation Blank (PBS)	One per digestion batch of 20 or fewer samples.	Less than PQL.	1) Investigate source of contamination. 2) Redigest and reanalyze all associated samples if sample concentration ≥ PQL and < 10x the blank concentration.
	Laboratory Control Sample (LCSS or LCSO)	One per digestion batch of 20 or fewer samples.	LCSS: Recovery within vendor-supplied acceptance limits. LCSO: Recovery within ± 20% of true value.	Redigest all affected samples.
	Matrix Spike Sample (S)	One per digestion batch of 20 or fewer samples.	Recovery ± 25% of true value, if sample > 4x spike value.	Flag results.
	Matrix Spike Duplicate Sample (P) or sample duplicate (D)	One per digestion batch of 20 or fewer samples.	1)Recovery ± 25% of true value, if sample < 4x spike added. 2)RPD ≤20% for duplicate spikes or duplicate samples.	Flag results
	Post-Digestion Matrix Spike Sample (PDS)	When matrix spike or MSD fail	Recovery ±20% of true value	Analyze serial dilution of sample
	Serial Dilution Test (L)	One per digestion batch or when PDS fails	1:5 dilution of sample must agree within 10% with undiluted result	If MS, MSD, PDS, and serial dilution fail, quantitate sample by method of standard additions

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TABLE 1

QC REQUIREMENTS (CONTINUED)

Parameter/ Method	QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action
Mercury/ USEPA Method 7471B	Instrument Detection Limit (IDL) Study	Quarterly.	IDL < PQL	1)Repeat IDL study. 2)Raise PQL.
	Method Detection Limit (MDL) Study	Refer to KAS SOP QA-806, “Method Detection Limit, Instrument Detection Limit and Reporting Limit Studies and Verifications”, current revision.		
	Limit of Detection (LOD) determination	Quarterly.	LOD = 2-3X MDL	Repeat LOD Determination.

TABLE 2

DoD QSM QC REQUIREMENTS

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 significant 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.
LOD determination and verification	(Refer to current revision of SOP QA-806)				
LOQ establishment and verification	(Refer to current revision of SOP QA-806)				
Initial calibration (ICAL) for Mercury: minimum 5 standards 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 (ICV)	Once after each ICAL, prior to beginning a sample run.	Value of second source for all analyte(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)	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 Q-flag to all results for the specific analyte(s) in all samples since the last acceptable calibration verification.	After every 10 field samples and at the end of the analysis sequence.	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.

TITLE: DIGESTION AND ANALYSIS OF SOLID SAMPLES FOR MERCURY BY USEPA METHOD 7471

TABLE 2

DoD QSM QC REQUIREMENTS

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. Contact Client if samples cannot be reprepped within hold time. For negative blanks, absolute value < LOD.	Correct the problem. Report sample results that are <LOD or >10x the blank concentration. Reprepare and reanalyze the method blank and all associated samples with results > LOD and < 10x the contaminated blank result. Contact Client if samples cannot be reprepped within hold time.	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. For negative blanks, absolute value < 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.	
LCS containing all analytes to be reported	One per preparatory batch.	Water: Recovery must be within ± 20% of the true value Soil: Recovery must be within vendor supplied limits (varies by lot).	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 (see Box D-7).	Recovery must be within ± 20% of the true value	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 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: Recovery must be within ± 20% of the true value. 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.

TABLE 2

DoD QSM QC REQUIREMENTS

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Method of standard additions (MSA)	When matrix interference is confirmed.	NA.	NA.	NA.	Document use of MSA in the case narrative.
Results reported between DL and LOQ	NA.	NA.	NA.	Apply J-flag to all results between DL and LOQ.	

TITLE: **DIGESTION AND ANALYSIS OF SOLID SAMPLES FOR MERCURY BY USEPA METHOD 7471**

TABLE 3

SUMMARY OF METHOD MODIFICATIONS

Topic	Katahdin SOP CA-611-08	USEPA Method 7471, current revision
Reagents	Stannous chloride dissolved in hydrochloric acid to prevent clogging of mercury analyzer, per instrument manufacturer's recommendation.	Stannous chloride dissolved/suspended in sulfuric acid.
Procedures	Sampling and gas stream switching performed automatically by mercury analyzer.	Sampling and gas stream switching performed manually by analyst.
QC – Calibration Verification	1)Known reference sample (ICV) analyzed daily. 2)Calibration verified after every 10 samples with CCV.	1)Known reference sample analyzed quarterly. 2)Calibration verified after every 20 samples.
QC - Calibration Blanks and Method Blanks	Acceptance Criterion: < PQL	Acceptance criteria: Low enough not to interfere with data quality objectives, or <10% of PQL, or <10% of regulatory limit, or <10% of lowest associated sample

TITLE: DIGESTION AND ANALYSIS OF SOLID SAMPLES FOR MERCURY BY USEPA METHOD 7471

FIGURE 1

EXAMPLE PAGE FROM MERCURY PREPARATION LOGBOOK

Katahdin Analytical Services, Inc. — **Metals Preparation Benchsheet**

Reagent Information:
HNO3: J41057 HCL: J350412 H2SO4: N/A
KMNO4: MR 981 K2S2O8: N/A NH2OH-HCl: MR 980
Method: 7471

REVIEWED DWM 12-7-10 KATAHDIN ANALYTICAL METALS SECTION

Standards/Spiking Information:
1ppm A : MW12757
1ppm B : MW12758
HHH 12-6-10 LCS$: .5mL of 1ppm A
Spike(S/P) = 100uL of 1ppm A to 100mL.

ICV = 600uL of 1ppm B to 100 mL.
S0.2 = 20uL of 1ppm A to 100 mL.
S0.5 = 50uL of 1ppm A to 100 mL.

S1.0 = 100uL of 1ppm A to 100 mL.
S5.0 = 500uL of 1ppm A to 100 mL.
S10.0 = 1000uL of 1ppm A to 100 mL.

Balance ID: BAL08
Water Bath ID : A
Digestion Start Time (@ 95 °C): 95 1420
Thermometer ID : PIG38
Digestion End Time(@ 100 °C): 100 1450

Sample ID	Batch ID	Initial Wt/Vol	Initial Units	Final Vol	Final Units	MX	Meth	Anal.	Date	Initial Color (HHH 12-6-10)	Initial Texture	Final Color	Final Clarity (HHH 12-6-10)	Artifacts	Bottle
HHH 12-6-10 LCS8AL06HGS0	AL06HGS0	0.1	g	0.10	L	SL	HG	HHH	12/06/2010	N/A	N/A	N/A	N/A		
PBSAL06HGS0	AL06HGS0	0.6	g		L	SL	HG	HHH	12/06/2010	N/A	N/A	N/A	N/A		
SD7209-001	AL06HGS0	0.63	g		L	SL	HG	HHH	12/06/2010						G
SD7209-002	AL06HGS0	0.73	g		L	SL	HG	HHH	12/06/2010						A
SD7209-003	AL06HGS0	0.67	g		L	SL	HG	HHH	12/06/2010						G
SD7209-004	AL06HGS0	0.61	g		L	SL	HG	HHH	12/06/2010						G
SD7209-005	AL06HGS0	0.65	g		L	SL	HG	HHH	12/06/2010						T
SD7209-006	AL06HGS0	0.78	g		L	SL	HG	HHH	12/06/2010						L
SD7209-007	AL06HGS0	0.62	g		L	SL	HG	HHH	12/06/2010						K
SD7209-008	AL06HGS0	0.68	g		L	SL	HG	HHH	12/06/2010						H
SD7209-009	AL06HGS0	0.65	g		L	SL	HG	HHH	12/06/2010						G
SD7421-001	AL06HGS0	0.71	g		L	SL	HG	HHH	12/06/2010						A
SD7421-001P	AL06HGS0	0.71	g		L	SL	HG	HHH	12/06/2010						↓
SD7421-001S	AL06HGS0	0.72	g		L	SL	HG	HHH	12/06/2010						

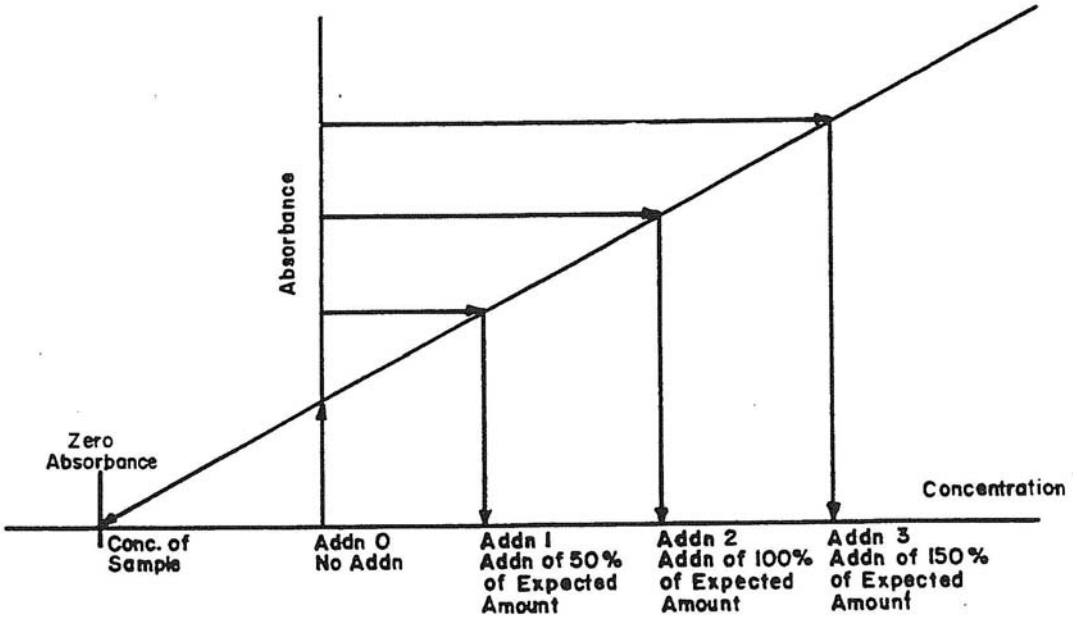
HHH 12-6-10

QA-067-Revision 1 - 09/23/2010 Digestion performed by: HHH On: 12-6-10 Page: AL024 Revision: 00

TITLE: **DIGESTION AND ANALYSIS OF SOLID SAMPLES FOR MERCURY BY USEPA METHOD 7471**

FIGURE 2

STANDARD ADDITIONS PLOT



TITLE: **DIGESTION AND ANALYSIS OF SOLID SAMPLES FOR MERCURY BY USEPA METHOD 7471**

FIGURE 3

EXAMPLE CERTIFICATE OF ANALYSIS FOR A SOLID REFERENCE MATERIAL

ENVIRONMENTAL RESOURCE ASSOCIATES®
The Industry Standard™

M51475

DataPacK™
Lot No. D051-540

Trace Metals in Soil
Catalog No. 540

Certification

Method 3050 HNO3, H2O2, HCl Parameter	Total Concentration [1] (mg/Kg)	Certified Value [2] (mg/Kg)	Performance Acceptance Limits™ [3] (mg/Kg)
aluminum	55600*	7870	4630 - 11100
antimony	160	70.5	D.L. - 149
arsenic	316	289	234 - 344
barium	869	211	174 - 247
beryllium	60.9	54.4	45.2 - 63.6
boron	129	91.3	58.8 - 124
cadmium	114	101	82.9 - 119
calcium	9750*	3680	2970 - 4390
chromium	249	224	180 - 268
cobalt	113	101	82.7 - 119
copper	94.9	88.0	73.3 - 103
iron	24400*	15700	6610 - 24900
lead	184	158	129 - 187
magnesium	3780*	2260	1760 - 2750
manganese	703	420	343 - 497
mercury	5.32	5.18	3.42 - 6.87
molybdenum	80.2	69.6	55.5 - 83.7
nickel	137	120	99.1 - 141
potassium	33000*	3000	2200 - 3800
selenium	146	130	101 - 159
silver	127	104	68.9 - 139
sodium	15600*	1080	692 - 1470
strontium	326	113	90.5 - 135
thallium	106	94.0	72.8 - 115
tin	175	149	104 - 194
titanium	3100*	284	116 - 453
vanadium	151	111	85.1 - 137
zinc	311	272	215 - 329

Method 3050 HNO3, H2O2 Parameter	Total Concentration [1] mg/Kg	Certified Value [2] mg/Kg	Performance Acceptance Limits™ [3] mg/Kg
aluminum	55600*	7380	4440 - 10300
antimony	160	75.2	D.L. - 198
arsenic	316	284	225 - 343
barium	869	217	177 - 257
beryllium	60.9	53.6	42.7 - 64.5
boron	129	89.5	58.9 - 120
cadmium	114	103	83.6 - 122
calcium	9750*	3540	2800 - 4270
chromium	249	224	172 - 275
cobalt	113	101	82.0 - 120
copper	94.9	85.5	70.4 - 100
iron	24400*	12500	5480 - 19500
lead	184	162	132 - 192
magnesium	3780*	2160	1650 - 2670
manganese	703	415	330 - 500
mercury	5.32	5.18	3.42 - 6.87
molybdenum	80.2	68.8	52.7 - 84.9
nickel	137	119	98.5 - 140
potassium	33000*	2840	2160 - 3520
selenium	146	135	104 - 166
silver	127	107	49.8 - 164
sodium	15600*	1010	709 - 1310
strontium	326	111	89.0 - 133
thallium	106	99.3	76.8 - 122
tin	175	148	70.6 - 225
titanium	3100*	283	104 - 463
vanadium	151	104	70.5 - 138
zinc	311	275	222 - 328

KATAHDIN ANALYTICAL SERVICES, INC.
STANDARD OPERATING PROCEDURE

SOP Number: CA-615
Revision History
Cover Page
Page 1

TITLE: DIGESTION AND ANALYSIS OF AQUEOUS SAMPLES FOR MERCURY BY USEPA METHOD 7470

Prepared By: George Brewer Date: 01/01

Approved By:

Group Supervisor: George Brewer Date: 01/29/01

Operations Manager: Joel C. Burton Date: 1/29/01

QA Officer: Deborah J. Nadeau Date: 1·29·01

General Manager: Dennis F. Hufham Date: 1/29/01

Revision History:

SOP Revision	Changes	Approval Initials	Approval Date	Effective Date
00 7470A	NA	DH	1·29·01	1/29/01
01	Revised Sect. 4, 5 and 7 to reflect current practice. Revised Sect. 8 to reflect current QC Limits. Revised sect. 10 to reflect current Applicable Documents and references. Removed figure 2. Update table 1 to reflect current QC Limits. Minor changes throughout	LAD	02-16-05	02-16-05
02	Updated Fig. 1 - new prep Logbook page	LAD	04/08	04/08
03	Updated Figure 1 - Example of a mercury Preparation Logbook page.	LAD	03/09	03/09
04	Added LOD definition. Updated sections 8, 9, 10 and Table 1 for DOD QSM version 4.1 compliance.	DH	08/09	08/09

TITLE: **DIGESTION AND ANALYSIS OF AQUEOUS SAMPLES FOR MERCURY BY USEPA METHOD 7470**

Revision History:

SOP Revision	Changes	Approval Initials	Approval Date	Effective Date
05	Added Table 2 - DoD QSM Version 4.1 QC Requirements	LAD	04/10	04/10

TITLE: **DIGESTION AND ANALYSIS OF AQUEOUS SAMPLES FOR MERCURY BY USEPA METHOD 7470**

Please acknowledge receipt of this standard operating procedure by signing and dating both of the spaces provided. Return the bottom half of this sheet to the QA Department.

I acknowledge receipt of copy ___ of document **SOP CA-615-05,** titled **DIGESTION AND ANALYSIS OF AQUEOUS SAMPLES FOR MERCURY BY USEPA METHOD 7470.**

Recipient: _____Date:_____

KATAHDIN ANALYTICAL SERVICES, INC.
STANDARD OPERATING PROCEDURE

I acknowledge receipt of copy ___ of document **SOP CA-615-05,** titled **DIGESTION AND ANALYSIS OF AQUEOUS SAMPLES FOR MERCURY BY USEPA METHOD 7470.**

Recipient: _____Date:_____

TITLE: DIGESTION AND ANALYSIS OF AQUEOUS SAMPLES FOR MERCURY BY USEPA METHOD 7470

1.0 SCOPE AND APPLICATION

The purpose of this SOP is to describe the procedure used by Katahdin Analytical Services, Inc. personnel for the digestion and analysis aqueous samples for mercury using cold vapor atomic absorption spectrophotometry.

This method is applicable to the determination of mercury in groundwaters, aqueous wastes, and mobility-procedure extracts under USEPA Method 7470 (Test Methods for Evaluating Solid Wastes: Physical/Chemical Methods, SW-846, 2nd edition, 1982 (revised 1984), 3rd edition, 1986, and Updates I, II, IIA, and III 1996, Office of Solid Waste and Emergency Response, U.S. EPA.

1.1 Definitions

CCB - Continuing Calibration Blank - An analyte-free solution consisting of acidified laboratory grade reagent water used to verify calibration accuracy periodically during analysis.

CCV - Continuing Calibration Verification - A midrange standard used to verify calibration accuracy periodically during analysis.

Duplicate - A second aliquot of a sample that is prepared and analyzed in the same way as the original sample in order to determine the precision of the method.

ICB - Initial Calibration Blank - An analyte-free solution consisting of acidified laboratory grade reagent water used to verify calibration accuracy.

ICV - Initial Calibration Verification - A standard made from a source independent from the calibration standards and with analyte concentrations different from those in the CCV; used to verify the accuracy of the instrument calibration.

IDL - Instrument Detection Limit - The lowest concentration of an analyte that can be determined with 95% confidence by the instrument.

LCS - Laboratory Control Sample - A standard or solid reference material that has been brought through the sample preparation process.

LOD – Limit of Detection – An estimate of the minimum amount of a substance that an analytical process can reliably detect. An LOD is analyte and matrix-specific and is used for DoD QSM acceptance criteria.

PB - Preparation Blank - Laboratory grade reagent water that has been brought through the sample preparation process.

PQL - Practical Quantitation Limit - The lowest concentration of an analyte that is routinely reported by the laboratory; nominally three to five times the IDL.

Matrix Spike - An aliquot of a sample to which a known amount of analyte has been added before digestion.

MDL - Method Detection Limit - The minimum concentration of an analyte that can be identified, measured, and reported with 99% confidence that the analyte concentration is greater than zero.

1.2 Responsibilities

This method is restricted to use by, or under the supervision of analysts experienced in the analysis of mercury by USEPA Method 7470. Each analyst must demonstrate and document their ability to generate acceptable results with this method. Refer to Katahdin SOP QA-805, current revision, “Personnel Training & Documentation of Capability”.

It is the responsibility of all Katahdin technical personnel involved in analysis of mercury by USEPA Method 7470 to read and understand this SOP, to adhere to the procedures outlined, and to properly document their data in the appropriate lab notebook. Any deviations from the test or irregularities with the samples should also be recorded in the lab notebook and reported to the Department Manager or designated qualified data reviewer responsible for this data.

It is the responsibility of the Department Manager to ensure that members of their group follow this SOP, that their work is properly documented, and to indicate periodic review of the associated logbooks.

1.3 Safety

Many of the samples and reagents used in cold vapor atomic absorption are toxic or corrosive. Rubber gloves, safety glasses, lab coats, and other protective clothing should be worn whenever these materials are handled. Because of the toxic nature of mercury vapor, care must be taken to avoid its inhalation. The instrument exhaust fan must be in operation whenever the mercury analyzer is in use (the fan should never be shut off).

Users of this procedure must be cognizant of inherent laboratory hazards, proper disposal procedures for contaminated materials and appropriate segregation of hazardous wastes. The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical should be treated as a potential health hazard. A reference file of material safety data sheets is available to all personnel involved in the chemical analysis. Everyone involved with

the procedure must be familiar with the MSDSs for all the materials used in this procedure.

Each qualified analyst or technician must be familiar with the Katahdin Analytical Environmental Health and Safety Manual including the Katahdin Hazardous Waste Management Plan and follow appropriate procedures such as wearing safety glasses and gloves when working with chemicals or near an instrument and not taking food or drink into the laboratory. Each analyst should know the location and use of all safety equipment.

1.4 Pollution Prevention/Waste Disposal

Whenever possible, laboratory personnel should use pollution prevention techniques to address their waste generation. Refer to the current revision of the Katahdin Hazardous Waste Management Plan for further details on pollution prevention techniques.

Samples, sample digestates, standards, and other reagents used in cold vapor atomic absorption may contain high concentrations of acids, mercury, and other toxic metals. They should be disposed of in a manner appropriate to the types of hazards they present. All digested mercury samples and standards and excess reagents and standards should be disposed of in the satellite waste container for corrosive wastes (labeled “Waste Stream A”) that is located in the Metals Prep lab. Further information regarding waste classification and disposal may be obtained by consulting the laboratory's Hazardous Waste Management Plan and Safety Manual and the Department Manager.

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. It relies on the volatility of elemental mercury at room temperature. During preparation, organic mercurials are oxidized and elemental mercury is ionized to Hg^{3+}. During instrumental analysis, mercuric ions are reduced to elemental mercury by the addition of stannous chloride. Elemental mercury is then aerated from solution and passes through a cell positioned in the path of a mercury spectrophotometer, where absorbance (peak height) is measured as a function of mercury concentration and recorded by the associated computer. The mercury vapor is then swept out of the instrument into an exhaust hood, where it is evacuated from the laboratory.

3.0 INTERFERENCES

In addition to inorganic forms of mercury, organic mercurials may be present in environmental samples. These organo-mercury compounds will not respond to the cold

vapor atomic absorption technique unless they are first broken down and converted to mercuric ions. The presence of undigested organo-mercurials in samples will result in a low bias for analytical results. Certain volatile organic materials will also non-specifically absorb radiation at the 253.7 nm analytical wavelength. The presence of such compounds may result in a high bias for analytical results. For these reasons, complete digestion using potassium permanganate and potassium persulfate is required for all environmental samples. Complete digestion is indicated by the persistence of the purple permanganate color (indicating the presence of excess permanganate) following digestion.

Sea waters, brines, and industrial effluents high in chlorides may require additional permanganate to maintain a persistent purple color following digestion. During the oxidation step, chlorides are converted to free chlorine which will absorb radiation at the 253.7 nm analytical wavelength. Any free chlorine thus generated will be present in the headspace of the digestion vessel following digestion. Because samples are poured into autosampler tubes prior to analysis by the mercury analyzer, any free chlorine present in the headspace of the digestion vessels is not sampled by the instrument and the analysis is free of chlorine interference.

4.0 APPARATUS AND MATERIALS

4.1 40 mL VOA vials, for use as digestion vessels.

4.2 250 mL Pyrex media bottles with plastic screw caps, for use in digesting calibration standards.

4.3 Water bath capable of maintaining a constant temperature of 95° C.

4.4 Adjustable volume automatic pipettes - 2 to 20 uL, 10 to 100 uL, 100 to 1000 uL. Calibrated Eppendorf Reference pipets and Finn digital pipets are appropriate.

4.5 Repipetters (adjustable repeating pipetters with reservoirs) for dispensing concentrated nitric acid, concentrated sulfuric acid, and other reagents

4.6 Spirit-filled thermometer, NIST-traceable, covering the range from 20° to 110° C, for monitoring the temperature of the water bath. Mercury-filled thermometers are not acceptable for use in the metals laboratory, due to the possibility of breakage and consequent contamination.

4.7 Disposable graduated polystyrene sample cups, 200 mL capacity

4.8 CETAC M-6100 automated mercury analyzer and associated peripherals and parts

4.9 Disposable graduated dose cups, 30 mL capacity

TITLE: DIGESTION AND ANALYSIS OF AQUEOUS SAMPLES FOR MERCURY BY USEPA METHOD 7470

Refer to Katahdin SOP CA-629, current revision, "Operation and Maintenance of the CETAC M-6100 Automated Mercury Analyzer" for additional required materials.

5.0 REAGENTS

5.1 Laboratory grade reagent water – mercury-free water meeting the specifications of ASTM Type II water

5.2 Concentrated sulfuric acid, trace metals grade

5.3 Concentrated nitric acid, trace metals grade

5.4 Concentrated hydrochloric acid, trace metal grade

5.5 Potassium permanganate solution, 5% w/v: Dissolve 50 g of potassium permanganate in 1 L laboratory grade reagent water. The source reagent should be labeled as suitable for use in mercury determination.

5.6 Potassium persulfate solution, 5% w/v: Dissolve 50g of potassium permanganate in 1L laboratory grade reagent water. The source reagent should be labeled as suitable for use in mercury determination.

5.7 Sodium chloride – hydroxylamine hydrochloride solution: Dissolve 120 g sodium chloride and 120 g hydroxylamine hydrochloride in laboratory grade reagent water and dilute to a final volume of 1 L.

5.8 Stannous chloride solution: Add 70 mL concentrated hydrochloric acid to 500 mL of laboratory grade reagent water. Add 100 g stannous chloride and bring to a final volume of 1 L. Mix to dissolve. Reagent should be labeled as suitable for use in mercury determination.

5.9 Intermediate Mercury Standard A: Appropriately dilute a mercury stock standard to obtain a solution containing 1000 ug of mercury per liter in 2% nitric acid. This intermediate standard is used to prepare calibration standards, matrix spikes, CCVs, and laboratory control samples (refer to Section 8). The identity of the stock standard currently used to prepare this intermediate may be obtained by consulting the Standards Preparation Logbook maintained in the Section. Intermediate Mercury Standard A must be prepared fresh monthly ,and disposed of appropriately after use. (Note: the concentrations of all stock standards must be certified by the vendors as traceable to NIST reference materials).

5.10 Intermediate Mercury Standard B: Appropriately dilute a mercury stock standard to obtain a solution containing 1000 ug of mercury per liter in 2% nitric acid. The source of the stock standard used to prepare Intermediate Mercury Standard B must

be distinct from that used to prepare Intermediate Mercury Standard A (i.e. obtained from a separate vendor). Intermediate Mercury Standard B is used to prepare the ICV (refer to Section 8). The identity of the stock standard currently used to prepare this intermediate standard may be obtained by consulting the Standards Preparation Logbook maintained in the Section. Intermediate Mercury Standard B must be prepared fresh monthly, and disposed of appropriately after use.

6.0 SAMPLE COLLECTION, PRESERVATION AND HANDLING

Aqueous samples to be analyzed for mercury should be collected and preserved as described in the following table.

Matrix	Container[1]	Collection Volume/ Weight	Preservation/ Treatment	Holding Time
Aqueous (total)	P, G	250 mL	HNO_3 to pH < 2	28 days
Aqueous (dissolved)	P, G	250 mL	HNO_3 to pH < 2	28 days

[1] P = polyethylene or G = glass

7.0 PROCEDURES

BOTTLE PREPARATION

7.1 Mercury digestions are performed in two different types of vessels. Calibration standards, the Initial Calibration Verification (ICV) standard, and the Initial/Continuing Calibration Blank (ICB/CCB) are prepared in 250 mL Pyrex media bottles. Large bottles are used to provide sufficient volumes of these standards to allow for multiple reanalyses when required. Field samples, Method Blanks, and Laboratory Control Samples are digested in 40 mL VOA vials. These smaller vials provide enough digestate to allow one or two reanalyses when required, but reduce the amounts of samples consumed and waste generated.

VOA vials are reused if the samples they have contained have no measurable mercury above the PQL. After the previous contents of the vials have been discarded, these vials are segregated according to whether the measured mercury concentrations of the previous contents were above the PQL (contaminated vials) or below the PQL (uncontaminated vials). Labels are removed from the vials by wiping with a paper towel saturated with toluene. Uncontaminated vials are rinsed with laboratory grade reagent water. Contaminated vials are discarded.

The Pyrex media bottles in which standards are prepared are emptied, rinsed, and reused. Each of these bottles is permanently marked with the concentration of the standard it contains.

PREPARATION OF STANDARDS, QC SAMPLES, AND BLANKS

7.2 Prior to performing the digestion, make a list of the samples that are to be digested. Enter digestion information (Katahdin Sample Numbers, QC Batch ID, preparation date, analyst initials, etc.) into the ACCESS Metals database and print out a copy of the sample prep bench sheet. All necessary details of sample preparation (standards preparation information, digestion times, initial and final volumes, pertinent observations, etc.) must be recorded on this spreadsheet, which will be bound in the Mercury Preparation Logbook. Refer to Figure 1 for an example page from the Mercury Preparation Logbook.

7.3 Using a silver paint marker, label clean VOA vials with the appropriate sample numbers and standard identifications for each sample and standard to be digested.

7.4 Use a bottle-top dispenser to add 100 mL of laboratory grade reagent water to 6 standards digestion bottles (250 mL media bottles). Using calibrated adjustable pipettes, prepare calibration standards by adding 0 uL, 20 uL, 50 uL, 100 uL, 500 uL, and 1000 uL of Intermediate Mercury Standard A to separate appropriately-labeled media bottles containing 100 mL of laboratory grade reagent water. The mercury concentrations of these calibration standards are, respectively, 0 ug/L (calibration blank), 0.2 ug/L, 0.5 ug/L, 1.0 ug/L, 5.0 ug/L, and 10.0 ug/L. The 0.2 ug/L and 0.5 ug/L standards are analyzed after calibration as the PQL standard and the CCV (refer to Section 8.0), respectively, as well as being used in the creation of the calibration curve.

7.5 Add 100 mL of laboratory grade reagent water to the media bottle labeled “ICV”. Using a calibrated adjustable pipette, prepare the Initial Calibration Verification standard (refer to Section 8) by adding 600 uL of Intermediate Mercury Standard B to the water in this bottle, and record the bottle number in the Mercury Preparation Logbook. The mercury concentration of the ICV is 6.0 ug/L.

7.6 Prepare an appropriate number of preparation blanks (PBW) by adding 25 mL of laboratory grade reagent water to labeled vials.

7.7 Prepare an appropriate number of laboratory control samples (LCSW) by adding 125 uL of Intermediate Mercury Standard A to labeled digestion vials containing 25 mL of laboratory grade reagent water. The mercury concentration of each LCSW is 5.0 ug/L.

7.8 Matrix spikes are prepared by adding 25 uL of Intermediate Mercury Std A to 25 mL aliquots of samples. The concentration of mercury added to each matrix spike is 1.0 ug/L.

7.9 All QC samples and blanks are digested in the same manner as client samples. Refer to Sample Preparation and Digestion, sections 7.10 through 7.13 of this SOP. The volumes of reagents added to the standards prepared in the media bottles are four times those listed in sections 7.10 through 7.13.

SAMPLE PREPARATION AND DIGESTION

7.10 Using a graduated disposable dosecup, transfer 25 mL of sample, or an aliquot diluted to 25 mL, to a digestion vial. Add 1.25 mL of concentrated sulfuric acid and 0.625 mL of concentrated nitric acid, swirling to mix after each addition. Add 3.75 mL of potassium permanganate solution, swirl to mix, and allow to stand for at least 15 minutes. Samples that contain large amounts of organic substances may require additional 3.75 mL aliquots of potassium permanganate solution. This is indicated by the failure of the purple permanganate color to persist for the entire 15 minute waiting period. Add additional 3.75 mL aliquots to samples as necessary until the purple color persists for 15 minutes. If any of the samples require these additional aliquots of potassium permanganate solution, record the additional volume used for each sample on the mercury preparation benchsheet.

7.11 Add 2 mL of potassium persulfate solution to each sample. Cap the vials and place them in a preheated water bath. Monitor the temperature of the bath with a spirit thermometer throughout the digestion. The temperature of the water bath will fall below 95° C upon addition of the digestion vials. After the temperature of the bath has risen back to 95° C, continue heating the samples at 95° C for two hours. Record initial and final digestion times and temperatures in the mercury prepareation benchsheet.

7.12 Remove bottles from the water bath and allow to cool to room temperature. If the purple permanganate color has failed to persist after digestion in any of the samples, add additional 3.75 mL aliquots of potassium permanganate solution as required to the samples, and record these additions in the mercury preparation benchsheet. Heat the samples that required additional permanganate in the water bath at 95° C for an additional two hours. Remove the bottles from the water bath and allow to cool to room temperature. If the purple color fails to persist after the second heating step, consult the Department Manager for advice on how to proceed.

7.13 Add 1.5 mL of sodium chloride – hydroxylamine hydrochloride solution to each digestion vial and swirl to mix. This will reduce the excess permanganate, and the sample will change from purple to colorless. Wait at least 30 seconds before proceeding with analysis.

INSTRUMENTAL ANALYSIS

7.14 Digested mercury samples are analyzed using the CETAC M-6100 Automated Mercury Analyzer. Analysis is automated and is controlled by the QuickTrace Mercury Analyzer software running on a dedicated PC. Detailed instructions for setting up the instrument and analyzing samples are given Katahdin SOP CA-629, "Operation and Maintenance of the CETAC M-6100 Automated Mercury Analyzer".

METHOD OF STANDARD ADDITIONS

7.15 The standard addition technique involves adding known amounts of standard to one or more aliquots of the processed sample solution. This technique compensates for a sample constituent that enhances or depresses the analyte signal, thus producing a different slope from that of the calibration standards. It will not correct for additive interferences which cause a baseline shift. The method of standard additions shall be used for analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

7.15.1 The simplest version of this technique is the single-addition method, in which two identical aliquots of the sample solution, each of volume V_x, are taken. To the first (labeled A) is added a known volume V_S of a standard analyte solution of concentration C_S. To the second aliquot (labeled B) is added the same volume V_S of the solvent. The analytical signals of A and B are measured and corrected for nonanalyte signals. The unknown sample concentration C_x is calculated:

$$C_X = \frac{S_B V_S C_S}{(S_A - S_B) V_X}$$

where S_A and S_B are the analytical signals (corrected for the blank) of solutions A and B, respectively. V_s and C_s should be chosen so that S_A is roughly twice S_B on the average, avoiding excess dilution of the sample. If a separation or concentration step is used, the additions are best made first and carried through the entire procedure.

7.15.2 Improved results can be obtained by employing a series of standard additions. To equal volumes of the sample are added a series of standard solutions containing different known quantities of the analyte, and all solutions are diluted to the same final volume. For example, addition 1 should be prepared so that the resulting concentration is approximately 50 percent of the expected absorbance from the endogenous analyte in the sample. Additions 2 and 3 should be prepared so that the concentrations are approximately 100 and 150 percent of the expected endogenous sample absorbance. The absorbance of each solution is determined and then plotted on the vertical axis of a graph, with the concentrations of the known

standards plotted on the horizontal axis. When the resulting line is extrapolated to zero absorbance, the point of interception of the abscissa is the endogenous concentration of the analyte in the sample. The abscissa on the left of the ordinate is scaled the same as on the right side, but in the opposite direction from the ordinate. An example of a plot so obtained is shown in Figure 3. A linear regression program may be used to obtain the intercept concentration.

7.15.3 For the results of this MSA technique to be valid, the following limitations must be taken into consideration:

- The apparent concentrations from the calibration curve must be linear over the concentration range of concern. For the best results, the slope of the MSA plot should be nearly the same as the slope of the standard curve. If the slope is significantly different (greater than 20%), caution should be exercised.

- The effect of the interference should not vary as the ratio of analyte concentration to sample matrix changes, and the standard addition should respond in a similar manner as the analyte.

- The determination must be free of spectral interference and corrected for nonspecific background interference.

DATA REDUCTION AND REPORTING

7.16 Results are obtained in concentration units (ug/L) from the instrument. Electronic instrument data files are imported into the Metals ACCESS database for data reduction. Sample preparation information (initial sample volumes and final digestate volumes) are entered directly into the Metals ACCESS database to allow calculation of final results for reporting. Results are calculated as follows:

$$\text{Mercury concentration (ug/L)} = \frac{MC \times DF \times IV}{FV}$$

Where: MC = Measured mercury concentration (ug/L)
DF = Dilution factor at instrument
IV = Initial sample volume (mL)
FV = Final digestate volume (mL)

7.17 Results that exceed the calibration range of the instrument may not be reported - the sample must be appropriately diluted and reanalyzed. Results for diluted samples should be multiplied by the dilution factor prior to reporting. If additional aliquots of potassium permanganate were added during digestion, the resulting dilution must be corrected for before reporting.

7.18 Results are reported down to the laboratory's practical quantitation level (PQL), unless otherwise requested. Results below the PQL should be reported to the PQL and flagged with a "U" qualifier.

8.0 QUALITY CONTROL AND ACCEPTANCE CRITERIA

USEPA Method 7470 requires the laboratory to perform specific quality control checks to assess laboratory performance and data quality. Minimum frequencies, acceptance criteria, and corrective actions for these control checks are tabulated in Table 1 and are described below. Preparation instructions and the resulting mercury concentrations for calibration standards, QC standards, and matrix spikes are detailed in Sections 7.4 through 7.8 of this SOP. Table 1 criteria are intended to be guidelines for analysts. The table does not cover all possible situations. If any of the QC requirements are outside the recovery ranges listed in Table 1, all associated samples must be evaluated against all the QC. In some cases data may be reported, but may be reanalyzed in other cases. Making new reagents and standards may be necessary if the standardization is suspect. The corrective actions listed in Table 1 may rely on analyst experience to make sound scientific judgments. These decisions are based on holding time considerations and client and project specific Data Quality Objectives. The Department Manager, Operations Manager, General Manager and/or Quality Assurance Officer may be consulted to evaluate data. Some samples may not be able to be reanalyzed within hold time. In these cases "qualified" data with narration may be advisable after consultation with the client.

In some cases the standard QC requirements listed in Table 1 may not be sufficient to meet the Data Quality Objectives of the specific project. Much of the work performed at the lab is analyzed in accordance with specific QC requirements spelled out in a project specific Quality Assurance Project Plan (QAPP) or in a program specific Quality Systems Manual (QSM). The reporting limits, acceptance criteria and/or corrective actions may be different than those specified in this SOP. In these cases the appropriate information will be communicated to the Department Manager and/or senior chemists before initiation of the analyses so that specific product codes can be produced for the project. In addition, the work order notes for each project will describe the specific QAPP or QSM to be followed.
INITIAL DEMONSTRATION OF PERFORMANCE

8.1 Instrument detection limits (IDL) are determined quarterly for each analyte analyzed on each instrument by each method. This determination requires seven replicate analyses of a laboratory grade reagent water spiked at 3-5 times the anticipated detection limit for each analyte, performed on three non-consecutive days. The standard deviation of the 21 analyses is multiplied by three to obtain the IDL. For more information on performing IDL determinations, refer to the current revision of Katahdin SOP QA-806.

8.2 Method detection limits (MDL) are determined annually for each analyte analyzed on each instrument. This determination requires at least seven replicate digestions

and analyses of laboratory grade reagent water spiked at 3-5 times the anticipated MDL for each analyte. MDLs differ from IDLs in that the replicates are digested prior to analysis, and they may be analyzed on a single day. The standard deviation of the 7 (or more) replicate analyses is multiplied by the Student's t-value to obtain the MDL. For more information on performing MDL determinations, refer to the current revision of Katahdin SOP QA-806.

8.3 Limits of Detection (LOD) are used when evaluating data using DoD QSM. The LOD is established by spiking a quality system matrix at 2-3 times the detection limit for a single analyte standard and 1-4 times the detection limit for a multi-analyte standard. The LOD must be verified quarterly. For more information on performing LOD determinations, refer to the current revision of Katahdin SOP QA-806.

8.4 Instrument calibration - The instrument must be calibrated each time it is set up, and calibration standards must be digested each day that samples are digested. Calibration includes analysis of a calibration blank and five calibration standards with graduated concentrations in the appropriate range. The concentration of one of the calibration standards must be at the Practical Quantitation Level (PQL). The intermediate standards used for preparing the calibration standards are prepared at least once per month in 2% nitric acid. Because mercury may be adsorbed onto the walls of glass and plastic containers, the calibration standards must be prepared fresh daily. The correlation coefficient for the calibration curve must be at least 0.995. If the calibration curve does not pass this test, analysis must be halted, the problem corrected, and the instrument recalibrated.

8.5 An Initial Calibration Verification (ICV) solution is analyzed after the initial calibration to check calibration accuracy. The ICV solution is prepared from a standard source different than that of the calibration standard and at a concentration within the working range of the instrument. The result of the ICV must fall within 90% to 110% of the expected value. If the ICV fails, results may not be reported from the run until the problem is corrected and a passing ICV has been analyzed.

8.6 The Continuing Calibration Verification (CCV) solution is analyzed after the initial calibration, after every ten samples, and at the end of the analytical run. The CCV solution is prepared using the same standard used for calibration at a concentration near the mid-point of the calibration curve. Results of the CCVs must fall within 80% to 120% of the expected value. If a CCV fails, associated sample results may not be reported from the run until the problem is corrected and a passing CCV has been analyzed. Also, all samples analyzed after the last passing CCV must be reanalyzed.

8.7 A calibration blank is analyzed after each ICV and CCV. A calibration blank that is analyzed after the ICV is called an Initial Calibration Blank (ICB). A calibration blank that is analyzed after a CCV is called a Continuing Calibration Blank (CCB). The absolute values of results of ICBs and CCBs must be less than the Practical

Quantitation Level (PQL) for each element. If samples are being run using DoD QSM criteria, the absolute values of ICBs and CCBs must be less than the Limit of Detection (LOD). If an ICB or a CCB fails, results for the failing elements may not be reported from the run until the problem is corrected and a passing ICB or CCB has been analyzed. Also, all samples analyzed after the last passing CCB must be reanalyzed.

8.8 A standard with a mercury concentration that is at the Practical Quantitation Limit (PQL) is analyzed at the beginning of the run to determine calibration accuracy at the reporting limit. Result of the PQL standard should fall within 70% to 130% of the expected values. No corrective action has been established at this time.

PREPARATION BATCH QC SAMPLES

8.9 Preparation blank (PBW or PBS), consisting of reagent water carried through the same process as associated samples, is prepared with each digestion batch of twenty or fewer samples. The results of preparation blanks must be less than the Practical Quantitation Level (PQL) for each element. For DoD QSM acceptance criteria the results must be less than ½ the PQL except for common contaminants which must be less than the PQL. If a preparation blank fails, results for the failing elements may not be reported from the digestion batch, and all associated samples must be redigested, with the following exception. If the result for a preparation blank is greater than the PQL (greater than ½ PQL for DoD), associated sample results that are less than the PQL (less than ½ PQL for DoD) or greater than or equal to ten times the measured preparation blank concentration may be reported.

8.10 A laboratory control sample (LCSW), consisting of spiked reagent carried through the same process as associated samples, is prepared with each digestion batch of twenty or fewer samples. Results for laboratory control samples must fall within 80% to 120% of the expected value, unless laboratory-generated statistical limits are available. If a laboratory control sample fails, results may not be reported from the digestion batch, and all associated samples must be redigested.

SAMPLE MATRIX QC SAMPLES

8.11 Matrix spiked duplicate samples are prepared at a minimum frequency of one per digestion batch. Matrix spike recoveries for these samples are calculated as follows:

$$\text{Recovery (\%)} = \frac{(P - S)}{A} \times 100\%$$

where: P = Spiked sample value
S = Original sample value
A = Spike amount

The recovery for each element in a spiked sample or spiked duplicate sample must fall within 75% to 125% of the actual value if the result for the unspiked sample is less than four times the amount of spike added. If one or both spike recoveries fail, a matrix interference should be suspected and the associated sample result should be flagged on the report of analysis. If DoD QSM acceptance criteria are being used, recoveries must be the same as stated for laboratory control samples.

The relative percent difference between matrix spiked duplicate sample results is calculated as follows:

$$\text{RPD (\%)} = \frac{|D_1 - D_2|}{(|D_1 + D_2|)/2} \times 100$$

where: D_1 = Spike sample result
D_2= Spike duplicate sample result

A control limit of 20% RPD is applied to matrix spike duplicate analysis. If the matrix spike duplicate analysis fails, the associated sample result should be flagged on the report of analysis.

9.0 METHOD PERFORMANCE

The method detection limit (MDL) and the limit of detection (LOD) are defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. The MDLs and LODs are determined prior to sample analysis per type of instrument and filed with the Inorganic Department Manager and with the QAO. Refer to the current revision of Katahdin SOP QA-806, Method Detection Limit, Instrument Detection Limit and Reporting Limit Studies and Verifications, for procedures on determining the MDL.

Refer to the current revision of USEPA Method 7470 for other method performance parameters and requirements.

10.0 APPLICABLE DOCUMENTS/REFERENCES

Department of Defense Quality Systems Manual for Environmental Laboratories (DOD QSM), Version 4.1, 04/22/09.

Katahdin SOP CA-101, Equipment Maintenance, current revision.

Katahdin SOP QA-806, Method Detection Limit, Instrument Detection Limit and Reporting Limit Studies and Verifications.

TITLE: DIGESTION AND ANALYSIS OF AQUEOUS SAMPLES FOR MERCURY BY USEPA METHOD 7470

The National Environmental Laboratory Accreditation Conference (NELAC) Standards, June 2003.

Test Methods for Evaluating Solid Wastes, United States Environmental Protection Agency, USEPA SW 846, Third Edition, Final Update III (9/94), Method 7470A.

QuickTrace M6100 Mercury Analyzer Operator Manual Version 1.0.1, CETAC Technologies.

QuickTrace Mercury Analyzer Software Manual, CETAC Technologies.

List of Tables and Figures

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Table 2 DoD QSM Version 4.1 QC Requirements
Table 3 Method Modifications
Figure 1 Example Mercury Preparation Logbook Page
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TABLE 1

QC REQUIREMENTS

Parameter/ Method	QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action
Mercury/ USEPA 7470	Initial Calibration, 5 points plus a calibration blank.	Daily prior to sample analysis.	Correlation coefficient ≥ 0.995.	Correct problem and repeat calibration.
	Initial Calibration Verification (ICV), prepared from a second source.	Before beginning a sample run.	Recovery within ± 10% of true value.	Correct problem and repeat calibration.
	Initial Calibration Blank (ICB)	Before beginning a sample run.	Less than PQL.	Correct problem and repeat calibration.
	Practical Quantitation Level Standard (PQL)	Before beginning a sample run.	Recovery within ± 30% of true value.	No corrective action required at this time.
	Continuing Calibration Verification (CCV)	At beginning or run, after every 10 samples, and at end of the run	Recovery within ± 20% of true value	Repeat calibration and reanalyze all samples analyzed since the last successful CCV.
	Continuing Calibration Blank (CCB)	At beginning or run, after every 10 samples, and at end of the run	Less than PQL.	Repeat calibration and reanalyze all samples analyzed since the last successful CCB.
	Preparation Blank (PBW)	One per digestion batch of 20 or fewer samples.	Less than PQL.	1) Investigate source of contamination. 2) Redigest and reanalyze all associated samples if sample concentration ≥ PQL and < 10x the blank concentration.
	Laboratory Control Sample (LCSW)	One per digestion batch of 20 or fewer samples.	Recovery within ± 20% of true value.	Redigest all affected samples.
	Matrix Spike Sample (S)	One per digestion batch of 20 or fewer samples.	Recovery ±25% of true value, if sample > 4x spike value.	Flag results.
	Matrix Spike Duplicate Sample (P)	One per digestion batch of 20 or fewer samples.	1) Recovery ± 25% of true value, if sample < 4x spike added. 2) RPD ≤20% for duplicate spikes.	Flag results
	Instrument Detection Limit (IDL) Study	Quarterly.	IDL < PQL	1) Repeat IDL study. 2) Raise PQL.
	Limit of Detection (LOD) determination	Quarterly.	LOD = 2-3X MDL	Repeat LOD Determination.
	Method Detection Limit (MDL) Study	Refer to KAS SOP QA-806, "Method Detection Limit, Instrument Detection Limit and Reporting Limit Studies and Verifications", current revision.		

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TABLE 2

DOD QSM VERSION 4.1 QC REQUIREMENTS

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 significant 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.
LOD determination and verification	(Refer to current revision of SOP QA-806)				
LOQ establishment and verification	(Refer to current revision of SOP QA-806)				
Initial calibration (ICAL) for mercury - minimum 5 standards and a calibration blank	Daily ICAL prior to sample analysis.	5 points plus a calibration blank, 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 (ICV)	Once after each ICAL, prior to beginning a sample run.	Value of second source for all analyte(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)	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 Q-flag to all results for the specific analyte(s) in all samples since the last acceptable calibration verification.	After every 10 field samples and at the end of the analysis sequence.	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.

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TABLE 2

DOD QSM VERSION 4.1 QC REQUIREMENTS

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Method blank	One per preparatory batch.	No analytes detected > ½ RL (> RL for common lab contaminants) 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 the problem. Report sample results that are <LOD or >10x the blank concentration. Reprepare and reanalyze the method blank and all associated samples with results > LOD and < 10x the contaminated blank result. Contact Client if samples cannot be reprepped within hold time.	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.	
LCS	One per preparatory batch.	Water: Recovery must be within + 20% of the true value Soil: Recovery must be within vendor supplied limits (varies by lot).	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).	Recovery must be within + 20% of the true value.	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 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 (see Box D-7).	MSD: Recovery must be within + 20% of the true value. 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.

TITLE: DIGESTION AND ANALYSIS OF AQUEOUS SAMPLES FOR MERCURY BY USEPA METHOD 7470

TABLE 2

DOD QSM VERSION 4.1 QC REQUIREMENTS

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Method of standard additions (MSA)	When matrix interference is confirmed.	NA.	NA.	NA.	Document use of MSA in the case narrative.
Results reported between DL and LOQ	NA.	NA.	NA.	Apply J-flag to all results between DL and LOQ.	

TITLE: DIGESTION AND ANALYSIS OF AQUEOUS SAMPLES FOR MERCURY BY USEPA METHOD 7470

TABLE 3

SUMMARY OF METHOD MODIFICATIONS

TOPIC	KATAHDIN SOP CA-615-04	USEPA METHOD 7470
Reagents	Stannous chloride dissolved in hydrochloric acid to prevent clogging of mercury analyzer, per instrument manufacturer's recommendation.	Stannous chloride dissolved/suspended in sulfuric acid.
Procedures	1)Sampling and gas stream switching performed automatically by mercury analyzer. 2)Working Mercury standard prepared monthly in 2% nitric; calibration standards prepared fresh daily.	1)Sampling and gas stream switching performed manually by analyst. 2)Working Mercury standard prepared fresh daily and acidity maintained at 0.15% nitric.
QC – Calibration Verification	1) Known reference sample (ICV) analyzed daily. 2) Calibration verified after every 10 samples with CCV.	1) Known reference sample analyzed quarterly. 2) Calibration verified after every 20 samples.
QC - Calibration Blanks	Acceptance criteria employed for 245.1: ± PQL	Acceptance criteria stated in 245.1: ± MDL

TITLE: DIGESTION AND ANALYSIS OF AQUEOUS SAMPLES FOR MERCURY BY USEPA METHOD 7470

FIGURE 1

EXAMPLE PAGE FROM MERCURY PREPARATION LOGBOOK

Katahdin Analytical Services, Inc.

Metals Preparation Benchsheet

Reagent Information:

JT Baker HNO3: G41034 JT Baker HCL: N/A JT Baker H2SO4: G20022 Method: 7470

JT Baker KMNO4: MR781 JT Baker K2S2O8: MR780 JT Baker NH2OH-HCl: MR778

Standards/Spiking Information:

1ppm A : ~~[illegible]~~ MW11565

1ppm B : DWM 2-25-09 MW11566

LCSW = 125uL of 1ppm A to 25mL

Spike(S/P) = 25uL of 1ppm A to 25mL

ICV = 600uL of 1ppm B to 100 mL

S0.2 = 20uL of 1ppm A to 100 mL

S0.5 = 50uL of 1ppm A to 100 mL

S1.0 = 100uL of 1ppm A to 100 mL

S5.0 = 500uL of 1ppm A to 100 mL

S10.0 = 1000uL of 1ppm A to 100 mL

Balance ID: N/A

Water Bath ID : B

Digestion Start Time (@ 96 °C): 13:30

Thermometer ID : ALC-5

Digestion End Time(@ 95 °C): 15:30

Sample ID	Batch ID	Initial Wt/Vol	Initial Units	Final Vol	Final Units	MX	Meth	Anal.	Date	Initial Color	Initial Clarity	Final Color	Final Clarity	Artifacts	Bottle
LCSWZB24HGW0	ZB24HGW0	0.025	L	0.025	L	AQ	HG	DWM	02/24/2009	N/A	N/A	N/A	N/A		
PBWZB24HGW0	ZB24HGW0		L		L	AQ	HG	DWM	02/24/2009	N/A	N/A	N/A	N/A		
SC0797-001T	ZB24HGW0		L		L	AQ	HG	DWM	02/24/2009						
SC0805-007T	ZB24HGW0		L		L	AQ	HG	DWM	02/24/2009						
SC0834-013T	ZB24HGW0		L		L	AQ	HG	DWM	02/24/2009						
SC0834-002 DWM 2-25-09	ZB24HGW0		L		L	AQ	HG	DWM	02/24/2009						E
SC0836-001	ZB24HGW0		L		L	AQ	HG	DWM	02/24/2009						E
SC0846-013	ZB24HGW0		L		L	AQ	HG	DWM	02/24/2009						E
SC0858-001T	ZB24HGW0		L		L	AQ	HG	DWM	02/24/2009						
SC0858-002T	ZB24HGW0		L		L	AQ	HG	DWM	02/24/2009						
SC0868-013	ZB24HGW0		L		L	AQ	HG	DWM	02/24/2009						E
SC0868-015	ZB24HGW0		L		L	AQ	HG	DWM	02/24/2009						E
SC0834-013TD			L		L										
013TS			L		L										

DWM 2-25-09

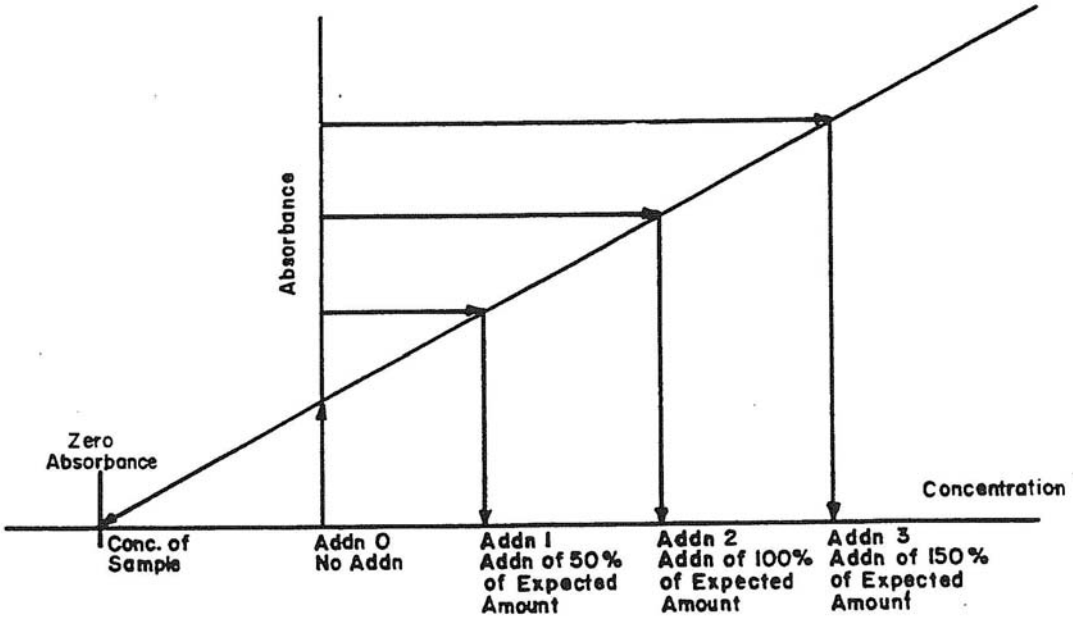
Digestion performed by: DWM On: 2-24-09

Page: ZB071 Revision: 00

TITLE: **DIGESTION AND ANALYSIS OF AQUEOUS SAMPLES FOR MERCURY BY USEPA METHOD 7470**

FIGURE 2

STANDARD ADDITIONS PLOT



KATAHDIN ANALYTICAL SERVICES, INC.
STANDARD OPERATING PROCEDURE

SOP Number: CA-627
Revision History
Cover Page
Page 1

TITLE: **TRACE METALS ANALYSIS BY ICP-MS USING USEPA METHOD 6020**

Prepared By: George Brewer Date: 03/01

Approved By:

Group Supervisor: George Brewer Date: 04/02/01

Operations Manager: Joel C. Burton Date: 3/29/01

QA Officer: Deborah J. Nadeau Date: 03·27·01

General Manager: Dennis P. Hufford Date: 04/03/01

Revision History:

SOP Revision	Changes	Approval Initials	Approval Date	Effective Date
01	Changed acid solution conc. changed Run ID naming convention added data reduction and reporting procedures updated standards tables (4-8) updated Table 10 in include ISIS configuration	LAD	02-16-05	02-16-05
02	Sect. 4.2 - changed tubing size Sect. 5 - changed acid conc.'s Sect. 7 - major changes to reflect current practises including reporting data in the metals database. Sect. 8 - major changes updating acceptance criteria. Updated Tables 1, 3 → 8, 10 & 11	LAD	04/06	04/06
03	Updated Tables 4, 5 and 6 with current standards. Updated Table 1 with serial dilution, Post Digestion Matrix spike, MSA, ICS-A, ICS-AB and IDL minimum frequency or criteria. Updated Sect. 8 regarding client specific requirements.	LAD	07/07	07/07
04	Section 7.18-changed instrument identifier to reflect new instrument; section 8-changed acceptance criteria and ICSAB analyte list; Table 1-updated acceptance criteria and corrective actions to QC. Table 3-added all analytes to list-removed "for information only" list.	LAD	04/08	04/08
05	Updates to reflect changes from 6020 to 602A. Added Hardness by calculation attachment. Added LL QC requirement and criteria to Sect 8 and Table 1. Added criteria to analyze PQL Std. at beginning and END of run.	LAD	02/09	02/09

TITLE: TRACE METALS ANALYSIS BY ICP-MS USING USEPA METHOD 6020

SOP Revision	Changes	Approval Initials	Approval Date	Effective Date
06	Sect. 8 and QC Tables - Added DoD QSM references and criteria. Section 10 - Added references. Tables 4 → 7 - Added information pertaining to CCV conc. change	LAD	08/09	08/09
07	Added Table 2 with DoD QSM ver. 4.1 QC requirements. Updated Section 4.1, Table 10 and Table 11 with new autosampler information.	LAD	04/10	04/10

TITLE: **TRACE METALS ANALYSIS BY ICP-MS USING USEPA METHOD 6020**

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STANDARD OPERATING PROCEDURE

I acknowledge receipt of copy ___ of document **SOP CA-627-07**, titled **TRACE METALS ANALYSIS BY ICP-MS USING USEPA METHOD 6020**

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TITLE: **TRACE METALS ANALYSIS BY ICP-MS USING USEPA METHOD 6020**

1.0 SCOPE AND APPLICATION

Inductively coupled plasma-mass spectrometry (ICP-MS) is applicable to the determination of sub-ppb (ug/L) concentrations of a large number of elements in water samples and in waste extracts or digests. When dissolved constituents are required, samples must be filtered and acid-preserved prior to analysis. No digestion is required prior to analysis for dissolved elements in water samples. Acid digestion prior to filtration and analysis is required for groundwater, aqueous samples, industrial wastes, soils, sludges, sediments, and other solid wastes for which total (acid-leachable) elements are required.

ICP-MS has been applied to the determination of over 60 elements in various matrices. Analytes for which EPA has demonstrated the acceptability Method 6020 in a multi-laboratory study on solid wastes are listed as "analytes" in Table 4. Instrument detection limits, sensitivities, and linear ranges will vary with the matrices, and operating conditions. If Method 6020 is used to determine any analyte not listed in Table 4, it is the responsibility of the analyst to demonstrate the accuracy and precision of the method in the waste to be analyzed. The analyst is always required to monitor potential sources of interferences and take appropriate action to ensure data of known quality.

An appropriate internal standard is required for each analyte determined by ICP-MS. Recommended internal standards are ^{6}Li, ^{45}Sc, ^{89}Y, ^{103}Rh, ^{115}In, ^{159}Tb, ^{165}Ho, and ^{209}Bi. The lithium internal standard should have an enriched abundance of ^{6}Li, so that interference from lithium native to the sample is minimized. Other elements may need to be used as internal standards when samples contain significant amounts of the recommended internal standards.

1.1 Definitions:

CCB - Continuing Calibration Blank - An analyte-free solution consisting of acidified reagent water used to verify calibration accuracy periodically during analysis.

CCV - Continuing Calibration Verification - A midrange standard used to verify calibration accuracy periodically during analysis.

Duplicate - A second aliquot of a sample that is prepared and analyzed in the same way as the original sample in order to determine the precision of the method.

ICB - Initial Calibration Blank - An analyte-free solution consisting of acidified reagent water used to verify calibration accuracy.

ICP-MS - Inductively Coupled Plasma Mass Spectrometry.

ICS - Interference Check Samples - Two standards (ICS-A and ICS-AB) used to

verify the effectiveness of interference correction equations. Solution ICS-A contains only interferents (Al, Ca, Fe, Mg, Na, K, P, S, Mo, Ti, C, Cl) at high concentrations; solution ICS-AB contains interferents at the same concentrations as well as analytes at low (20 ug/L) concentrations.

ICV - Initial Calibration Verification - A standard made from a source independent from the calibration standards and with analyte concentrations different from those in the CCV; used to verify the accuracy of the instrument calibration.

IDL - Instrument Detection Limit - The lowest concentration of an analyte that can be determined with 95% confidence.

LCS - Laboratory Control Sample - A standard or solid reference material that has been brought through the sample preparation process.

PB - Preparation Blank - Reagent water that has been brought through the sample preparation process.

Post-Digestion Spike - An aliquot of a sample to which a known amount of analyte has been added before analysis and after digestion, if digestion is required.

PQL - Practical Quantitation Limit - The lowest concentration of an analyte that is routinely reported by the laboratory; nominally three to five times the IDL.

Matrix Spike - An aliquot of a sample to which a known amount of analyte has been added before digestion.

Serial Dilution - The dilution of a sample by a factor of five. When corrected by the dilution factor, the measured analyte concentrations of the diluted sample should agree with those of the original undiluted sample within specified limits. Serial dilution may reflect the influence of interferents.

1.2 Responsibilities

This method is restricted to use by, or under the supervision of, analysts experienced in ICP-MS analysis by USEPA Method 6020 who are knowledgeable in the recognition and in the correction of spectral, chemical, and physical interferences in ICP-MS. Each analyst must demonstrate and document their ability to generate acceptable results with this method. Refer to Katahdin SOP QA-805, current revision, "Personnel Training & Documentation of Capability".

It is the responsibility of all Katahdin technical personnel involved in ICP-MS analysis by USEPA Method 6020 to read and understand this SOP, to adhere to the procedures outlined, and to properly document their data in the appropriate lab notebook. Any deviations from the test or irregularities with the samples should also

be recorded in the lab notebook and reported to the Department Manager or designated qualified data reviewer responsible for this data.

It is the responsibility of the Department Manager to oversee that members of their group follow this SOP, to ensure that their work is properly documented, and to initiate periodic review of the associated logbooks.

1.3 Safety

Users of this procedure must be cognizant of inherent laboratory hazards, proper disposal procedures for contaminated materials and appropriate segregation of hazardous wastes. The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical should be treated as a potential health hazard. A reference file of material safety data sheets is available to all personnel involved in the chemical analysis. Everyone involved with the procedure must be familiar with the MSDSs for all the materials used in this procedure.

Each qualified analyst or technician must be familiar with Katahdin Analytical Environmental Health and Safety Manual including the Katahdin Hazardous Waste Plan and must follow appropriate procedures. These include the use of appropriate personal protective equipment (PPE) such as safety glasses, gloves and lab coats when working with chemicals or near an instrument and not taking food or drink into the laboratory. Each analyst should know the location of all safety equipment. Each analyst shall receive a safety orientation from their Department Manager, or designee, appropriate for the job functions they will perform.

Samples, sample digestates, standards, and other reagents used in ICP analysis may contain high concentrations of acids and toxic metals. Spilled samples and reagents should be cleaned up from instrument and laboratory surfaces immediately.

Liquid argon represents a potential cryogenic and suffocation hazard and safe handling procedures should be employed at all times when handling liquid argon tanks and fittings. Safety glasses and cryogenic-resistant gloves should be worn when changing or adjusting argon tanks.

The Agilent 7500 ICP-MS spectrometer is safety-interlocked to prevent user exposure to harmful electrical voltages, radio frequency emissions, ultraviolet radiation, high temperatures, and other hazards. At no time should the operator attempt to disable these interlocks or operate the instrument if any safety interlock is suspected to be disabled

1.4 Pollution Prevention/Waste Disposal

Whenever possible, laboratory personnel should use pollution prevention and waste minimization techniques to address their waste generation. Refer to the current revision of the Katahdin Hazardous Waste Management Program for further details on pollution prevention techniques.

Samples, sample digestates, standards, and other reagents used in ICP-MS spectrometry may contain high concentrations of acids and toxic metals. They should be disposed of in a manner appropriate to the types of hazards they present. All digested samples and excess reagents and standards should be disposed of in the satellite waste container for corrosive wastes (labeled "Waste Stream A") that is located in the Metals Instrument lab. Further information regarding waste classification and disposal may be obtained by consulting Katahdin Analytical Environmental Health and Safety Manual and the Department Manager.

2.0 SUMMARY OF METHOD

2.1 Prior to analysis, samples that require total ("acid-leachable") values must be digested using appropriate sample preparation methods (such as USEPA Methods 3005 - 3051).

2.2 USEPA Method 6020 describes the multi-elemental determination of analytes by ICP-MS. The method measures ions produced by a radio-frequency inductively coupled argon plasma. Analyte species originating in a liquid are nebulized and the resulting aerosol transported by argon gas into the plasma torch. The ions produced are entrained in the plasma gas and introduced, by means of a vacuum interface, into a mass spectrometer. The ions produced in the plasma are sorted according to their mass-to-charge ratios and quantified with a channel electron multiplier. Interferences must be assessed and valid corrections applied or the data flagged to indicate problems. Interference correction must include compensation for background ions contributed by the plasma gas, reagents, and constituents of the sample matrix.

3.0 INTERFERENCES

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). The Agilent 7500 ChemStation data system is used to correct for these interferences. This involves determining the signal for another isotope of the interfering element and subtracting the appropriate signal from the analyte isotope signal. 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 which could affect ICP-MS

determinations have been identified. Examples include $ArCl^+$ ions on the 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 isotopic abundances from the literature, the most precise coefficients for an instrument must be determined from the ratio of the net isotope signals observed for a standard solution at a concentration providing suitable (<1 percent) counting statistics. Because the ^{35}Cl natural abundance of 75.77 percent is 3.13 times the ^{37}Cl abundance of 24.23 percent, the chloride correction for arsenic can be calculated (approximately) as follows (where the $^{38}Ar^{37}Cl^+$ contribution at m/z 75 is a negligible 0.06 percent of the $^{40}Ar\ ^{35}Cl^+$ signal):

Corrected ^{75}As signal (using natural isotopic abundances for coefficient approximations) =

(m/z 75 signal) - (3.13) (m/z 77 signal) + (2.73) (m/z 82 signal),

where the final term adjusts for any selenium contribution at 77 m/z.

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

Corrected ^{114}Cd signal (using natural isotopic abundances for coefficient approximations) =(m/z 114 signal) - (0.027)(m/z 118 signal) - (1.63)(m/z 108 signal),

where last 2 terms adjust for any tin or MoO^+ contributions at m/z 114.

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

NOTE: As for the arsenic equation above, the coefficients in the Cd equation are only illustrative. The most appropriate coefficients for an instrument can be determined from the ratio of the net isotope signals observed for a standard solution at a concentration providing suitable (<l percent) counting precision.

The interference correction equations that are used by this laboratory in performing USEPA Method 6020 are listed in Table 4. The accuracy of these types of equations is based upon the constancy of the observed isotopic ratios for the interfering species. Corrections that presume a constant fraction of a molecular ion relative to the "parent" ion have not been found to be reliable, e.g., oxide levels can vary. If a correction for an oxide ion is based upon the ratio of parent-to-oxide ion intensities, the correction must be adjusted for the degree of oxide formation by the use of an appropriate oxide internal standard previously demonstrated to form a similar level of oxide as the interferent. This type of

correction has been reported for oxide-ion corrections using ThO^+/Th^+ for the determination of rare earth elements. The use of aerosol desolvation and/or mixed plasmas have been shown to greatly reduce molecular interferences (the Agilent 7500 ICP-MS spectrometer employs spray chamber cooling to effect aerosol desolvation). These techniques can be used provided that method detection limit, accuracy, and precision requirements for analysis of the samples can be met.

3.1 Physical interferences are associated with the sample nebulization and transport processes as well as with ion-transmission efficiencies. Nebulization and transport processes can be affected if a matrix component causes a change in surface tension or viscosity. Changes in matrix composition can cause significant signal suppression or enhancement. Dissolved solids can deposit on the nebulizer tip of a pneumatic nebulizer and on the interface skimmers (reducing the orifice size and the instrument performance). Total solid levels below 0.2% (2,000 mg/L) are recommended to minimize solid deposition. An internal standard can be used to correct for physical interferences, if it is carefully matched to the analyte so that the two elements are similarly affected by matrix changes. The internal standard used should differ from the analyte of interest by no more than 50 amu. See table 14 for a list of internal standards used. When the intensity level of an internal standard is less than 70 percent or greater than 120 percent of the intensity of the first standard used during calibration, the sample must be reanalyzed after a fivefold (1+4) or greater dilution has been performed.

3.2 Memory interferences can occur when there are large concentration differences between samples or standards that are analyzed sequentially. Sample deposition on the sampler and skimmer cones, spray chamber design, and the type of nebulizer affect the extent of the memory interferences that are observed. The rinse period between samples must be long enough to eliminate significant memory interference.

4.0 APPARATUS AND MATERIALS

4.1 Agilent 7500 ICP-MS system, consisting of the Agilent 7500 ICP-mass spectrometer and its controlling computer data station. The spectrometer is capable of providing resolution better than or equal to unit resolution at 10% peak height. The Agilent 7500 mass range of 2-260 amu exceeds the method requirement of 2- 240 amu. The Agilent 7500 ChemStation software allows automatic corrections for isobaric interferences and correction for internal standard responses as required by the method. All critical argon flows including nebulizer argon are under mass flow controller control and a peristaltic pump is used for sample introduction. Peripheral equipment includes a Elemental Scientific SC-4 PX Fast Autosampler and Sample Introduction system, and an Agilent LaserJet printer.

4.2 Peristaltic pump tubing – 3-stop Tygon white-white (1.02 mm ID), orange-blue (0.25 mm ID), and 2-stop red-red (1.14 mm ID). 3-stop Pharmed blue-yellow (1.52 mm ID).

4.3 15 ml 17x100 mm polypropylene or polystyrene disposable test tubes for samples and 50 ml polypropylene centrifuge tubes for standards.

4.4 Automatic adjustable-volume pipetters of suitable precision and accuracy. Calibrated Eppendorf Reference pipets and Finn digital pipets are appropriate.

4.5 Trace metal grade pipette tips.

4.6 Volumetric glassware or plasticware of suitable precision and accuracy.

4.7 Talc free vinyl gloves.

4.8 Argon gas supply (high purity grade gas or liquid, 99.99%).

4.9 For the determination of trace levels of elements, contamination and loss are of prime consideration. Potential contamination sources include improperly cleaned laboratory apparatus and general contamination within the laboratory environment from dust etc. A clean laboratory work area, designed for trace element sample handling must be used. Standards, samples and blanks should be exposed to the laboratory environment as little as possible. The use of preparation blanks and spikes should be used to verify the absence of sources of contamination and loss. If necessary, polypropylene sample tubes should be rinsed and stored in dilute acid prior to use.

NOTE: Chromic acid must not be used for cleaning glassware for trace metals analysis.

5.0 REAGENTS

5.1 Acids used in the preparation of standards and for sample processing must be of high purity. Redistilled acids are recommended because of the high sensitivity of ICP-MS. Mallincrodt/Baker "Instra-Analyzed" trace-metals grade acids are appropriate. It is important to match the acid concentration in standards and samples. Concentrations of antimony and silver between 50-500 ug/L require 1% (v/v) HCl for stability; for concentrations above 500 ug/L additional HCl will be needed. For this reason, it is recommended that antimony and silver concentrations in samples and standards be maintained below 500 ppb wherever possible. Acids are received in poly-coated glass bottles, and are stored under the hood in the Metals sample preparation laboratory at room temperature until use. All acids are considered to have a shelf life of three years from date of receipt unless

otherwise indicated by the vendor. Refer to the current revision of Katahdin SOP CA-105, Reagent and Solvent Handling, for further details.

5.2 Reagent water, trace metals free, equivalent to ASTM Type 1 (ASTM D 1193), >18 Megohm/centimeter resistivity. Polyethylene carboys are filled with reagent water in the glassware prep room and are transported to the laboratory for use. Reagent water is replaced at least weekly.

5.3 Single element and multielement stock standard solutions – purchased standards prepared from high purity salts or metals, and supplied by the vendors with certificates of purity and analysis. Refer to Tables 5 and 6 for a listing of stock standards required, and to Table 9 for element concentrations in stock standards. Purchased stock standards are received in polyethylene containers and are stored in their original containers at room temperature in the Metals Standards Preparation Laboratory. All purchased stock standards are given an expiration date as indicated by the manufacturer. Refer to the current revision of Katahdin SOP CA-106, Standard Preparation, Documentation and Traceability, for further details.

5.4 Intermediate standard solutions – laboratory-prepared multielement standards that are used in the subsequent preparation of working standards. Refer to Table 6 for a listing of intermediate standards required and for preparation instructions. Refer to Table 8 for element concentrations in intermediate standards. Intermediate standards are stored at room temperature in acid-washed polyethylene containers in the Metals Standards Preparation Laboratory. Intermediate standards are assigned an expiration date of three months from the date of preparation, or the earliest expiration date of a component standard, whichever comes first. Refer to the current revision of Katahdin SOP CA-106, Standard Preparation, Documentation and Traceability, for further details.

5.5 Working standard solutions – laboratory-prepared multielement standards that are used to calibrate the instrument, to provide internal standardization through on-line addition, and to perform all necessary QC checks. Refer to Table 5 for a listing of working standards and for preparation instructions. Refer to Table 7 for element concentrations in working standards. Working standards are stored at room temperature in acid-washed polyethylene containers in the Metals Standards Preparation Laboratory. All working standards except the ICSA and ICSAB solutions are assigned an expiration date of three months from the date of preparation, or the earliest expiration date of a component standard, whichever comes first. The ICSA and ICSAB solutions are assigned an expiration date of one week from the date of preparation, or the earliest expiration date of a component standard, whichever comes first. Refer to the current revision of Katahdin SOP CA-106, Standard Preparation, Documentation and Traceability, for further details.

5.6 Blanks: Three types of blanks are required for the analysis. The calibration blank is used in establishing the calibration curve. The preparation blank is used to monitor

for possible contamination resulting from the sample preparation procedure. The rinse blank is used to flush the system between all samples and standards.

5.6.1 The calibration blank consists of the same concentrations of the same acid(s) used to prepare the final dilution of the analyte calibration solutions (currently 1% HNO_3 and 0.5% HCl, v/v, in laboratory reagent grade water). Use of HCl for antimony and silver is cited in Section 5.1.

5.6.2 The preparation blank must be carried through the complete preparation procedure and contain the same volumes of reagents as the associated digested sample solutions.

5.6.3 The rinse blank consists of 4% HNO_3 and 0.5% HCl,v/v, in reagent water. Prepare a sufficient quantity to flush the system between standards and samples.

6.0 SAMPLE COLLECTION, PRESERVATION AND HANDLING

Samples to be analyzed for trace metals by ICP-MS should be collected and preserved as described in the following table.

Matrix	Container[1]	Collection Volume/ Weight	Preservation/ Treatment	Holding Time
Aqueous (total)	P, G	250 mL	HNO_3 to pH < 2	6 months
Aqueous (dissolved)	P, G	250 mL	Filter, HNO_3 to pH < 2	6 months
Solid	P, G	10 g	Cool, 4°C	6 months

[1] P = polyethylene or, G = glass

7.0 PROCEDURES

7.1 Instrument control and data acquisition are completely automated through the use of the Agilent Chemstation software. The main Chemstation screen is accessed by double-clicking the "ICP-MS Top" icon on the Windows desktop. Autosampler tables are edited by double clicking the "Edit Sample Log Table" icon on the Windows desktop. In the following discussion, software menu items that are to be selected are printed in boldface. The instrument operating conditions, acquisition parameters, acquisition masses, and internal standards for analysis USEPA Method 6020 are detailed in Table 11.

7.2 Turn on the argon supply at the tank and set the pressure to >700 kPa.

7.3 Turn on the water chiller/recirculator.

7.4 Verify that the exhaust hood is in operation.

7.5 Ensure that the internal standard solution bottle is adequately full. Consumption is approximately 2.5 mL/hour.

7.6 Verify that the rinse station reservoir has an adequate supply of reagent water.

7.7 Verify that the drain reservoir has adequate room to accept the day's drain waste. Empty the reservoir as necessary into an appropriate waste container (Waste Stream A) located in the Hazardous Waste Storage Area.

7.8 Inspect the peristaltic pump tubes for signs of flattening and wear, and replace them as necessary. Clamp the peristaltic pump tubes into the peristaltic pump.

7.9 Open the Chemstation software by double-clicking the "ICP-MS Top" icon. Initiate the plasma by selecting **Instrument>>Instrument Control>>Plasma>>Plasma On** and allow the instrument to aspirate calibration blank solution for at least 15 minutes. During this warm-up, select **Tune>>Sensitivity>>Start** to start the instrument scanning the mass range. Verify that the flow of sample and internal standard solutions through the uptake lines and into the nebulizer is free from pulsations by introducing an air bubble into each line and observing its progress. Adjust the pump clamp tension on each line to obtain a constant, pulse-free flow.

7.10 After the 15 minute warm-up, check the responses of masses 82 and 83 to insure minimal krypton intereference with selenium. Mass 83 response should be < 2000 counts per second. Then aspirate the Instrument Tune Solution (10 ppb Li, Y, Ce, Tl) and check the responses and RSDs at masses 7, 89, and 205.

7.11 Generate a tune report by selecting **Tune>>File>>Generate Report**. Evaluate the tune report against the tune specifications listed in Table 12. If the tune passes all specifications, proceed to step 7.14.

7.12 If the tune report indicates unacceptable instrument performance for any parameter, initiate an autotune by selecting **Tune>>Autotune>>Run**. The Chemstation software will attempt to tune the instrument to meet the tune specifications, and will generate a new tune report after autotuning. Evaluate the new tune report against the tune specifications listed in Table 12.

7.13 Repeat step 7.12 until all tune specifications have been met. File the final tune report.

7.14 Aspirate a 100 ppb solution of all analytes and run a P/A autotune by selecting **Tune>>Tune>>P/A Factor>>Run**. This will calibrate the pulse and analog modes of the detector. File the P/A report with the Tune report.

7.15 Load the instrument analytical method and calibrations table for USEPA Method 6020 into memory by selecting **Methods>>Load>>K6020.M>>K6020.C**.

7.16 Edit the sequence template "K6020.S" to create an analytical sequence table listing all of the samples to be analyzed. To do this, double click the "Edit Sample Log Table" icon on the Windows desktop. Select **Open>>K6020.S**. Click the drop-down menu at the top left of the screen, and select the **Sample** block. Fill in the sample table with sample IDs, vial numbers, analytical method (K6020.M for all samples), dilution factors, and failure actions. When the sample table is complete, click the drop-down menu at the top left of the screen, and select **Whole List** to view the entire analytical sequence, including all calibration standards and QC samples. Select **Print** to print this table. Save the sample log table under a new name by selecting **Save** and then typing the name. Close the "Edit Sample Log Table" window.

7.17 Load the autosampler racks according to the analytical sequence printout.

7.18 Select **Sequence>>Load and Run Sequence**, and select the appropriate autosampler sequence table from the displayed list. Enter the analyst's initials in the Operator box. Change data file name to appropriate designation. The protocol for naming data files is as follows: the 1st character is a letter that identifies the instrument ("J" for the Agilent 75000 ICP-MS), the 2nd character is a letter that identifies the year of the run ("X" for 2007, "Y" for 2008, etc.), the 3rd character is a letter that identifies the month of the run ("A" for January, "B" for February, etc.), the 4th and 5th characters are numbers that identify the date of the run ("01" for the first day of the month, etc.), and the 6th character is a letter that sequentially identifies the run ("A" for the first run of the day on that instrument, "B" for the second run, etc.). For example, the run identified as "JYA16A" is the first run of the day that was performed on January 16, 2008, using the Agilent 7500 ICP-MS. Select **Run**. The instrument will analyze all samples in the order listed in the table. Analysis must proceed in the sequence described in Table 10 to ensure that all necessary quality control samples are analyzed at the appropriate frequencies. A minimum of three replicate scans is required for all standards and samples. Analysis always begins with the analysis of a calibration blank followed by at least three multielement calibration standards to calibrate the instrument. The system is flushed with rinse blank between each sample and standard, and each sample and standard is aspirated for at least one minute prior to the beginning of mass scanning.

7.19 Analysis continues with analysis of the initial calibration verification standard (ICV) and the initial calibration blank (ICB) to verify the accuracy of the calibration. Refer to Section 8 and Table 1 for additional information.

7.20 A practical quantitation limit standard (PQL) is analyzed at the beginning of the run to verify calibration accuracy at the reporting limit. Refer to Section 8 and Table 1 for additional information.

7.21 A continuing calibration verification standard (CCV) and a continuing calibration blank (CCB) must be analyzed at the beginning of the run, after every ten samples, and at the end of the run to verify the continued accuracy of the calibration. Refer to Section 8 and Table 1 for additional information.

7.22 Interference check standard solutions ICS-A and ICS-AB must be analyzed at the beginning of each run and every 12 hours to verify the adequacy of interference corrections. Refer to Section 8 and Table 1 for additional information.

7.23 All sample analytical results for a particular element that are bracketed (preceded or followed) by failing results in a calibration verification sample (ICV, ICB, CCV, or CCB) for that element must not be reported, except as noted in Sections 8.5, 8.6, and 8.9. The sample must be reanalyzed for the element in question.

7.24 All samples that exceed the linear dynamic range must be diluted and reanalyzed.

7.25 If dilutions of digested samples are performed, the measured element concentrations must be multiplied by the dilution factor prior to reporting. This is accomplished automatically by entering the dilution factor in the sample log table prior to initiation of analysis.

7.26 If an element has more than one monitored isotope, examination of the concentration calculated for each isotope, or the isotope ratios, will provide useful information for the analyst in detecting a possible spectral interference. Consideration should therefore be given to both primary and secondary isotopes in the evaluation of the element concentration. In some cases, secondary isotopes may be less sensitive or more prone to interferences than the primary recommended isotopes, therefore differences between the results do not necessarily indicate a problem with data calculated for the primary isotopes. In the case of Pb, quantitation is based on the sum of isotopes 206, 207 and 208 to compensate for any variation in naturally occurring isotope ratios. This is accomplished through the use of the interference correction equation for lead.

7.27 Calculations, aqueous samples: Final element concentrations for aqueous samples are reported in units of micrograms per liter (ug/L). The reported concentrations are calculated from measured digestate concentrations as follows:

$$\text{Concentration (ug/L)} = \frac{MC \times DF \times FV}{IV}$$

where: MC = Measured digestate concentration (ug/L)
DF = Instrument dilution factor
FV = Final digestate volume (L)
IV = Digested sample volume (L)

7.28 Calculations, solid samples: Final element concentrations for solid samples are reported in units of milligrams per kilogram (mg/kg) on a dry weight basis. The reported concentrations are calculated from measured digestate concentrations as follows:

$$\text{Concentration (mg/kg dry weight)} = \frac{MC \times DF \times FV \times 100}{W \times S}$$

where: MC = Measured digestate concentration (ug/L)
DF = Instrument dilution factor
FV = Final digestate volume (L)
W = Weight of digested wet sample (g)
S = Percent solids

DATA REDUCTION AND REPORTING

7.29 When the analytical run is completed, the analyst should print a run summary and create a data import file.

7.30 Follow these steps to print the run summary: Open the FileView program using the "FIVIEW" icon on the Windows Desktop. Select the data file of interest and move the required samples into the "Process List". Make sure the "Corrected Data" box is checked. Click the "Process" button. The data will be displayed in a spreadsheet format.

7.31 Select "Configure" from the top menu and "Sublists" from the displayed options. Select "Load Sublist" and then select "K6020" from this list of options. Make sure the "Enable Sublist" box is checked. Click the "OK" button. This will display only the analyte masses in the spreadsheet.

7.32 Select "Quant Info" from the top menu and "Quant Results" from the displayed options. This will display the data in concentration units. Click on the cell in the top left corner of the spreadsheet to highlight all data. Select "Tools" from the top menu and "Import Data into Spreadsheet Application" from the displayed options. Click the "Save" button. The data is transferred to a Microsoft Excel spreadsheet. Minimize this window and return to the FileView spreadsheet.

7.33 Select "Configure" from the top menu and "Sublists" from the displayed options. Select "Load Sublist" and then select "INTSTDS" from this list of options. Make sure the "Enable Sublist" box is checked. Click the "OK" button. This will display only the internal standard masses in the spreadsheet.

7.34 Select "Count Info" from the top menu and "Counts/sec" from this list of options. This will display the data in counts per second units. Click on the cell in the top left corner of the spreadsheet to highlight all data. Select "Tools" from the top menu and "Import Data into Spreadsheet Application" from the displayed options. Click the "Save" button. The data is transferred to a Microsoft Excel spreadsheet. Copy the internal standard names and results and paste into the analyte results Excel spreadsheet.

7.35 In a separate cell of the Excel spreadsheet, input a formula to calculate the percent recovery of the internal standard relative to that of the calibration blank for each internal standard measurement of each sample.

7.36 Input a formula into the sample results cells to correct the data for dilution.

7.37 Format, print and save (as FileName.XLS, e.g. JYA28A.XLS) this run summary.

7.38 Follow these steps to create the data import file: Open the FileViewNT program using the "FIVIEWNT" icon on the Windows Desktop. Select the data file of interest and move the required samples into the "Process List". Make sure the "Corrected Data" box is checked. Click the "Process" button. The data will be displayed in a spreadsheet format.

7.39 Select "Configure" from the top menu and "Sublists" from the displayed options. Select "Load Sublist" and then select "K6020" from this list of options. Make sure the "Enable Sublist" box is checked. Click the "OK" button. This will display only the analyte masses in the spreadsheet.

7.40 Select "Quant Info" from the top menu and "Quant Results" from the displayed options. This will display the data in concentration units.

7.41 Select the "Transpose" from the menu.

7.42 Select "Tools" from the top menu and "Copy Selected Data to CSV File" from this list of options. Set the name the file as "FileName.CSV", e.g., "JYA28A.CSV". Click the "Save" button.

To import data into the Metals Database:

7.43 Select the "ICPMS Import" icon from the Windows Desktop, the ICPMS Import window will appear. Enter the datafile name without extension, (e.g., "JYA28A") and click the "Import" button.

7.44 When the "Import finished" message appears, close the ICPMS Import window and select the "KIMS_METALS" icon from the Windows Desktop. The Metals Database Main Menu will appear.

7.45 Select the "Reporting Menu" button. From the Reporting Menu screen select the Batch QC Menu button and then the "Calculate Batch QC" button.

7.46 From the resulting list of QC results, deselect any items that fail run QC or do not need ICP-MS analysis. Click on the "Accept Selected Batch QC" button.

7.47 From the Metals Main Menu, select the "Additional Data Handling" button. The Data Menu will appear. Select the "Report Added Compounds" button.

7.48 From the resulting list of sample results, deselect any items that fail run QC or do not need ICP-MS analysis. Click on the "Accept Data" button.

7.49 Once all associated data from an analysis run have been processed, go to the Generate Coverage portion of the Export Menu and print the Run Log and Logbook Page for the analysis run.

7.50 Combine these reports with the raw data printout and the Run Info Sheet and scan into a PDF format. Save in the "ICPMS DATA" section of the "METPDF" directory on the IMAGESERVER.

8.0 QUALITY CONTROL AND ACCEPTANCE CRITERIA

USEPA Method 6020 requires the laboratory to perform specific quality control checks to assess laboratory performance and data quality. Minimum frequencies, acceptance criteria, and corrective actions for these control checks are tabulated in Table 1 and are described below. Table 1 criteria are intended to be guidelines for analysts. The table does not cover all possible situations. If any of the QC requirements are outside the recovery ranges listed in Table 1, all associated samples must be evaluated against all the QC. In some cases data may be reported, but may be reanalyzed in other cases. Making new reagents and standards may be necessary if the standardization is suspect. The corrective actions listed in Table 1 may rely on analyst experience to make sound scientific judgements. These decisions are based on holding time considerations and client and project specific Data Quality Objectives. The Department Manager, Operations Manager, and/or Quality Assurance Officer may be consulted to evaluate data. Some samples may not be able to be reanalyzed within hold time. In these cases "qualified" data with narration may be advisable after consultation with the client.

In some cases the standard QC requirements listed in this section and in Table 1 may not be sufficient to meet the Data Quality Objectives of the specific project. Much of the work performed at the lab is analyzed in accordance with specific QC requirements spelled out in a project specific Quality Assurance Project Plan (QAPP) or in a program specific Quality Systems Manual (QSM). The reporting limits, acceptance criteria and/or corrective actions may be different than those specified in this SOP. In these cases the appropriate information will be communicated to the Department Manager and/or senior chemists before initiation of

the analyses so that specific product codes can be produced for the project. In addition, the work order notes for each project will describe the specific QAPP or QSM to be followed.

INITIAL DEMONSTRATION OF PERFORMANCE

8.1 Instrument detection limits (IDL) are determined quarterly for each analyte analyzed on each instrument. This determination requires seven replicate analyses of a reagent blank, performed on three non-consecutive days. The standard deviation of the 21 analyses is multiplied by three to obtain the IDL. For more information on performing IDL determinations, refer to the current revision of Katahdin SOP QA-806.

8.2 Method detection limits (MDL) are determined annually for each analyte analyzed by each method on each instrument. This determination requires at least seven replicate digestions and analyses of reagent water spiked at 3-5 times the anticipated MDL for each analyte. MDLs differ from IDLs in that the seven replicates are digested prior to analysis, and they may be analyzed on a single day. The standard deviation of the 7 (or more) replicate analyses is multiplied by the Student's t-value to obtain the MDL. For more information on performing MDL determinations, refer to the current revision of Katahdin SOP QA-806.

8.3 A Lower Limit of Quantitation Check (LLQC) sample must be prepared and analyzed annually or on an as-needed basis to confirm the laboratory's Practical Quantitation Limits (PQLs). The LLQC sample is equivalent to the PQL standard (Section 8.9) but is carried through the entire sample preparation and analysis process. Element recoveries for the LLQC sample must fall within 70% to 130% of the expected concentrations to confirm the previously established PQLs.

ANALYTICAL RUN QC SAMPLES

8.4 Initial instrument calibration: The instrument is calibrated by running a calibration blank and at least three multielement calibration standards. For each element, calibration is performed fitting a single order equation to the calibration data, as follows:

$$Y=aX + [Blank]$$

where: Y = Concentration (ug/L)
X = Measured signal intensity (counts per second)
a = Slope of the calibration line
[Blank] = Measured signal intensity of the calibration blank

Fitting the calibration equation through the measured intensity of the calibration blank, rather than through the y-intercept of the line, provides the best calibration accuracy at the low end of the calibration range. When this equation is used,

however, the Agilent software does not calculate a calibration coefficient. For this reason, calibration accuracy at the high end of the calibration range is checked by reanalyzing the highest calibration standard as a sample immediately after instrument calibration. Recoveries for all elements must be within 90% to 110% of the true value in the high calibration standard. If the high calibration standard fails, result for the failing elements may not be reported from the run until the problem is corrected and a passing high calibration standard has been analyzed. Calibration accuracy in the middle of the calibration range is verified by analysis of the CCV solution (see Section 8.6 below). Calibration accuracy at the reporting limit is verified by analysis of the PQL Check Standard (see Section 8.7 below).

8.5 The intensities of all internal standards must be monitored for every analysis. When the intensity of any internal standard fails to fall between 70 and 120 percent of the intensity of that internal standard in the initial calibration standard, the following procedure is followed. The sample must be diluted fivefold (1+4) and reanalyzed with the addition of appropriate amounts of internal standards. This procedure must be repeated until the internal standard intensities fall within the prescribed window. The intensity levels of the internal standards for the calibration blanks (ICB and CCBs) and calibration verification standards (ICV and CCVs) must agree within ± 20 percent of the intensity level of the internal standard of the original calibration solution. If they do not agree, terminate the analysis, correct the problem, recalibrate, verify the new calibration, and reanalyze the affected samples.

8.6 An Initial Calibration Verification (ICV) solution is analyzed after the initial calibration to check calibration accuracy. The ICV solution is prepared by combining compatible elements from standard sources different than those of the calibration standards and at concentrations within the linear working range of the instrument. The results of the ICV must fall within 90% to 110% of the expected values. If the ICV fails, result for the failing elements may not be reported from the run, unless the ICV recovery is greater than 110% and the sample result is less than the PQL.

8.7 Continuing Calibration Verification (CCV) solutions are analyzed after the initial calibration, after every ten samples, and at the end of the analytical run. The CCV solution is prepared using the same standards used for calibration at concentrations near the mid-point of the calibration curve. Results of the CCVs must fall within 90% to 110% of the expected values. If a CCV fails, results for the failing elements may not be reported from the run, unless the CCV recovery is greater than 110% and the sample result is less than the PQL.

8.8 A Practical Quantitation Limit (PQL) Check Standard or low level conintuing calibration verification (LLCCV) is analyzed at the beginning of each run (after the ICV and ICB samples) and at the end of each run. Element concentrations in this solution are one-fifth the laboratory's practical quantitation limit (assuming a 5-fold dilution of all digestates during analysis). Element recoveries for the PQL Check Standard must fall within 70% to 130% of the expected values (unless the samples

analyzed are for the Department of Defense (80% to 120% recovery limits) or other client-specific limits are imposed). If the PQL Check Standard fails, results for the failing elements may not be reported from the run, unless the PQL Check Standard recovery is greater than the high limit and the sample result is less than the PQL.

8.9 A calibration blank solution is analyzed after each ICV and CCV. A calibration blank that is analyzed after the ICV is called an Initial Calibration Blank (ICB). A calibration blank that is analyzed after a CCV is called a Continuing Calibration Blank (CCB). The absolute values of results of ICBs and CCBs must be less than the applicable reporting limit (or PQL) for each element. The reporting limit should be determined on a project specific basis, taking into account the data quality objectives for the project. This information must be communicated through a project QAPP and through the Katahdin project manager. When no project specific reporting limit is specified, the laboratory PQL shall be used. Some project specific limits may require reporting down to the MDL or IDL and taking corrective action based on these levels. Results that fall between the PQL and the IDL or MDL must always be flagged as "estimated" with a "J".

8.10 If an ICB or a CCB fails the acceptance criteria of less than the reporting limit, results for the failing elements may not be reported from the run until the problem is corrected and a passing ICB or CCB has been analyzed, with the following exception. If the result for an ICB or CCB is greater than the PQL (or reporting limit), sample results that are less than the PQL (or reporting limit) or that are greater than or equal to ten times the measured ICB or CCB concentration may be reported. Also, for failing elements, all samples analyzed after the last passing CCB must be reanalyzed, with the exception noted above.

8.11 To obtain analyte data of known quality, it is necessary to measure more than the analytes of interest in order to apply corrections or to determine whether interference corrections are necessary. If the concentrations of interference sources (such as C, Cl, Mo, Zr, W) are such that, at the correction factor, the analyte is less than the limit of quantitation and the concentration of interferents are insignificant, then the data may go uncorrected. Note that monitoring the interference sources does not necessarily require monitoring the interferent itself, but that a molecular species may be monitored to indicate the presence of the interferent. When correction equations are used, all QC criteria must also be met. Extensive QC for interference corrections are required at all times. The monitored masses must include those elements whose hydrogen, oxygen, hydroxyl, chlorine, nitrogen, carbon and sulfur molecular ions could impact the analytes of interest. Interference check solutions ICS-A and ICS-AB are analyzed at the beginning of each run and at least every 12 hours during the run to verify the effectiveness of interference corrections. Solution ICS-A contains high concentrations of interferents (Al, Ca, Fe, Mg, Na, P, K, S, C, Cl, Mo, and Ti) only. These should recover between 80% and 120% of the true value. The measured concentrations of other elements in this solution should be very low, indicating that interfering mass

correction equations are adequate. Solution ICS-AB contains interferents at the same high concentrations, and all other analytes at 20 ug/L. Measured recoveries for all analytes should be within 80% to 120% of the true values.

PREPARATION BATCH QC SAMPLES

Each digestion batch of twenty or fewer samples will contain a preparation blank and a laboratory control sample. Each batch will also contain one or more of the following QC samples: laboratory control sample duplicate, sample duplicate, matrix spiked sample, or matrix spiked sample duplicate.

8.12 A preparation blank (PBW or PBS), consisting of reagent water carried through the same process as associated samples, is prepared with each digestion batch of twenty or fewer samples. The results of preparation blanks must be less than the Practical Quantitation Level (PQL) (or project specific reporting limit, if applicable) for each element. If a preparation blank fails, results for the failing elements may not be reported from the digestion batch, and all associated samples must be redigested, with the following exception. If the result for a preparation blank is greater than the PQL or reporting limit, associated sample results that are less than the PQL or reporting limit or that are greater than or equal to ten times the measured preparation blank concentration may be reported.

8.13 A laboratory control sample (LCSW, LCSO, or LCSS), consisting of spiked reagent water or a solid reference material carried through the same process as associated samples, is prepared with each digestion batch of twenty or fewer samples. Results for laboratory control samples must fall within 80% to 120% of the expected value, unless vendor-supplied limits (for solid reference materials) or laboratory-generated statistical limits are available. If a laboratory control sample fails, results for the failing elements may not be reported from the digestion batch, and all associated samples must be redigested, with the following exception. If the recovery of a laboratory control sample is greater than 120%, associated sample results that are less than the PQL or reporting limit may be reported.

SAMPLE MATRIX QC SAMPLES

8.14 The relative percent difference (RPD) between matrix duplicate, matrix spike duplicate, or laboratory control duplicate sample results is calculated as follows:

$$\text{RPD (\%)} = \frac{|D_1 - D_2|}{(|D_1 + D_2|)/2} \times 100$$

where: D_1 = First sample or LCS result
D_2= Second (duplicate) sample or LCS result

A control limit of 20% RPD is applied to duplicate analysis, if the result is greater than 100 times the instrument detection limit. If the matrix duplicate analysis fails, the associated sample result must be flagged on the report of analysis.

8.15 The recovery for each element in a spiked sample must fall within 75% to 125% of the actual value if the result for the unspiked sample is less than four times the amount of spike added. If a recovery fails, the associated sample result must be flagged on the report of analysis. The spike recovery should be calculated as follows:

$$\text{Recovery (\%)} = \frac{S-U}{SA} * 100\%$$

where: S = Measured concentration of spiked aliquot
U = Measured concentration of unspiked aliquot
SA = Amount of spike added

8.16 A serial dilution is analyzed to check for chemical or physical interferences. If the analyte concentration of a sample is sufficiently high (minimally, 50 x IDL), the measured concentration of a five-fold dilution (1:5 dilution) of the sample should agree within 90% to 110% of the original determination. The percent difference between the original sample and the serial dilution should be calculated as follows:

$$\text{Difference (\%)} = \frac{|L-S|}{S} * 100\%$$

where: L = Serial dilution result (corrected for dilution)
S = Original sample result

If the serial dilution analysis fails, a matrix interference should be suspected. The action taken is dependent upon project requirements. The associated sample result may be flagged on the report of analysis, the sample may be reanalyzed at dilution to eliminate the interference, or a post-digestion spike may be performed (see section 8.16).

8.17 An analyte spike that is added to an aliquot of a prepared sample, or its dilution, should be recovered within 80% to 120% of the known value if the result for the unspiked aliquot is less than four times the amount of spike added. If the post-digestion spike is not recovered within these limits, the sample should be diluted and reanalyzed to compensate for the matrix interference or the method standard additions may be employed.

9.0 METHOD PERFORMANCE

The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. The MDLs are determined prior to sample analysis per type of instrument and filed with the Metals Department Manager and with the QAO.

Refer to the current revision of Katahdin SOP QA-806, Method Detection Limit, Instrument Detection Limit and Reporting Limit Studies and Verifications, for procedures on determining the MDL. Refer to the current revisions of USEPA Method 6020 for other method performance parameters and requirements.

10.0 APPLICABLE DOCUMENTS/REFERENCES

Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, USEPA SW846, 3rd Edition, Final Updates I, II, IIA, IIB, III, IIIA, IIIB and IV, February 2007, Method 6020A.

Department of Defense Quality Systems Manual for Environmental Laboratories (DOD QSM), Version 4.1, 04/22/09

The National Environmental Laboratory Accreditation Conference (NELAC) Standards, June 2003

Katahdin SOP CA-101, Equipment Maintenance and Troubleshooting, current revision.

Katahdin SOP QA-806, Method Detection Limit, Instrument Detection Limit and Reporting Limit Studies and Verifications, current revision

Agilent 7500 ICP-MS ChemStation Operator's Manual, Agilent Technologies, Inc., 2000.

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TABLE 1

QC REQUIREMENTS

QC Sample	Minimum Frequency	Acceptance Criteria	Corrective Action
Initial Calibration, minimum 3 points plus a calibration blank.	Daily prior to sample analysis.	Correlation coefficient (r) ≥ 0.998	Recalibrate
Initial Calibration Verification (ICV), prepared from a second source.	Before beginning a sample run.	Recovery within ± 10% of true value.	Do not use results for failing elements, unless ICV >110% and sample result < PQL/reporting limit.
Initial Calibration Blank (ICB)	Immediately after the ICV.	Absolute value of ICB < PQL or project specific reporting limit.	Do not use results if sample ≥ PQL/reporting limit and < 10x ICB level.
PQL Standard or LLCCV	At beginning and end of run	70-130% of true value	Do not use results for failing elements, unless PQL rec.> upper limit and sample result < PQL/reporting limit.
Continuing Calibration Verification (CCV)	At beginning of run, after every 10 samples, and at end of run.	Recovery within ± 10% of true value.	Do not use sample results for failing elements, unless CCV >110% and sample result < PQL/reporting limit.
Continuing Calibration Blank (CCB)	Immediately after every CCV	Absolute value of CCB < PQL or project specific reporting limit.	Do not use sample results if ≥ PQL/reporting limit and < 10x CCB level.
Interference Check Solution A (ICS-A)	Before analyzing samples, and every 12 hours during a run.	Interferents: Recovery within ± 20% of true value. Analytes: No criteria established (Project specific criteria may apply)	Do not use sample results for failing elements.
Interference Check Solution AB (ICS-AB)	Before analyzing samples, and every 12 hours during a run.	Recovery within ± 20% of true value.	Do not use sample results for failing elements, unless ICSAB >120% and sample result < PQL/reporting limit.
Preparation Blank (PBW/PBS)	One per digestion batch of 20 or fewer samples.	Less than PQL (standard practice), or based on the project specific guidelines.	1) Investigate source of contamination. 2) Redigest and reanalyze all associated samples if sample concentration ≥ PQL and <10x the blank conc.

TABLE 1 (continued)

QC REQUIREMENTS

QC Sample	Minimum Frequency	Acceptance Criteria	Corrective Action
Laboratory Control Sample (LCSW/LCSS/LCSO)	At least one per digestion batch of 20 or fewer samples.	Recovery within ± 20% of true value, unless vendor-supplied or statistical limits have been established.	1) Investigate source of problem. 2) Redigest and reanalyze all associated samples, unless LCS >120% and sample result < PQL.
Matrix Spike Sample (S)	See section 8.11	Recovery ± 25% of true value, if sample < 4x spike added.	Flag results and/ or perform post-digestion spike.
Duplicate Sample (D), Matrix Spike Duplicate (P), or LCS Duplicate (LC2W/LC2S/LC2O)	See section 8.11	1) RPD ≤ 20%, if sample > 100x IDL.	Flag results
Post-Digestion Matrix Spike (A)	When serial dilution fails and analyte concentration < 100 x MDL.	Recovery ± 20% of true value, if sample < 4x spike added.	Flag results and/or analyze sample by method of standard additions.
Serial Dilution (L)	1 per digestion batch	If original sample result is at least 50x IDL, 5-fold dilution must agree within ± 10% of the original result.	Flag result or dilute and reanalyze sample to eliminate interference.
Internal Standard (IS) Appropriate IS required for all analytes in all samples. Mass of IS must be <50 amu different from that of analyte.		1) For each sample, IS intensity within 70%-120% of that of initial calib. blank. 2) For ICV, ICB, CCV, and CCB, IS intensity within 80%-120% of that in initial calib. blank.	Do not use results for failing elements.
Instrument Detection Limit (IDL) Study	Quarterly.	IDL < MDL PQL at least 2-3x IDL	1) Repeat IDL study. 2) Raise PQL.
Method Detection Limit (MDL) Study	Refer to KAS SOP QA-806, "Method Detection Limit, Instrument Detection Limit and Reporting Limit Studies and Verifications", current revision.		
Lower Limit of Quantitation Check (LLQC) Sample	Digest and analyze annually or as needed to confirm PQLs	70% - 130% of true value	Reevaluate PQLs
Method of Standard Additions	When matrix interference is suspected	r ≥ 0.995	Dilute and reanalyze sample to eliminate interference.

TABLE 2

DoD QSM VERSION 4.1 QC REQUIREMENTS

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.
LOD determination and verification	Refer to current revision of SOP QA-806				
LOQ establishment and verification	Refer to current revision of SOP QA-806				
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 2 (cont)

DoD QSM VERSION 4.1 QC REQUIREMENTS

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 (> RL for common lab contaminants) 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 the problem. Report sample results that are <LOD or >10x the blank concentration. Reprepare and reanalyze the method blank and all associated samples with results > LOD and < 10x the contaminated blank result.	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-AB)	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 verified trace impurity from one of the spiked analytes); ICS-AB: Within ± 20% of true value. May use < LOD for some projects.	Terminate analysis, locate and correct problem, reanalyze ICS, reanalyze all samples.	If corrective action fails, apply Q-flag to all results for specific analyte(s) in all samples associated with the ICS.	

TABLE 2 (cont)

DoD QSM VERSION 4.1 QC REQUIREMENTS

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
LCS containing all analytes to be reported	One per preparatory batch.	Water: Recovery must be within + 20% of the true value Soil: Recovery must be within vendor supplied limits (varies by lot).	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 additions (MSA)	When matrix interference is confirmed.	NA.	NA.	NA.	Document use of MSA in the case narrative.
Internal standards (IS)	Every sample.	IS intensity within 30-120% of intensity of the IS in the ICAL.	Flagging criteria are not appropriate.	Reanalyze sample at 5-fold dilution with addition of appropriate amounts of internal standards.	
Results reported between DL and LOQ	NA.	NA.	NA.	Apply J-flag to all results between DL and LOQ.	

TABLE 3

SUMMARY OF METHOD MODIFICATIONS

TOPIC	KATAHDIN SOP CA-627-07	METHOD 6020, current revision
Apparatus/Materials		
Reagents		
Sample preservation/ handling		
Procedures		
QC - Spikes		
QC - LCS		
QC - Accuracy/Precision		
QC - MDL		
QC - Calibration Blanks	Acceptance criteria employed for 6020: ± PQL	Acceptance criteria stated in 6020: <10% of PQL

TITLE: **TRACE METALS ANALYSIS BY ICP-MS USING USEPA METHOD 6020**

TABLE 4

ISOTOPES MONITORED AND CORRECTION EQUATIONS USED FOR USEPA METHOD 6020

Element Class	Element	Sym-bol	Isotopes Monitored	Correction Equations [See note 1]
Analytes	Aluminum	Al	27	
	Antimony	Sb	121, 123	
	Arsenic	As	75	^{75}As = (75)*1 - (77)*2.95 + (82)*2.548 – (83)*2.571 [See note 2]
	Barium	Ba	135, 137	
	Beryllium	Be	9	
	Boron	B	11	
	Cadmium	Cd	106, 108, 111, 114	^{111}Cd = (111)*1 – (108)*1.073 + (106)*0.764 [See note 3] ^{114}Cd = (114)*1 – (118)*0.0268 [See note 4]
	Calcium	Ca	44	^{44}Ca = (44)*1 – (88)*0.0169 [See note 7]
	Chromium	Cr	52, 53	
	Cobalt	Co	59	
	Copper	Cu	63, 65	
	Iron	Fe	54, 56, 57	^{54}Fe = (54)*1 – (52)*0.0282 [See note 8] ^{57}Fe = (57)*1 – (43)*0.03 [See note 9]
	Lead	Pb	206, 207, 208	^{208}Pb = (208)*1 + (206)*1 + (207)*1 [See note 5]
	Magnesium	Mg	25	
	Manganese	Mn	55	
	Molybdenum	Mo	98	^{98}Mo = (98)*1 – (99)*0.146 [See note 10]
	Nickel	Ni	60, 61	
	Potassium	K	39	
	Selenium	Se	82	^{82}Se = (82)*1 – (83)*1.009 [See note 11]
	Silver	Ag	107, 109	
	Sodium	Na	23	
	Strontium	Sr	88	
	Thallium	Tl	203, 205	
	Thorium	Th	232	
	Tin	Sn	118, 120	
	Tungsten	W	182	
	Uranium	U	238	
	Vanadium	V	51	^{51}V = (51)*1 – (53)*2.95 + (52)*0.333 [See note 12]
	Zinc	Zn	66, 67, 68	
Internal Stan-dards.	Bismuth	Bi	209	
	Germanium	Ge	72	
	Indium	In	115	^{115}In = (115)*1 – (118)*0.016 [See note 6]
	Lithium	Li	6	
	Scandium	Sc	45	
	Terbium	Tb	159	
	Yttrium	Y	89	

TABLE 4 (continued)

ISOTOPES MONITORED AND CORRECTION EQUATIONS USED FOR USEPA METHOD 6020

Notes:

1) Numbers in parentheses, e.g "(51)", indicate measured counts at the indicated mass.
2) Corrects for ArCl interference, taking into account secondary interferences from Se and Kr
3) Corrects for MoO interference, taking into account secondary interference from ^{108}Cd
4) Corrects for Sn interference
5) Corrects for variations in isotopic composition of lead
6) Corrects for Sn interference
7) Corrects for interference from $^{88}Sr^{2+}$
8) Corrects for Cr interference
9) Corrects for Ca interference
10) Corrects for Ru interference
11) Corrects for Kr interference
12) Corrects for ClO, taking into account secondary interference from Cr

TABLE 5

PREPARATION OF CALIBRATION AND QUALITY CONTROL STANDARDS

Sample or Solution Name	Component Solution Name	Source of Component	Amount of Component Added per 100 mL Final Volume (mL)
Calibration Standard 1 (S1) (1.0% HNO_3 / 0.5% HCl)	MS-MIX-Z	Lab Prepared	0.010
	Instrument Calibration Sol'n 1	Spex Industries	0.0025
	Instrument Calibration Sol'n 2	Spex Industries	0.005
Calibration Standard 2 (S2) (1.0% HNO_3 / 0.5% HCl)	MS-MIX-Z	Lab Prepared	0.10
	Instrument Calibration Sol'n 1	Spex Industries	0.025
	Instrument Calibration So'ln 2	Spex Industries	0.050
Calibration Standard 3 (S3) / CCV (1.0% HNO_3 / 0.5% HCl)	MS-MIX-Z	Lab Prepared	0.50
	Instrument Calibration Sol'n 1	Spex Industries	0.125
	Instrument Calibration Sol'n 2	Spex Industries	0.25
Calibration Standard 4 (S4) / High Standard (1.0% HNO_3 / 0.5% HCl)	MS-MIX-Z	Lab Prepared	1.0
	Instrument Calibration Sol'n 1	Spex Industries	0.25
	Instrument Calibration Sol'n 2	Spex Industries	0.50
Initial Calibration Verification (ICV) (1.0% HNO_3 / 0.5% HCl)	CL-ICS-1,CL-ICS-4, CL-ICS-5	Spex Industries	0.20 of each
	CL-ICS-3	Spex Industries	2.0
	1000 mg/L Si	Inorganic Ventures	0.040
	1000 mg/L Al	Inorganic Ventures	0.038
	1000 mg/L B, W	Inorganic Ventures	0.002 of each

TABLE 5 (continued)

PREPARATION OF CALIBRATION AND QUALITY CONTROL STANDARDS

Sample or Solution Name	Component Solution Name	Source of Component	Amount of Component Added per 100 mL Final Volume (mL)
Practical Quantitation Limit Solution (PQL) (1.0% HNO_3 / 0.5% HCl)	ICP-MS PQL Intermediate 1	Lab Prepared	1.0
	ICP-MS PQL Intermediate 2	Lab Prepared	0.1
Interference Check Solution A (ICS-A) (1.0% HNO_3 / 0.5% HCl)	6020ICS-0A	Inorganic Ventures	10.0
Interference Check Solution AB (ICS-AB) (1.0% HNO_3 / 0.5% HCl)	6020ICS-0A	Inorganic Ventures	10.0
	Instrument Calibration Sol'n 1	Spex Industries	0.1
	ICP-MS ICSAB Intermediate	Lab Prepared	1.0
P/A Tuning Solution (1.0% HNO_3 / 0.5% HCl)	CL-CAL-1	Spex Industries	1.0 of each
Instrument Tuning Solution (1.0% HNO_3 / 0.5% HCl)	ICP-MS-TS-2	High Purity Standards	0.10
Internal Standard Solution (5.0% HNO_3 / 0.5% HCl)	Internal Standard Mix	Spex Industries	10
Method Tuning Solution (1.0% HNO_3 / 0.5% HCl)	ICP-MS Method Tune Intermediate	Lab Prepared	1.0

TABLE 6

PREPARATION OF INTERMEDIATE STANDARDS

Sample or Solution Name	Component Solution Name	Source of Component	Amount of Component Added per 100 mL Final Volume (mL)
ICP-MS PQL Intermediate 1 (1.0% HNO_3 / 0.5% HCl)	1000 mg/L As, Se	High Purity Standards	0.01 of each
	1000 mg/L Zn 10,000 mg/L Ca, Fe, Mg	High Purity Standards	0.02 of each
	10,000 mg/L Si	High Purity Standards	0.04
	10,000 mg/L Al	High Purity Standards	0.06
	1000 mg/L B	High Purity Standards	0.08
	10,000 mg/L K, Na	High Purity Standards	0.20 of each
	CL-ICS-4	Spex Industries	2.0
ICP-MS PQL Intermediate 2 (1.0% HNO_3 / 0.5% HCl)	1000 mg/L Sb, Ba, Be, Cd, Co, Cu, Pb, Mn, Ni, Ag, Sr, Sn	High Purity Standards or Inorganic Ventures	0.02 of each
	1000 mg/L Tl	High Purity Standards	0.04
	1000 mg/L Cr	High Purity Standards	0.06
	1000 mg/L Mo	High Purity Standards	0.08
	1000 mg/L V, W	High Purity Standards or Inorganic Ventures	0.1 of each
ICP-MS Method Tune Intermediate (1.0% HNO_3 / 0.5% HCl)	1000 mg/L Be, Co, In, Pb, Li, Tl 10,000 mg/L Mg	High Purity Standards or Inorganic Ventures	1.0 of each
MS-MIX-Z (1.0% HNO_3 / 0.5% HCl)	10,000 mg/L Ca, Fe, Mg, K, Na	High Purity Standards or Inorganic Ventures	5.0 of each
	10,000 mg/L Si	High Purity Standards	1.0
	10,000 mg/L Al	High Purity Standards	0.95
	1000 mg/L B, Sr, Sn, Ti, W	High Purity Standards	0.50 of each
ICP-MS ICSAB Intermediate (1.0% HNO_3 / 0.5% HCl)	10,000 mg/L Si	High Purity	0.50
	1,000 mg/L B, Sn, Sr, W	High Purity or Inorganic Ventures	0.20 each

TITLE: **TRACE METALS ANALYSIS BY ICP-MS USING USEPA METHOD 6020**

TABLE 7

ELEMENT CONCENTRATIONS IN WORKING STANDARDS

Element	CONCENTRATION IN SOLUTION, ug/L						
	S1	S2	S3/CCV	S4	ICV	PQL	P/A Tune Soln.
Aluminum	10.0	100.0	500.0	1000.0	400.0	60.0	200
Antimony	0.5	5.0	25.0	50.0	20.0	0.2	200
Arsenic	0.5	5.0	25.0	50.0	20.0	1.0	200
Barium	0.5	5.0	25.0	50.0	20.0	0.2	200
Beryllium	0.5	5.0	25.0	50.0	20.0	0.2	200
Boron	0.5	5.0	25.0	50.0	20.0	8.0	
Cadmium	0.5	5.0	25.0	50.0	20.0	0.2	200
Calcium	100.0	1000.0	5000.0	10000.0	4000.0	20.0	
Chromium	0.5	5.0	25.0	50.0	20.0	0.6	200
Cobalt	0.5	5.0	25.0	50.0	20.0	0.2	200
Copper	0.5	5.0	25.0	50.0	20.0	0.2	200
Iron	100.0	1000.0	5000.0	10000.0	4000.0	20.0	
Lead	0.5	5.0	25.0	50.0	20.0	0.2	200
Magnesium	100.0	1000.0	5000.0	10000.0	4000.0	20.0	
Manganese	0.5	5.0	25.0	50.0	20.0	0.2	200
Molybdenum	0.5	5.0	25.0	50.0	40.0	1.0	200
Nickel	0.5	5.0	25.0	50.0	20.0	0.2	200
Potassium	100.0	1000.0	5000.0	10000.0	4000.0	20.0	
Selenium	0.5	5.0	25.0	50.0	20.0	1.0	200
Silicon	10.0	100.0	500.0	1000.0	400.0	40.0	
Silver	0.5	5.0	25.0	50.0	20.0	0.2	200
Sodium	100.0	1000.0	5000.0	10000.0	4000.0	20.0	
Strontium	0.5	5.0	25.0	50.0	20.0	0.2	
Thallium	0.5	5.0	25.0	50.0	20.0	0.4	200
Thorium	0.5	5.0	25.0	50.0	20.0	0.2	200
Tin	0.5	5.0	25.0	50.0	20.0	0.2	
Tungsten	0.5	5.0	25.0	50.0	20.0	1.0	
Uranium	0.5	5.0	25.0	50.0	20.0	0.2	200
Vanadium	0.5	5.0	25.0	50.0	20.0	1.0	200
Zinc	0.5	5.0	25.0	50.0	20.0	2.0	200

TABLE 7 (continued)

ELEMENT CONCENTRATIONS IN WORKING STANDARDS

Element	CONCENTRATION IN SOLUTION, ug/L			
	ICSA[1]	ICSAB[1]	Internal Std Solution	Instrument Tuning Solution
Aluminum	100000	100000		
Antimony		20		
Arsenic		20		
Barium		20		
Beryllium		20		
Boron		20		
Cadmium		20		
Calcium	100000	100000		
Chromium		20		
Cobalt		20		
Copper		20		
Iron	100000	100000		
Lead		20		
Magnesium	100000	100000		
Manganese		20		
Molybdenum	2000	2000		
Nickel		20		
Potassium	100000	100000		
Selenium		20		
Silver		20		
Sodium	100000	100000		
Strontium		20		
Thallium		20		10.0
Tin		20		
Tungsten		20		
Uranium		20		
Vanadium		20		
Zinc		20		
Bismuth			1000.0	
Germanium			1000.0	
Lithium (^{6}Li)			1000.0	
Scandium			1000.0	
Terbium			1000.0	
Yttrium			1000.0	10.0
Cerium				10.0
Lithium(^{7}Li)				10.0

1) Solution also contains 1000 mg/L Chloride, 200 mg/L Carbon, and 100 mg/L Phosphorus and Sulfur, and 2mg/L Titanium.

TABLE 8

ELEMENT CONCENTRATIONS IN INTERMEDIATE STANDARDS

ELEMENT	CONCENTRATION IN SOLUTION, mg/L				
	MS-MIX-Z	ICP-MS PQL Intermediate 1	ICP-MS PQL Intermediate 2	ICP-MS Method Tune Intermediate	ICP-MS ICSAB Intermediate
Aluminum	95.0	6.0			
Antimony			0.20		2
Arsenic		0.10			
Barium			0.20		2
Beryllium			0.20	10.0	2
Boron	5.0	0.8			2
Cadmium			0.20		
Calcium	500	2.0			
Chromium			0.60		
Cobalt			0.20	10.0	
Copper			0.20		
Indium				10.0	
Iron	500	2.0			
Lead			0.20	10.0	2
Lithium				10.0	
Magnesium	500	2.0		10.0	
Manganese			0.20		
Molybdenum		0.02	0.80		2
Nickel			0.20		
Potassium	500	20.0			
Selenium		0.10			2
Silicon	100	4.0			50
Silver			0.20		
Sodium	500	20.0			
Strontium	5.0		0.20		2
Thallium			0.40	10.0	2
Thorium		0.020			
Tin	5.0		0.20		2
Tungsten	5.0		1.0		2
Uranium		0.020			2
Vanadium			1.0		2
Zinc		0.20			

TITLE: **TRACE METALS ANALYSIS BY ICP-MS USING USEPA METHOD 6020**

TABLE 9

ELEMENT CONCENTRATIONS IN STOCK STANDARDS

Element	CONCENTRATION IN SOLUTION, mg/L					
	Instrument Calibration Standard 1 (Spex)	Instrument Calibration Standard 2 (Spex)	CL-ICS-1 (Spex)	CL-ICS-3 (Spex)	CL-ICS-4 (Spex)	CL-ICS-5 (Spex)
Aluminum	20.0		10.0			
Antimony	20.0		10.0			
Arsenic	20.0		10.0			
Barium	20.0		10.0			
Beryllium	20.0		10.0			
Boron						
Cadmium	20.0		10.0			
Calcium		1000		200.0		
Chromium	20.0		10.0			
Cobalt	20.0		10.0			
Copper	20.0		10.0			
Iron		1000		200.0		
Lead	20.0		10.0			
Magnesium		1000		200.0		
Manganese	20.0		10.0			
Molybdenum	20.0				10.0	10.0
Nickel	20.0		10.0			
Potassium		1000		200.0		
Selenium	20.0		10.0			
Silver	20.0		10.0			
Sodium		1000		200.0		
Strontium						10.0
Thallium	20.0		10.0			
Thorium	20.0				10.0	
Tin						10.0
Tungsten						
Uranium	20.0				10.0	
Vanadium	20.0		10.0			
Zinc	20.0		10.0			

TABLE 9 (continued)

ELEMENT CONCENTRATIONS IN STOCK STANDARDS

Element	CONCENTRATION IN SOLUTION, ug/L		
	6020ICS-0A[1] (Inorganic Ventures)		**ICP-MS-TS-2 (High Purity)**
Aluminum	1000		
Arsenic			
Cadmium			
Calcium	1000		
Chromium			
Cobalt			
Copper			
Iron	1000		
Magnesium	1000		
Manganese			
Molybdenum	20.0		
Nickel			
Potassium	1000		
Silver			
Sodium	1000		
Zinc			
Cerium			10000
Lithium			10000
Thallium			10000
Yttrium			10000

1) Solution also contains 10000 mg/L Chloride, 2000 mg/L Carbon, and 1000 mg/L Phosphorus and Sulfur, and 20 mg/L Titanium.

TABLE 10

REQUIRED ANALYTICAL SEQUENCE

Sequence Number	Standard/Sample	Purpose
1	Method Tuning Solution	Verify mass calibration and resolution
2	S0 (Calibration Blank)	Initial calibration
3	S1 (Calibration Standard)	Initial calibration
4	S2 (Calibration Standard)	Initial calibration
5	S3 (Calibration Standard)	Initial calibration
6	S4 (Calibration Standard)	Initial calibration
7	ICV (Initial Calibration Verification)	Check calibration accuracy
8	ICB (Initial Calibration Blank)	Check calibration accuracy
9	PQL (Practical Quantitation Limit)	Check calibration accuracy at low concentration
10	ICS-A (Interference Check Solution A)	Verify accuracy of mass correction equations
11	ICS-AB (Interference Check Solution AB)	Verify accuracy of mass correction equations
12	CCV (Continuing Calibration Verification)	Check calibration stability
13	CCB (Continuing Calibration Blank)	Check calibration stability
14-23	Analyze up to 10 samples	
24	CCV (Continuing Calibration Verification)	Check calibration stability
25	CCB (Continuing Calibration Blank)	Check calibration stability
...	Continue analyzing sequences of up to 10 samples, followed by a CCV and a CCB	
...	After last analytical sample, analyze PQL , followed by a CCV and a CCB	

TABLE 11

INSTRUMENT OPERATING CONDITIONS

Data Acquisition Program	Acquisition Mode	Spectrum
	Points per Mass	3
	Number of Replicates	3
	Detector Mode	Auto for all elements
	Integration Time per Point (for listed masses and their correction masses)	0.10 sec for Li, B, ^{29}Si, Sc, V, Cr, Mn, Ni, Cu, Zn, Y, Mo, Ag, In, Sn, Sb, Ba, Tb, W, Tl, Pb, Bi, Th, U
		0.30 sec for Be, As, Cd, Ge
		0.010 sec for Na, Al, K, ^{28}Si
		0.030 for Ca, Fe, Sr
		1.00 sec for Se
		0.050 sec for Mg, Co
	Spray Chamber Temperature	2° C
	Total Acquisition Time	105 sec for 3 replicates
Peristaltic Pump Program	Analysis Speed	0.15 rps
Before Acquisition	Uptake Speed	0.15 rps
	Uptake Time	5 sec
	Stabilization Time	15 sec
After Acquisition (Probe Rinse)	Rinse Speed	0.15 rps
	Rinse Time (sample)	5 sec
	Rinse Time (standard)	5 sec
After Acquisition (Rinse)	Rinse Vial	1
	Uptake Speed	0
	Uptake Time	0 sec
	Stabilization Time	0 sec
Calibration Curve fit	All quantitation masses	Y=ax+(blank)
	All internal standard masses	(Excluded)
	All interference correction masses	(Excluded)
Reporting Parameters	QC Reports	On-Printer
	All Other Reports	Off

TABLE 12

INSTRUMENT TUNE SPECIFICATIONS

Sensitivity	Li >5000 cts/0.1 sec/10 ppb
	Y >10,000 cts/0.1 sec/10 ppb
	Tl >5000 cts/0.1 sec/10 ppb
Precision	Li <8% RSD (0.1 sec integration time)
	Y <5% RSD (0.1 sec integration time)
	Tl <5% RSD (0.1 sec integration time)
Oxides	<1.0%
Doubly Charged (Ce^{++}/Ce^{+})	<2.0%
Background	Li <15 cps
	Y <15 cps
	Tl <15 cps
Mass Resolution	Width at 10% peak height: 0.7-0.8 amu
Mass Axis	Li ±0.1 amu of nominal mass
	Y ±0.1 amu of nominal mass
	Tl ±0.1 amu of nominal mass

TABLE 13

METHOD TUNE SPECIFICATIONS

Precision	≤5% RSD of 4 replicates
Mass Resolution	Width at 10% peak height: <0.9 amu
Mass Calibration	±0.1 amu of nominal mass

TABLE 14

REPORTED ISOTOPES AND INTERNAL STANDARDS

ELEMENT	MASS	INTERNAL STANDARD (mass)
Aluminum	27	Scandium (45)
Antimony	123	Terbium (159)
Arsenic	75	Germanium (72)
Barium	135	Terbium (159)
Beryllium	9	Lithium (6)
Boron	11	Lithium (6)
Cadmium	114	Germanium (72)
Calcium	44	Scandium (45)
Chromium	52	Germanium (72)
Cobalt	59	Germanium (72)
Copper	65	Germanium (72)
Iron	57	Germanium (72)
Lead	208	Bismuth (209)
Magnesium	25	Scandium (45)
Manganese	55	Germanium (72)
Molybdenum	98	Germanium (72)
Nickel	60	Germanium (72)
Potassium	39	Scandium (45)
Selenium	82	Germanium (72)
Silicon	29	Scandium (45)
Silver	107	Germanium (72)
Sodium	23	Scandium (45)
Strontium	88	Germanium (72)
Thallium	203	Bismuth (209)
Thorium	232	Bismuth (209)
Tin	118	Terbium (159)
Tungsten	182	Terbium (159)
Uranium	238	Bismuth (209)
Vanadium	51	Germanium (72)
Zinc	66	Germanium (72)

ATTACHMENT 1

HARDNESS BY CALCULATION

As referenced in "Standard Methods for the Examination if Water and Wastewater," Methods 2340 A & B, Hardness Introduction and Hardness by Calculation, American Public Health Association, 18th Edition, Revised 1992, total hardness is the sum of the calcium and magnesium concentrations, both expressed as calcium carbonate, in milligrams per liter.

Once the calcium and magnesium concentrations have been determined by EPA methods 6010, 6020, 200.7 or 200.8, the total hardness of an aqueous sample may be calculated as follows:

$$\text{Total Hardness, mg equivalent } CaCO_3/L = 2.497\ (Ca, mg/L) + 4.118\ (Mg, mg/L)$$

The calcium hardness of an aqueous sample may also be calculated as follows:

$$\text{Calcium Hardness, mg equivalent } CaCO_3/L = 2.497\ (Ca, mg/L)$$

LABORATORY ACCREDITATION BUREAU

Certificate Number L2223

Certificate of Accreditation

Accredited to DoD ELAP and ISO/IEC 17025:2005

Katahdin Analytical Services, Inc.

600 Technology Way
Scarborough, ME 04074

has met the requirements set forth in L-A-B's policies and procedures, all requirements of ISO/IEC 17025:2005 "General Requirements for the competence of Testing and Calibration Laboratories" and the U.S. Department of Defense Environmental Laboratory Accreditation Program (DoD ELAP).*

The accredited lab has demonstrated technical competence to a defined "Scope of Accreditation" and the operation of a laboratory quality management system (refer to joint ISO-ILAC-IAF Communiqué dated 8 January 2009).

Accreditation Granted through: November 4, 2012

R. Douglas Leonard, Jr., Managing Director
Laboratory Accreditation Bureau
Presented the 4th of November, 2009

*See the laboratory's Scope of Accreditation for details of the DoD ELAP requirements
Laboratory Accreditation Bureau is found to be in compliance with ISO/IEC 17011:2004 and recognized by ILAC (International Laboratory Accreditation Cooperation) and NACLA (National Cooperation for Laboratory Accreditation).

LABORATORY ACCREDITATION BUREAU

Certificate # L2223

Scope of Accreditation For Katahdin Analytical Services

600 Technology Way
Scarborough, ME 04074
Leslie Dimond
1- 207-874-2400

In recognition of a successful assessment to ISO/IEC 17025:2005 and the requirements of the DoD Environmental Laboratory Accreditation Program (DoD ELAP) as detailed in the DoD Quality Systems Manual for Environmental Laboratories (DoD QSM v4.1) based on the National Environmental Laboratory Accreditation Conference Chapter 5 Quality Systems Standard (NELAC Voted Revision June 5, 2003), accreditation is granted to Katahdin Analytical Services to perform the following tests:

Accreditation granted through: **November 4, 2012**

Testing - Environmental

Non-Potable Water		
Technology	**Method**	**Analyte**
GC/ECD	608 / 8081A,B/ SOM01.2	4 4`-DDD
GC/ECD	608 / 8081A,B/ SOM01.2	4 4`-DDE
GC/ECD	608 / 8081A,B / SOM01.2	4 4`-DDT
GC/ECD	608 / 8081A,B / SOM01.2	Aldrin
GC/ECD	608 / 8081A,B / SOM01.2	alpha-BHC (alpha-Hexachlorocyclohexane)
GC/ECD	8081A,B / SOM01.2	Alpha-Chlordane
GC/ECD	608 / 8081A,B / SOM01.2	beta-BHC (beta-Hexachlorocyclohexane)
GC/ECD	608 /8081A,B	Chlordane (tech.)
GC/ECD	608 / 8081A,B / SOM01.2	delta-BHC
GC/ECD	608 / 8081A,B / SOM01.2	Dieldrin
GC/ECD	608 / 8081A,B / SOM01.2	Endosulfan I
GC/ECD	608 / 8081A,B / SOM01.2	Endosulfan II
GC/ECD	608 / 8081A,B / SOM01.2	Endosulfan sulfate
GC/ECD	608 / 8081A,B / SOM01.2	Endrin
GC/ECD	608 / 8081A,B / SOM01.2	Endrin aldehyde
GC/ECD	8081A,B / SOM01.2	Endrin Ketone
GC/ECD	8081A,B / SOM01.2	gamma-BHC (Lindane gamma-Hexachlorocyclohexane)
GC/ECD	608 / 8081A,B / SOM01.2	Heptachlor
GC/ECD	608 / 8081A,B / SOM01.2	Heptachlor epoxide

LABORATORY ACCREDITATION BUREAU

Certificate # L2223

Non-Potable Water		
Technology	**Method**	**Analyte**
GC/ECD	8081A,B / SOM01.2	Methoxychlor
GC/ECD	608 / 8081A,B / SOM01.2	Toxaphene (Chlorinated camphene)
GC/ECD	608 / 8082/8082A / SOM01.2	Aroclor-1221 (PCB-1221)
GC/ECD	608 / 8082/8082A / SOM01.2	Aroclor-1232 (PCB-1232)
GC/ECD	608 / 8082/8082A / SOM01.2	Aroclor-1242 (PCB-1242)
GC/ECD	608 / 8082/8082A / SOM01.2	Aroclor-1248 (PCB-1248)
GC/ECD	608 / 8082/8082A / SOM01.2	Aroclor-1254 (PCB-1254)
GC/ECD	608 / 8082/8082A / SOM01.2	Aroclor-1260 (PCB-1260)
GC/ECD	8082/8082A	Aroclor-1262 (PCB-1262)
GC/ECD	8082/8082A	Aroclor-1268 (PCB-1268)
GC/ECD	8082/8082A	2 2' 3 3' 4 4' 5 5' 6-Nonachlorobiphenyl (BZ 206)
GC/ECD	8082/8082A	2 2' 3 3' 4 4' 5 6-Octachlorobiphenyl (BZ 195)
GC/ECD	8082/8082A	2 2' 3 3' 4 4' 5-Heptachlorobiphenyl (BZ 170)
GC/ECD	8082/8082A	2 2' 3 3' 4 4'-Hexachlorobiphenyl (BZ 128)
GC/ECD	8082/8082A	2 2' 3 4 4' 5 5'-Heptachlorobiphenyl (BZ 180)
GC/ECD	8082/8082A	2 2' 3 4 4' 5' 6-Heptachlorobiphenyl (BZ 183)
GC/ECD	8082/8082A	2 2' 3 4 4' 5'-Hexachlorobiphenyl (BZ 138)
GC/ECD	8082/8082A	2 2' 3 4 4' 6 6'-Heptachlorobiphenyl (BZ 184)
GC/ECD	8082/8082A	2 2' 3 4' 5 5' 6-Heptachlorobiphenyl (BZ 187)
GC/ECD	8082/8082A	2 2' 3 4 5'-Pentachlorobiphenyl (BZ 87)
GC/ECD	8082/8082A	2 2' 3 5'-Tetrachlorobiphenyl (BZ 44)
GC/ECD	8082/8082A	2 2' 4 4' 5 5'-Hexachlorobiphenyl (BZ 153)
GC/ECD	8082/8082A	2 2' 4 5 5'-Pentachlorobiphenyl (BZ 101)
GC/ECD	8082/8082A	2 2' 4' 5-Tetrachlorobiphenyl (BZ 49)
GC/ECD	8082/8082A	2 2' 5 5'-Tetrachlorobiphenyl (BZ 52)
GC/ECD	8082/8082A	2 2' 5-Trichlorobiphenyl (BZ 18)
GC/ECD	8082/8082A	2 3 3' 4 4' 5-Hexachlorobiphenyl (BZ 156)
GC/ECD	8082/8082A	2 3 3' 4 4' 5'-Hexachlorobiphenyl (BZ 157)
GC/ECD	8082/8082A	2 3 3' 4 4'-Pentachlorobiphenyl (BZ 105)
GC/ECD	8082/8082A	2 3 3’ 4 4’ 5 5’-Heptachlorobiphenyl (BZ 189)
GC/ECD	8082/8082A	2 3' 4 4' 5 5'-Hexachlorobiphenyl (BZ 167)
GC/ECD	8082/8082A	2 3' 4 4' 5-Pentachlorobiphenyl (BZ 118)
GC/ECD	8082/8082A	2 3' 4 4'5-Pentachlorobiphenyl (BZ 123)
GC/ECD	8082/8082A	2 3' 4 4'-Tetrachlorobiphenyl (BZ 66)
GC/ECD	8082/8082A	2 3’ 4 4’ 5-Pentachlorobiphenyl (BZ 114)
GC/ECD	8082/8082A	2 4 4'-Trichlorobiphenyl (BZ 28)
GC/ECD	8082/8082A	2 4'-Dichlorobiphenyl (BZ 8)
GC/ECD	8082/8082A	3 3' 4 4' 5 5'-Hexachlorobiphenyl (BZ 169)
GC/ECD	8082/8082A	3 3' 4 4' 5-Pentachlorobiphenyl (BZ 126)
GC/ECD	8082/8082A	3 3' 4 4'-Tetrachlorobiphenyl (BZ 77)
GC/ECD	8082/8082A	3 4 4’ 5-Tetrachlorobiphenyl (BZ 81)
GC/ECD	8082/8082A	Decachlorobiphenyl (BZ 209)
GC/ECD	8151A	2 4 5-T
GC/ECD	8151A	2 4-D
GC/ECD	8151A	2 4-DB

Non-Potable Water		
Technology	**Method**	**Analyte**
GC/ECD	8151A	Dalapon
GC/ECD	8151A	Dicamba
GC/ECD	8151A	Dichloroprop
GC/ECD	8151A	DInoseb
GC/ECD	8151A	MCPA
GC/ECD	8151A	MCPP
GC/ECD	8151A	Pentachlorophenol
GC/ECD	8151A	Silvex (2 4 5-TP)
GC/FID	8015B/C	Diesel range organics (DRO)
GC/FID	8015B/C	Gasoline range organics (GRO)
GC/FID	8011 / 504	1 2-Dibromoethane (EDB)
GC/FID	8011 / 504	1 2-Dibromo-3-chloropropane
GC/FID	RSK-175	Methane Ethane Ethene
GC/MS	8260B,C / 524.2	1 1 1 2-Tetrachloroethane
GC/MS	624 / 8260B,C / SOM01.2 / 524.2	1 1 1-Trichloroethane
GC/MS	624 / 8260B,C / SOM01.2 / 524.2	1 1 2 2-Tetrachloroethane
GC/MS	SOM01.2	1 1 2-Trichloro-1 2 2-trifluoroethane
GC/MS	624 / 8260B,C / SOM01.2 / 524.2	1 1 2-Trichloroethane
GC/MS	624 / 8260B,C / SOM01.2 / 524.2	1 1-Dichloroethane
GC/MS	624 / 8260B,C / SOM01.2 / 524.2	1 1-Dichloroethene
GC/MS	8260B,C / 524.2	1 1-Dichloropropene
GC/MS	8260B,C / SOM01.2 / 524.2	1 2 3-Trichlorobenzene
GC/MS	8260B,C / 524.2	1 2 3-Trichloropropane
GC/MS	8260B,C / SOM01.2 / 524.2	1 2 4-Trichlorobenzene
GC/MS	8260B,C / 524.2	1 2 4-Trimethylbenzene
GC/MS	8260B,C / SOM01.2 / 524.2	1 2-Dibromo-3-chloropropane
GC/MS	8260B,C / SOM01.2 / 524.2	1 2-Dibromoethane (EDB)
GC/MS	624 / 8260B,C / SOM01.2 / 524.2	1 2-Dichlorobenzene
GC/MS	624 / 8260B,C / SOM01.2 / 524.2	1 2-Dichloroethane
GC/MS	624 / 8260B,C / SOM01.2 / 524.2	1 2-Dichloropropane
GC/MS	8260B,C / 524.2	1 3 5-Trimethylbenzene
GC/MS	624 / 8260B,C / SOM01.2 / 524.2	1 3-Dichlorobenzene
GC/MS	8260B,C / 524.2	1 3-Dichloropropane
GC/MS	624 / 8260B,C / SOM01.2 / 524.2	1 4-Dichlorobenzene
GC/MS	8260B,C / SOM01.2	1 4-Dioxane
GC/MS	8260B,C / 524.2	2 2-Dichloropropane

Non-Potable Water		
Technology	**Method**	**Analyte**
GC/MS	8260B,C / SOM01.2 / 524.2	2-Butanone
GC/MS	624 / 8260B,C	2-Chloroethyl vinyl ether
GC/MS	8260B,C / 524.2	2-Chlorotoluene
GC/MS	8260B,C / SOM01.2 / 524.2	2-Hexanone
GC/MS	8260B,C / 524.2	4-Chlorotoluene
GC/MS	8260B,C / SOM01.2 / 524.2	4-Methyl-2-pentanone
GC/MS	8260B,C / SOM01.2 / 524.2	Acetone
GC/MS	8260B,C	Acetonitrile
GC/MS	624 / 8260B,C	Acrolein
GC/MS	624 / 8260B,C / 524.2	Acrylonitrile
GC/MS	8260B,C / 524.2	Allyl chloride
GC/MS	624 / 8260B,C / SOM01.2 / 524.2	Benzene
GC/MS	8260B,C / 524.2	Bromobenzene
GC/MS	8260B,C / SOM01.2 / 524.2	Bromochloromethane
GC/MS	624 / 8260B,C / SOM01.2 / 524.2	Bromodichloromethane
GC/MS	624 / 8260B,C / SOM01.2 / 524.2	Bromoform
GC/MS	8260B,C / SOM01.2 / 524.2	Carbon disulfide
GC/MS	624 / 8260B,C / SOM01.2 / 524.2	Carbon tetrachloride
GC/MS	624 / 8260B,C / SOM01.2 / 524.2	Chlorobenzene
GC/MS	624 / 8260B,C / SOM01.2 / 524.2	Chloroethane
GC/MS	624 / 8260B,C / SOM01.2 / 524.2	Chloroform
GC/MS	8260B,C	Chloroprene
GC/MS	8260B,C / SOM01.2 / 524.2	cis-1 2-Dichloroethene
GC/MS	624 / 8260B,C / SOM01.2 / 524.2	cis-1 3-Dichloropropene
GC/MS	SOM01.2	Cyclohexane
GC/MS	624 / 8260B,C / SOM01.2 / 524.2	Dibromochloromethane
GC/MS	8260B,C / 524.2	Dibromomethane
GC/MS	624 / 8260B,C / SOM01.2 / 524.2	Dichlorodifluoromethane
GC/MS	8260B,C / 524.2	Diethyl ether
GC/MS	8260B,C	Di-isopropylether
GC/MS	8260B,C / 524.2	Ethyl methacrylate
GC/MS	624 / 8260B,C / SOM01.2 / 524.2	Ethylbenzene
GC/MS	8260B,C	Ethyl-t-butylether
GC/MS	8260B,C / 524.2	Hexachlorobutadiene
GC/MS	8260B,C	Iodomethane
GC/MS	8260B,C	Isobutyl alcohol

Non-Potable Water		
Technology	**Method**	**Analyte**
GC/MS	8260B,C / SOM01.2 / 524.2	Isopropyl benzene
GC/MS	8260B,C / SOM01.2 / 524.2	m p-xylenes
GC/MS	8260B,C / 524.2	Methacrylonitrile
GC/MS	SOM01.2	Methyl acetate
GC/MS	624 / 8260B,C / SOM01.2 / 524.2	Methyl bromide (Bromomethane)
GC/MS	624 / 8260B,C / SOM01.2 / 524.2	Methyl chloride (Chloromethane)
GC/MS	8260B,C / 524.2	Methyl methacrylate
GC/MS	8260B,C / SOM01.2 / 524.2	Methyl tert-butyl ether
GC/MS	SOM01.2	Methylcyclohexane
GC/MS	624 / 8260B,C / SOM01.2 / 524.2	Methylene chloride
GC/MS	8260B,C / 524.2	Naphthalene
GC/MS	8260B,C / 524.2	n-Butylbenzene
Gc/ms	8260B,C / 524.2	n-Propylbenzene
GC/MS	8260B,C / SOM01.2 / 524.2	o-Xylene
GC/MS	8260B,C / 524.2	p-Isopropyltoluene
GC/MS	8260B,C / 524.2	Propionitrile
GC/MS	8260B,C / 524.2	sec-butylbenzene
GC/MS	8260B,C / SOM01.2 / 524.2	Styrene
GC/MS	8260B,C	t-Amylmethylether
GC/MS	8260B,C / 524.2	tert-Butyl alcohol
GC/MS	8260B,C	tert-Butylbenzene
GC/MS	624 / 8260B,C / SOM01.2 / 524.2	Tetrachloroethene (Perchloroethylene)
GC/MS	8260B,C / 524.2	Tetrahydrofuran
GC/MS	624 / 8260B,C / SOM01.2 / 524.2	Toluene
GC/MS	624 / 8260B,C / SOM01.2 / 524.2	trans-1 2-Dichloroethylene
GC/MS	624 / 8260B,C / SOM01.2 / 524.2	trans-1 3-Dichloropropylene
GC/MS	8260B,C / 524.2	trans-1 4-Dichloro-2-butuene
GC/MS	624 / 8260B,C / SOM01.2 / 524.2	Trichloroethene (Trichloroethylene)
GC/MS	624 / 8260B,C / SOM01.2 / 524.2	Trichlorofluoromethane
GC/MS	8260B,C	Vinyl acetate
GC/MS	624 / 8260B,C / SOM01.2 / 524.2	Vinyl chloride
GC/MS	624 8260B,C	Xylene
GC/MS	8270C,D / SOM01.2	1 2 4 5-Tetrachlorobenzene
GC/MS	625 / 8270C,D / SOM01.2	1 2 4-Trichlorobenzene
GC/MS	625 / 8270C,D / SOM01.2	1 2-Dichlorobenzene
GC/MS	8270C,D	1 2-Diphenylhydrazine

Non-Potable Water		
Technology	**Method**	**Analyte**
GC/MS	8270C,D	1 3 5-Trinitrobenzene
GC/MS	625 / 8270C,D / SOM01.2	1 3-Dichlorobenzene
GC/MS	8270C,D	1 3-Dinitrobenzene
GC/MS	625 / 8270C,D / SOM01.2	1 4-Dichlorobenzene
GC/MS	8270C,D	1 4-Dioxane
GC/MS	8270C,D	1 4-Naphthoquinone
GC/MS	8270C,D	1 4-Phenylenediamine
GC/MS	8270C,D	1-Naphthylamine
GC/MS	8270C,D / SOM01.2	2 3 4 6-Tetrachlorophenol
GC/MS	8270C,D / SOM01.2	2 4 5-Trochlorophenol
GC/MS	625 / 8270C,D / SOM01.2	2 4 6-Trichlorophenol
GC/MS	625 / 8270C,D / SOM01.2	2 4-Dichlorophenol
GC/MS	625 / 8270C,D / SOM01.2	2 4-Dimethylphenol
GC/MS	625 / 8270C,D / SOM01.2	2 4-Dinitrophenol
GC/MS	625 / 8270C,D / SOM01.2	2 4-Dinitrotoluene (2 4-DNT)
GC/MS	8270C,D	2 6-Dichlorophenol
GC/MS	625 / 8270C,D / SOM01.2	2 6-Dinitrotoluene (2 6-DNT)
GC/MS	8270C,D	2-Acetylaminofluorene
GC/MS	625 / 8270C,D / SOM01.2	2-Chloronaphthalene
GC/MS	625 / 8270C,D / SOM01.2	2-Chlorophenol
GC/MS	625 / 8270C,D / SOM01.2	2-Methyl-4 6-dinitrophenol
GC/MS	8270C,D / SOM01.2	2-Methylnaphthalene
GC/MS	8270C,D / SOM01.2	2-Methylphenol
GC/MS	8270C,D	2-Naphthylamine
GC/MS	8270C,D	2-Nitroaniline
GC/MS	625 / 8270C,D / SOM01.2	2-Nitrophenol
GC/MS	8270C,D	2-Picoline
GC/MS	625 / 8270C,D / SOM01.2	3 3'-Dichlorobenzidine
GC/MS	8270C,D	3 3'-Dimethylbenzidine
GC/MS	8270C,D	3-Methylcholanthrene
GC/MS	8270C,D / SOM01.2	3-Nitroaniline
GC/MS	8270C,D	4-Aminobiphenyl
GC/MS	625 / 8270C,D / SOM01.2	4-Bromophenyl phenyl ether
GC/MS	625 / 8270C,D / SOM01.2	4-Chloro-3-methylphenol
GC/MS	8270C,D / SOM01.2	4-Chloroaniline
GC/MS	625 / 8270C,D / SOM01.2	4-Chlorophenyl phenylether
GC/MS	8270C,D	4-Dimethyl aminoazobenzene
GC/MS	8270C,D / SOM01.2	4-Methylphenol
GC/MS	8270C,D / SOM01.2	4-Nitroaniline
GC/MS	625 / 8270C,D / SOM01.2	4-Nitrophenol
GC/MS	8270C,D	5-Nitro-o-toluidine
GC/MS	8270C,D	7,12-Dimethylphenethylamine
GC/MS	8270C,D	a a-Dimethylphenethylamine
GC/MS	625 / 8270C,D / SOM01.2	Acenaphthene
GC/MS	625 / 8270C,D / SOM01.2	Acenaphthylene

Non-Potable Water		
Technology	**Method**	**Analyte**
GC/MS	8270C,D / SOM01.2	Acetophenone
GC/MS	8270C,D	Aniline
GC/MS	625 / 8270C,D / SOM01.2	Anthracene
GC/MS	8270C,D	Aramite
GC/MS	8270C,D / SOM01.2	Atrazine
GC/MS	SOM01.2	Benzaldehyde
GC/MS	625 / 8270C,D	Benzidine
GC/MS	625 / 8270C,D / SOM01.2	Benzo(a)anthracene
GC/MS	625 / 8270C,D / SOM01.2	Benzo(a)pyrene
GC/MS	625 / 8270C,D / SOM01.2	Benzo(b)fluoranthene
GC/MS	625 / 8270C,D / SOM01.2	Benzo(g h i)perylene
GC/MS	625 / 8270C,D / SOM01.2	Benzo(k)fluoranthene
GC/MS	8270C,D	Benzoic Acid
GC/MS	8270C,D	Benzyl alcohol
GC/MS	8270C,D / SOM01.2	Biphenyl
GC/MS	625 / 8270C,D / SOM01.2	bis(2-Chloroethoxy)methane
GC/MS	625 / 8270C,D / SOM01.2	bis(2-Chloroethyl) ether
GC/MS	625 / 8270C,D / SOM01.2	bis(2-Chloroisopropyl) ether (2 2`-Oxybis(1-chloropropane))
GC/MS	625 / 8270C,D / SOM01.2	bis(2-Ethylhexyl) phthalate (DEHP)
GC/MS	625 / 8270C,D / SOM01.2	Butyl benzyl phthalate
GC/MS	SOM01.2	Caprolactam
GC/MS	8270C,D / SOM01.2	Carbazole
GC/MS	8270C,D	Chlorobenzilate
GC/MS	625 / 8270C,D / SOM01.2	Chrysene
GC/MS	8270C,D	Diallate
GC/MS	625 / 8270C,D / SOM01.2	Dibenz(a h)anthracene
GC/MS	8270C,D / SOM01.2	Dibenzofuran
GC/MS	625 / 8270C,D / SOM01.2	Diethyl phthalate
GC/MS	8270C,D	Dimethoate
GC/MS	625 / 8270C,D / SOM01.2	Dimethyl phthalate
GC/MS	625 / 8270C,D / SOM01.2	Di-n-butyl phthalate
GC/MS	625 / 8270C,D / SOM01.2	Di-n-octyl phthalate
GC/MS	8270C,D	Ethyl methanesulfonate
GC/MS	8270C,D	Famfur
GC/MS	625 / 8270C,D / SOM01.2	Fluoranthene
GC/MS	625 / 8270C,D / SOM01.2	Fluorene
GC/MS	625 / 8270C,D / SOM01.2	Hexachlorobenzene
GC/MS	625 / 8270C,D / SOM01.2	Hexachlorobutadiene
GC/MS	625 / 8270C,D / SOM01.2	Hexachlorocyclopentadiene
GC/MS	625 / 8270C,D / SOM01.2	Hexachloroethane
GC/MS	8270C,D	Hexachloropropene
GC/MS	625 / 8270C,D / SOM01.2	Indeno(1 2 3-cd)pyrene
GC/MS	8270C,D	Isodrin
GC/MS	625 / 8270C,D / SOM01.2	Isophorone

Non-Potable Water		
Technology	**Method**	**Analyte**
GC/MS	8270C,D	Isosafrole
GC/MS	8270C,D	Methapyriline
GC/MS	8270C,D	Methy methanesulfonate
GC/MS	8270C,D	Methyl parathion
GC/MS	625 / 8270C,D / SOM01.2	Naphthalene
GC/MS	625 / 8270C,D / SOM01.2	Nitrobenzene
GC/MS	8270C,D	Nitroquinoline-1-oxide
GC/MS	8270C,D	n-Nitrosodiethylamine
GC/MS	625 / 8270C,D / SOM01.2	n-Nitrosodimethylamine
GC/MS	8270C,D	n-Nitroso-di-n-butylamine
GC/MS	625 / 8270C,D / SOM01.2	n-Nitrosodi-n-propylamine
GC/MS	625 / 8270C,D / SOM01.2	n-Nitrosodiphenylamine
GC/MS	8270C,D	n-Nitrosomethylethylamine
GC/MS	8270C,D	n-Nitrosomorpholine
GC/MS	8270C,D	n-Nitrosopiperidine
GC/MS	8270C,D	n-Nitrosopyrrolidine
GC/MS	8270C,D	o o o-Triethyl phosphorothioate
GC/MS	8270C,D	o-Toluidine
GC/MS	8270C,D	Pentachlorobenzene
GC/MS	8270C,D	Pentachloronitrobenzene
GC/MS	625 / 8270C,D / SOM01.2	Pentachlorophenol
GC/MS	8270C,D	Phenacetin
GC/MS	625 / 8270C,D / SOM01.2	Phenanthrene
GC/MS	625 / 8270C,D / SOM01.2	Phenol
GC/MS	8270C,D	Phorate
GC/MS	8270C,D	Pronamide
GC/MS	625 / 8270C,D / SOM01.2	Pyrene
GC/MS	8270C,D	Pyrididne
GC/MS	8270C,D	Safrole
GC/MS	8270C,D	Thionazin
HPLC	8330/8330A/8330B	1 3 5-Trinitrobenzene
HPLC	8330/8330A/8330B	1 3-Dinitrobenzene
HPLC	8330/8330A/8330B	2 4 6-Trinitrotoluene
HPLC	8330/8330A/8330B	2 4-Dinitrotoluene
HPLC	8330/8330A/8330B	2 6-Dinitrotoluene
HPLC	8330/8330A/8330B	2-Amino-4 6 -dinitrotoluene
HPLC	8330/8330A/8330B	2-Nitrotoluene
HPLC	8330/8330A/8330B	3-Nitrotoluene
HPLC	8330/8330A/8330B	4-Amino-2,3-dinitrotoluene
HPLC	8330/8330A/8330B	4-Nitrotoluene
HPLC	8330/8330A/8330B	Hexahydro-1 3 5-trinitro-1 3 5-triazine (RDX)
HPLC	8330/8330A/8330B	Nitrobenzene
HPLC	8330/8330A/8330B	Nitroglycerin
HPLC	8330/8330A/8330B	Octahydro-1 3 5 7-tetrazocine (HMX)
HPLC	8330/8330A/8330B	Tetryl

Non-Potable Water		
Technology	**Method**	**Analyte**
CVAA	245.1 / 7470A / ILM05.3	Mercury
CVAF	1631E	Low Level Mercury
ICP	200.7 / 6010B,C / ILM05.3	Aluminum
ICP	200.7 / 6010B,C / ILM05.3	Antimony
ICP	200.7 / 6010B,C / ILM05.3	Arsenic
ICP	200.7 / 6010B,C / ILM05.3	Barium
ICP	200.7 / 6010B,C / ILM05.3	Beryllium
ICP	200.7 / 6010B,C	Boron
ICP	200.7 / 6010B,C / ILM05.3	Cadmium
ICP	200.7 / 6010B,C / ILM05.3	Calcium
ICP	200.7 / 6010B,C / ILM05.3	Chromium
ICP	200.7 / 6010B,C / ILM05.3	Cobalt
ICP	200.7 / 6010B,C / ILM05.3	Copper
ICP	200.7 / 6010B,C / ILM05.3	Iron
ICP	200.7 / 6010B,C / ILM05.3	Lead
ICP	200.7 / 6010B,C / ILM05.3	Magnesium
ICP	200.7 / 6010B,C / ILM05.3	Manganese
ICP	200.7 / 6010B,C	Molybdenum
ICP	200.7 / 6010B,C / ILM05.3	Nickel
ICP	200.7 / 6010B,C / ILM05.3	Potassium
ICP	200.7 / 6010B,C / ILM05.3	Selenium
ICP	200.7	Silicon
ICP	200.7 / 6010B,C / ILM05.3	Silver
ICP	200.7 / 6010B,C / ILM05.3	Sodium
ICP	6010B,C	Strontium
ICP	200.7 / 6010B,C / ILM05.3	Thallium
ICP	200.7 / 6010B,C	Tin
ICP	200.7 / 6010B,C	Titanium
ICP	200.7 / 6010B,C / ILM05.3	Vanadium
ICP	200.7 / 6010B,C / ILM05.3	Zinc
ICP/MS	200.8 / 6020/6020A / ILM05.3	Aluminum
ICP/MS	200.8 / 6020/6020A / ILM05.3	Antimony
ICP/MS	200.8 / 6020/6020A / ILM05.3	Arsenic
ICP/MS	200.8 / 6020/6020A / ILM05.3	Barium
ICP/MS	200.8 / 6020/6020A / ILM05.3	Beryllium
ICP/MS	200.8 / 6020/6020A	Boron
ICP/MS	200.8 / 6020/6020A / ILM05.3	Cadmium
ICP/MS	200.8 / 6020/6020A	Calcium
ICP/MS	200.8 / 6020/6020A / ILM05.3	Chromium
ICP/MS	200.8 / 6020/6020A / ILM05.3	Cobalt
ICP/MS	200.8 / 6020/6020A / ILM05.3	Copper
ICP/MS	200.8 / 6020/6020A	Iron
ICP/MS	200.8 / 6020/6020A / ILM05.3	Lead
ICP/MS	200.8 / 6020/6020A / ILM05.3	Magnesium
ICP/MS	200.8 / 6020/6020A	Manganese

Non-Potable Water		
Technology	**Method**	**Analyte**
ICP/MS	200.8 / 6020/6020A	Molybdenum
ICP/MS	200.8 / 6020/6020A / ILM05.3	Nickel
ICP/MS	200.8 / 6020/6020A	Potassium
ICP/MS	200.8 / 6020/6020A / ILM05.3	Selenium
ICP/MS	200.8 / 6020/6020A / ILM05.3	Silicon
ICP/MS	200.8 / 6020/6020A / ILM05.3	Silver
ICP/MS	200.8 / 6020/6020A	Sodium
ICP/MS	6020/6020A	Strontium
ICP/MS	200.8 / 6020/6020A / ILM05.3	Thallium
ICP/MS	200.8 / 6020/6020A	Tin
ICP/MS	200.8 / 6020/6020A	Titanium
ICP/MS	200.8	Uranium
ICP/MS	200.8 / 6020/6020A / ILM05.3	Vanadium
ICP/MS	200.8 / 6020/6020A / ILM05.3	Zinc
IC	300.0 / 9056/9056A	Bromide
IC	300.0 / 9056/9056A	Chloride
IC	300.0 / 9056/9056A	Nitrate as N
IC	300.0 / 9056/9056A	Nitrite as N
IC	300.0 / 9056/9056A	Nitrate + Nitrite
IC	300.0 / 9056/9056A	Orthophosphate as P
IC	300.0 / 9056/9056A	Sulfate
Titration	310.2 / 2320B	Alkalinity
Caculation	2340C	Hardness
Gravimetric	1664A	Oil and Grease
Gravimetric	2540 B, C, D	Solids
ISE	120.1 / 2510 B	Conductivity
ISE	2520B	Practical Salinity
ISE	4500F- C	Fluoride
ISE	4500H+ B	pH
ISE	5210B	TBOD / CBOD
Physical	1010 A	Ignitability
Physical	9040C	pH
Titration	2340B	Hardness
Titration	4500SO_3 B	Sulfite
Titration	9034 / 4500S^{2-} E	Sulfide
Titration	Chap. 7.3.4	Reactive Sulfide
TOC	9060A / 5310B	Total organic carbon
Turbidimetric	180.1 / 2130B	Turbidity
Turbidimetric	9038 / ASTM 516-02	Sulfate
UV/VIS	335.4 / 9012B / 4500-CN G	Amenable cyanide
UV/VIS	350.1 / 4500NH3 H	Ammonia as N
UV/VIS	3500Fe D	Ferrous Iron
UV/VIS	351.2	Kjeldahl nitrogen - total
UV/VIS	353.2 / 4500NO3 F	Nitrate + Nitrite

Non-Potable Water		
Technology	**Method**	**Analyte**
UV/VIS	353.2 / 4500NO3 F	Nitrate as N
UV/VIS	353.2 / 4500NO3 F	Nitrite as N
UV/VIS	365.1 / 4500P E	Orthophosphate as P
UV/VIS	365.4	Phosphorus total
UV/VIS	376.3	AVS-SEM
UV/VIS	410.4	COD
UV/VIS	420.1 / 9065	Total Phenolics
UV/VIS	4500Cl G	Total Residual Chlorine
UV/VIS	5540C	MBAS
UV/VIS	7196A / 3500-Cr D	Chromium VI
UV/VIS	9012B / ILM05.3/ 335.4	Total Cyanide
UV/VIS	9251 / 4500Cl E	Chloride
UV/VIS	Chap. 7.3.4	Reactive Cyanide
Preparation	**Method**	**Type**
Cleanup Methods	3640A	Gel Permeation Clean-up
Cleanup Methods	3630C	Silica Gel
Cleanup Methods	3660B	Sulfur Clean-Up
Cleanup Methods	3665A	Sulfuric Acid Clean-Up
Organic Preparation	3510C	Separatory Funnel Extraction
Organic Preparation	3520C	Continuous Liquid-Liquid Extraction
Inorganic Preparation	3010A	Hotblock
Volatile Organic Preparation	5030B,C	Purge and Trap

Solid and Chemical Waste		
Technology	**Method**	**Analyte**
GC/ECD	8081A,B/ SOM01.2	4 4`-DDD
GC/ECD	8081A,B / SOM01.2	4 4`-DDE
GC/ECD	8081A,B / SOM01.2	4 4`-DDT
GC/ECD	8081A,B / SOM01.2	Aldrin
GC/ECD	8081A,B / SOM01.2	alpha-BHC (alpha-Hexachlorocyclohexane)
GC/ECD	8081A,B / SOM01.2	Alpha-Chlordane
GC/ECD	8081A,B / SOM01.2	beta-BHC (beta-Hexachlorocyclohexane)
GC/ECD	608 /8081A,B	Chlordane (tech.)
GC/ECD	8081A,B / SOM01.2	delta-BHC
GC/ECD	8081A,B / SOM01.2	Dieldrin
GC/ECD	8081A,B / SOM01.2	Endosulfan I
GC/ECD	8081A,B / SOM01.2	Endosulfan II
GC/ECD	8081A,B / SOM01.2	Endosulfan sulfate
GC/ECD	8081A,B / SOM01.2	Endrin
GC/ECD	8081A,B / SOM01.2	Endrin aldehyde
GC/ECD	8081A,B / SOM01.2	Endrin Ketone

Solid and Chemical Waste		
Technology	**Method**	**Analyte**
GC/ECD	8081A,B / SOM01.2	gamma-BHC (Lindane gamma-Hexachlorocyclohexane)
GC/ECD	8081A,B / SOM01.2	Heptachlor
GC/ECD	8081A,B / SOM01.2	Heptachlor epoxide
GC/ECD	8081A,B / SOM01.2	Methoxychlor
GC/ECD	8081A,B / SOM01.2	Toxaphene (Chlorinated camphene)
GC/ECD	8082/8082A/ SOM01.2	Aroclor-1016 (PCB-1016)
GC/ECD	8082/8082A/ SOM01.2	Aroclor-1221 (PCB-1221)
GC/ECD	8082/8082A/ SOM01.2	Aroclor-1232 (PCB-1232)
GC/ECD	8082/8082A/ SOM01.2	Aroclor-1242 (PCB-1242)
GC/ECD	8082/8082A/ SOM01.2	Aroclor-1248 (PCB-1248)
GC/ECD	8082/8082A/ SOM01.2	Aroclor-1254 (PCB-1254)
GC/ECD	8082/8082A/ SOM01.2	Aroclor-1260 (PCB-1260)
GC/ECD	8082/8082A	Aroclor-1262 (PCB-1262)
GC/ECD	8082/8082A	Aroclor-1268 (PCB-1268)
GC/ECD	8082/8082A	2 2' 3 3' 4 4' 5 5' 6-Nonachlorobiphenyl (BZ 206)
GC/ECD	8082/8082A	2 2' 3 3' 4 4' 5 6-Octachlorobiphenyl (BZ 195)
GC/ECD	8082/8082A	2 2' 3 3' 4 4' 5-Heptachlorobiphenyl (BZ 170)
GC/ECD	8082/8082A	2 2' 3 3' 4 4'-Hexachlorobiphenyl (BZ 128)
GC/ECD	8082/8082A	2 2' 3 4 4' 5 5'-Heptachlorobiphenyl (BZ 180)
GC/ECD	8082/8082A	2 2' 3 4 4' 5' 6-Heptachlorobiphenyl (BZ 183)
GC/ECD	8082/8082A	2 2' 3 4 4' 5'-Hexachlorobiphenyl (BZ 138)
GC/ECD	8082/8082A	2 2' 3 4 4' 6 6'-Heptachlorobiphenyl (BZ 184)
GC/ECD	8082/8082A	2 2' 3 4' 5 5' 6-Heptachlorobiphenyl (BZ 187)
GC/ECD	8082/8082A	2 2' 3 4 5'-Pentachlorobiphenyl (BZ 87)
GC/ECD	8082/8082A	2 2' 3 5'-Tetrachlorobiphenyl (BZ 44)
GC/ECD	8082/8082A	2 2' 4 4' 5 5'-Hexachlorobiphenyl (BZ 153)
GC/ECD	8082/8082A	2 2' 4 5 5'-Pentachlorobiphenyl (BZ 101)
GC/ECD	8082/8082A	2 2' 4' 5-Tetrachlorobiphenyl (BZ 49)
GC/ECD	8082/8082A	2 2' 5 5'-Tetrachlorobiphenyl (BZ 52)
GC/ECD	8082/8082A	2 2' 5-Trichlorobiphenyl (BZ 18)
GC/ECD	8082/8082A	2 3 3' 4 4' 5-Hexachlorobiphenyl (BZ 156)
GC/ECD	8082/8082A	2 3 3' 4 4' 5'-Hexachlorobiphenyl (BZ 157)
GC/ECD	8082/8082A	2 3 3' 4 4'-Pentachlorobiphenyl (BZ 105)
GC/ECD	8082/8082A	2 3 3’ 4 4’ 5 5’-Heptachlorobiphenyl (BZ 189)
GC/ECD	8082/8082A	2 3' 4 4' 5 5'-Hexachlorobiphenyl (BZ 167)
GC/ECD	8082/8082A	2 3' 4 4' 5-Pentachlorobiphenyl (BZ 118)
GC/ECD	8082/8082A	2 3' 4 4'5-Pentachlorobiphenyl (BZ 123)
GC/ECD	8082/8082A	2 3' 4 4'-Tetrachlorobiphenyl (BZ 66)
GC/ECD	8082/8082A	2 3’ 4 4’ 5-Pentachlorobiphenyl (BZ 114)
GC/ECD	8082/8082A	2 4 4'-Trichlorobiphenyl (BZ 28)
GC/ECD	8082/8082A	2 4'-Dichlorobiphenyl (BZ 8)
GC/ECD	8082/8082A	3 3' 4 4' 5 5'-Hexachlorobiphenyl (BZ 169)
GC/ECD	8082/8082A	3 3' 4 4' 5-Pentachlorobiphenyl (BZ 126)
GC/ECD	8082/8082A	3 3' 4 4'-Tetrachlorobiphenyl (BZ 77)

Solid and Chemical Waste		
Technology	**Method**	**Analyte**
GC/ECD	8082/8082A	3 4 4' 5-Tetrachlorobiphenyl (BZ 81)
GC/ECD	8082/8082A	Decachlorobiphenyl (BZ 209)
GC/ECD	8151A	2 4 5-T
GC/ECD	8151A	2 4-D
GC/ECD	8151A	2 4-DB
GC/ECD	8151A	Dalapon
GC/ECD	8151A	Dicamba
GC/ECD	8151A	Dichloroprop
GC/ECD	8151A	DInoseb
GC/ECD	8151A	MCPA
GC/ECD	8151A	MCPP
GC/ECD	8151A	Pentachlorophenol
GC/ECD	8151A	Silvex (2 4 5-TP)
GC/FID	8015B,C	Diesel range organics (DRO)
GC/FID	8015B,C	Gasoline range organics (GRO)
GC/FID	8011	EDB
GC/FID	8011	1 2-Dibromo-3-chloropropane
GC/MS	8260B,C	1 1 1 2-Tetrachloroethane
GC/MS	8260B,C / SOM01.2	1 1 1-Trichloroethane
GC/MS	8260B,C / SOM01.2	1 1 2 2-Tetrachloroethane
GC/MS	SOM01.2	1 1 2-Trichloro-1 2 2-trifluoroethane
GC/MS	8260B,C / SOM01.2	1 1 2-Trichloroethane
GC/MS	8260B,C / SOM01.2	1 1-Dichloroethane
GC/MS	8260B,C / SOM01.2	1 1-Dichloroethylene
GC/MS	8260B,C	1 1-Dichloropropene
GC/MS	8260B,C / SOM01.2	1 2 3-Trichlorobenzene
GC/MS	8260B,C	1 2 3-Trichloropropane
GC/MS	8260B,C / SOM01.2	1 2 4-Trichlorobenzene
GC/MS	8260B,C	1 2 4-Trimethylbenzene
GC/MS	8260B,C / SOM01.2	1 2-Dibromo-3-chloropropane
GC/MS	8260B,C / SOM01.2	1 2-Dichlorobenzene
GC/MS	8260B,C / SOM01.2	1 2-Dichloroethane
GC/MS	8260B,C / SOM01.2	1 2-Dichloropropane
GC/MS	8260B,C	1 3 5-Trimethylbenzene
GC/MS	8260B,C / SOM01.2	1 3-Dichlorobenzene
GC/MS	8260B,C	1 3-Dichloropropane
GC/MS	8260B,C / SOM01.2	1 4-Dichlorobenzene
GC/MS	8260B,C / SOM01.2	1 4-Dioxane
GC/MS	8260B,C	2 2-Dichloropropane
GC/MS	8260B,C / SOM01.2	2-Butanone
GC/MS	8260B,C	2-Chloroethyl vinyl ether
GC/MS	8260B,C	2-Chlorotoluene
GC/MS	8260B,C / SOM01.2	2-Hexanone
GC/MS	8260B,C	4-Chlorotoluene
GC/MS	8260B,C / SOM01.2	4-Methyl-2-pentanone

Solid and Chemical Waste		
Technology	**Method**	**Analyte**
GC/MS	8260B,C / SOM01.2	Acetone
GC/MS	8260B,C	Acetonitrile
GC/MS	8260B,C	Acrolein
GC/MS	8260B,C	Acrylonitrile
GC/MS	8260B,C	Allyl chloride
GC/MS	8260B,C / SOM01.2	Benzene
GC/MS	8260B,C	Bromobenzene
GC/MS	8260B,C / SOM01.2	Bromochloromethane
GC/MS	8260B,C / SOM01.2	Bromodichloromethane
GC/MS	8260B,C / SOM01.2	Bromoform
GC/MS	8260B,C / SOM01.2	Carbon disulfide
GC/MS	8260B,C / SOM01.2	Carbon tetrachloride
GC/MS	8260B,C / SOM01.2	Chlorobenzene
GC/MS	8260B,C / SOM01.2	Chloroethane
GC/MS	8260B,C / SOM01.2	Chloroform
GC/MS	8260B,C	Chloroprene
GC/MS	8260B,C / SOM01.2	cis-1 2-Dichloroethene
GC/MS	8260B,C / SOM01.2	cis-1 3-Dichloropropene
GC/MS	SOM01.2	Cyclohexane
GC/MS	8260B,C / SOM01.2	Dibromochloromethane
GC/MS	8260B,C	Dibromomethane
GC/MS	624 / 8260B,C / SOM01.2	Dichlorodifluoromethane
GC/MS	8260B,C	Diethyl ether
GC/MS	8260B,C	Di-isopropylether
GC/MS	8260B,C / SOM01.2	EDB
GC/MS	8260B,C	Ethyl methacrylate
GC/MS	8260B,C / SOM01.2	Ethylbenzene
GC/MS	8260B,C	Ethyl-t-butylether
GC/MS	8260B,C	Hexachlorobutadiene
GC/MS	8260B,C	Iodomethane
GC/MS	8260B,C	Isobutyl alcohol
GC/MS	8260B,C / SOM01.2	Isopropyl benzene
GC/MS	SOM01.2	m p-xylenes
GC/MS	8260B,C	Methacrylonitrile
GC/MS	SOM01.2	Methyl acetate
GC/MS	8260B,C / SOM01.2	Methyl bromide (Bromomethane)
GC/MS	8260B,C / SOM01.2	Methyl chloride (Chloromethane)
GC/MS	8260B,C	Methyl methacrylate
GC/MS	8260B,C / SOM01.2	Methyl tert-butyl ether
GC/MS	SOM01.2	Methylcyclohexane
GC/MS	8260B,C / SOM01.2	Methylene chloride
GC/MS	8260B,C	Naphthalene
GC/MS	8260B,C	n-Butylbenzene
GC/MS	8260B,C	n-proplybenzene
GC/MS	8260B,C	o-Xylene

Solid and Chemical Waste		
Technology	**Method**	**Analyte**
GC/MS	8260B,C	p-Isopropyltoluene
GC/MS	8260B,C	Propionitrile
GC/MS	8260B,C	sec-butylbenzene
GC/MS	8260B,C / SOM01.2	Styrene
GC/MS	8260B,C	t-Amylmethylether
GC/MS	8260B,C	tert-Butyl alcohol
GC/MS	8260B,C	tert-Butylbenzene
GC/MS	8260B,C / SOM01.2	Tetrachloroethylene (Perchloroethylene)
GC/MS	8260B,C	Tetrahydrofuran
GC/MS	8260B,C / SOM01.2	Toluene
GC/MS	8260B,C / SOM01.2	trans-1 2-Dichloroethylene
GC/MS	8260B,C / SOM01.2	trans-1 3-Dichloropropylene
GC/MS	8260B,C	Trans-1 4-Dichloro-2-butuene
GC/MS	8260B,C / SOM01.2	Trichloroethene (Trichloroethylene)
GC/MS	8260B,C / SOM01.2	Trichlorofluoromethane
GC/MS	8260B,C	Vinyl acetate
GC/MS	8260B,C / SOM01.2	Vinyl chloride
GC/MS	8260B,C	Xylene
GC/MS	8270C,D	1-Naphthylamine
GC/MS	8270C,D	2-Acetylaminofluorene
GC/MS	8270C,D / SOM01.2	2-Chloronaphthalene
GC/MS	8270C,D / SOM01.2	2-Chlorophenol
GC/MS	8270C,D / SOM01.2	2-Methylnaphthalene
GC/MS	8270C,D / SOM01.2	2-Methylphenol
GC/MS	8270C,D	2-Naphthylamine
GC/MS	8270C,D	2-Nitroaniline
GC/MS	8270C,D / SOM01.2	2-Nitrophenol
GC/MS	8270C,D	2-Picoline
GC/MS	8270C,D	3-Methylcholanthrene
GC/MS	8270C,D / SOM01.2	3-Nitroaniline
GC/MS	8270C,D	4-Aminobiphenyl
GC/MS	8270C,D / SOM01.2	4-Bromophenyl phenyl ether
GC/MS	8270C,D / SOM01.2	4-Chloro-3-methylphenol
GC/MS	8270C,D / SOM01.2	4-Chloroaniline
GC/MS	8270C,D / SOM01.2	4-Chlorophenyl phenylether
GC/MS	8270C,D	4-Dimethyl aminoazobenzene
GC/MS	8270C,D / SOM01.2	4-Methylphenol
GC/MS	8270C,D / SOM01.2	4-Nitroaniline
GC/MS	8270C,D / SOM01.2	4-Nitrophenol
GC/MS	8270C,D	5-Nitro-o-toluidine
GC/MS	8270C,D	a a-Dimethylphenethylamine
GC/MS	8270C,D / SOM01.2	Acenaphthene
GC/MS	8270C,D / SOM01.2	Acenaphthylene
GC/MS	8270C,D / SOM01.2	Acetophenone
GC/MS	8270C,D	Aniline

Solid and Chemical Waste		
Technology	**Method**	**Analyte**
GC/MS	8270C,D / SOM01.2	Anthracene
GC/MS	8270C,D	Aramite
GC/MS	8270C,D / SOM01.2	Atrazine
GC/MS	SOM01.2	Benzaldehyde
GC/MS	8270C,D	Benzidine
GC/MS	8270C,D / SOM01.2	Benzo(a)anthracene
GC/MS	8270C,D / SOM01.2	Benzo(a)pyrene
GC/MS	8270C,D / SOM01.2	Benzo(b)fluoranthene
GC/MS	8270C,D / SOM01.2	Benzo(g h i)perylene
GC/MS	8270C,D / SOM01.2	Benzo(k)fluoranthene
GC/MS	8270C,D	Benzoic Acid
GC/MS	8270C,D	Benzyl alcohol
GC/MS	8270C,D / SOM01.2	Biphenyl
GC/MS	8270C,D / SOM01.2	bis(2-Chloroethoxy)methane
GC/MS	8270C,D / SOM01.2	bis(2-Chloroethyl) ether
GC/MS	8270C,D / SOM01.2	bis(2-Ethylhexyl) phthalate (DEHP)
GC/MS	8270C,D / SOM01.2	Butyl benzyl phthalate
GC/MS	SOM01.2	Caprolactam
GC/MS	8270C,D / SOM01.2	Carbazole
GC/MS	8270C,D	Chlorobenzilate
GC/MS	8270C,D / SOM01.2	Chrysene
GC/MS	8270C,D	Diallate
GC/MS	8270C,D / SOM01.2	Dibenz(a h)anthracene
GC/MS	8270C,D / SOM01.2	Dibenzofuran
GC/MS	8270C,D / SOM01.2	Diethyl phthalate
GC/MS	8270C,D	Dimethoate
GC/MS	8270C,D / SOM01.2	Dimethyl phthalate
GC/MS	8270C,D / SOM01.2	Di-n-butyl phthalate
GC/MS	8270C,D / SOM01.2	Di-n-octyl phthalate
GC/MS	8270C,D	Ethyl methanesulfonate
GC/MS	8270C,D	Famfur
GC/MS	8270C,D / SOM01.2	Fluoranthene
GC/MS	8270C,D / SOM01.2	Fluorene
GC/MS	8270C,D / SOM01.2	Hexachlorobenzene
GC/MS	8270C,D / SOM01.2	Hexachlorobutadiene
GC/MS	8270C,D / SOM01.2	Hexachlorocyclopentadiene
GC/MS	8270C,D / SOM01.2	Hexachloroethane
GC/MS	8270C,D	Hexachloropropene
GC/MS	8270C,D	Isodrin
GC/MS	8270C,D / SOM01.2	Isophorone
GC/MS	8270C,D	Isosafrole
GC/MS	8270C,D	Methapyriline
GC/MS	8270C,D	Methyl methanesulfonate
GC/MS	8270C,D	Methyl parathion
GC/MS	8270C,D / SOM01.2	Naphthalene

Solid and Chemical Waste		
Technology	**Method**	**Analyte**
GC/MS	8270C,D / SOM01.2	Nitrobenzene
GC/MS	8270C,D	Nitroquinoline-1-oxide
GC/MS	8270C,D	n-Nitrosodiethylamine
GC/MS	8270C,D / SOM01.2	n-Nitrosodimethylamine
GC/MS	8270C,D	n-Nitroso-di-n-butylamine
GC/MS	8270C,D / SOM01.2	n-Nitrosodi-n-propylamine
GC/MS	8270C,D / SOM01.2	n-Nitrosodiphenylamine
GC/MS	8270C,D	n-Nitrosomethylethylamine
GC/MS	8270C,D	n-Nitrosomorpholine
GC/MS	8270C,D	n-Nitrosopiperidine
GC/MS	8270C,D	n-Nitrosopyrrolidine
GC/MS	8270C,D	o o o-Triethyl phosphorothioate
GC/MS	8270C,D	o-Toluidine
GC/MS	8270C,D	Pentachlorobenzene
GC/MS	8270C,D	Pentachloronitrobenzene
GC/MS	8270C,D/ SOM01.2	Pentachlorophenol
GC/MS	8270C,D	Phenacetin
GC/MS	8270C,D / SOM01.2	Phenanthrene
GC/MS	8270C,D / SOM01.2	Phenol
GC/MS	8270C,D	Phorate
GC/MS	8270C,D	Pronamide
GC/MS	8270C,D / SOM01.2	Pyrene
GC/MS	8270C,D	Pyrididne
GC/MS	8270C,D	Safrole
GC/MS	8270C,D	Thionazin
GC/MS	8270C,D / SOM01.2	Indeno(1 2 3-cd)pyrene
GC/MS	8270C,D / SOM01.2	1 2 4-Trichlorobenzene
GC/MS	8270C,D	1 3 5-Trinitrobenzene
GC/MS	8270C,D / SOM01.2	1 2 4 5-Tetrachlorobenzene
GC/MS	8270C,D / SOM01.2	2 4 5-Trochlorophenol
GC/MS	8270C,D / SOM01.2	2 4 6-Trichlorophenol
GC/MS	8270C,D / SOM01.2	2 3 4 6-Tetrachlorophenol
GC/MS	8270C,D / SOM01.2	1 2-Dichlorobenzene
GC/MS	8270C,D	1 2-Diphenylhydrazine
GC/MS	8270C,D / SOM01.2	1 3-Dichlorobenzene
GC/MS	8270C,D	1 3-Dinitrobenzene
GC/MS	8270C,D / SOM01.2	1 4-Dichlorobenzene
GC/MS	8270C,D	1 4-Dioxane
GC/MS	8270C,D	1 4-Naphthoquinone
GC/MS	8270C,D	1 4-Phenylenediamine
GC/MS	8270C,D / SOM01.2	bis(2-Chloroisopropyl) ether (2 2`-Oxybis(1-chloropropane))
GC/MS	8270C,D / SOM01.2	2 4-Dichlorophenol
GC/MS	8270C,D / SOM01.2	2 4-Dimethylphenol
GC/MS	8270C,D / SOM01.2	2 4-Dinitrophenol

Solid and Chemical Waste		
Technology	**Method**	**Analyte**
GC/MS	8270C,D / SOM01.2	2 4-Dinitrotoluene (2 4-DNT)
GC/MS	8270C,D	2 6-Dichlorophenol
GC/MS	8270C,D / SOM01.2	2 6-Dinitrotoluene (2 6-DNT)
GC/MS	8270C,D / SOM01.2	3 3`-Dichlorobenzidine
GC/MS	8270C,D	3 3'-Dimethylbenzidine
GC/MS	8270C,D / SOM01.2	2-Methyl-4 6-dinitrophenol
GC/MS	8270C,D	7,12-Dimethylphenethylamine
HPLC	8330/8330A/8330B (Analysis Only)	1 3 5-Trinitrobenzene
HPLC	8330/8330A/8330B (Analysis Only)	1 3-Dinitrobenzene
HPLC	8330/8330A/8330B (Analysis Only)	2 4 6-Trinitrotoluene
HPLC	8330/8330A/8330B (Analysis Only)	2 4-Dinitrotoluene
HPLC	8330/8330A/8330B (Analysis Only)	2 6-Dinitrotoluene
HPLC	8330/8330A/8330B (Analysis Only)	2-Amino-4 6 -dinitrotoluene
HPLC	8330/8330A/8330B (Analysis Only)	2-Nitrotoluene
HPLC	8330/8330A/8330B (Analysis Only)	3-Nitrotoluene
HPLC	8330/8330A/8330B (Analysis Only)	4-Amino-2,3-dinitrotoluene
HPLC	8330/8330A/8330B (Analysis Only)	4-Nitrotoluene
HPLC	8330/8330A/8330B (Analysis Only)	Hexahydr-1 3 5-trinitro-1 3 5-triazine (RDX)
HPLC	8330/8330A/8330B (Analysis Only)	Nitrobenzene
HPLC	8330/8330A/8330B (Analysis Only)	Nitroglycerin
HPLC	8330/8330A/8330B (Analysis Only)	Octahydro-1 3 5 7-tetrazocine (HMX)
HPLC	8330/8330A/8330B (Analysis Only)	Tetryl
CVAA	7471B/ ILM05.3	Mercury
CVAF	1631E	Low Level Mercury
ICP	6010B,C /ILM05.3	Aluminum
ICP	6010B,C /ILM05.3	Antimony
ICP	6010B,C /ILM05.3	Arsenic
ICP	6010B,C /ILM05.3	Barium
ICP	6010B,C /ILM05.3	Beryllium
ICP	6010B,C	Boron
ICP	6010B,C /ILM05.3	Cadmium

Solid and Chemical Waste		
Technology	**Method**	**Analyte**
ICP	6010B,C /ILM05.3	Calcium
ICP	6010B,C /ILM05.3	Chromium
ICP	6010B,C /ILM05.3	Cobalt
ICP	6010B,C /ILM05.3	Copper
ICP	6010B,C /ILM05.3	Iron
ICP	6010B,C /ILM05.3	Lead
ICP	6010B,C /ILM05.3	Magnesium
ICP	6010B,C /ILM05.3	Manganese
ICP	6010B,C	Molybdenum
ICP	6010B,C /ILM05.3	Nickel
ICP	6010B,C /ILM05.3	Potassium
ICP	6010B,C /ILM05.3	Selenium
ICP	200.7	Silicon
ICP	6010B,C /ILM05.3	Silver
ICP	6010B,C /ILM05.3	Sodium
ICP	6010B,C	Strontium
ICP	6010B,C /ILM05.3	Thallium
ICP	6010B,C	Tin
ICP	6010B,C	Titanium
ICP	6010B,C /ILM05.3	Vanadium
ICP	6010B,C /ILM05.3	Zinc
ICP/MS	6020/6020A / ILM05.3	Aluminum
ICP/MS	6020/6020A / ILM05.3	Antimony
ICP/MS	6020/6020A / ILM05.3	Arsenic
ICP/MS	6020/6020A / ILM05.3	Barium
ICP/MS	6020/6020A / ILM05.3	Beryllium
ICP/MS	6020/6020A	Boron
ICP/MS	6020/6020A / ILM05.3	Cadmium
ICP/MS	6020/6020A	Calcium
ICP/MS	6020/6020A / ILM05.3	Chromium
ICP/MS	6020/6020A / ILM05.3	Cobalt
ICP/MS	6020/6020A / ILM05.3	Copper
ICP/MS	6020/6020A	Iron
ICP/MS	6020/6020A / ILM05.3	Lead
ICP/MS	6020/6020A / ILM05.3	Magnesium
ICP/MS	6020/6020A	Manganese
ICP/MS	6020/6020A	Molybdenum
ICP/MS	6020/6020A / ILM05.3	Nickel
ICP/MS	6020/6020A	Potassium
ICP/MS	6020/6020A / ILM05.3	Selenium
ICP/MS	6020/6020A / ILM05.3	Silver
ICP/MS	6020/6020A	Sodium
ICP/MS	6020/6020A	Strontium
ICP/MS	6020/6020A / ILM05.3	Thallium
ICP/MS	6020/6020A	Tin

LABORATORY ACCREDITATION BUREAU

Certificate # L2223

Solid and Chemical Waste		
Technology	**Method**	**Analyte**
ICP/MS	6020/6020A	Titanium
ICP/MS	6020/6020A / ILM05.3	Vanadium
ICP/MS	6020/6020A / ILM05.3	Zinc
IC	9056/9056A	Chloride
IC	9056/9056A	Fluoride
IC	9056/9056A	Nitrate as N
IC	9056/9056A	Nitrite as N
IC	9056/9056A	Sulfate
Gravimetric	9070A / 9071B	Oil and Grease
Physical	1010A	Ignitability
Physical	9045D	pH
Titration	Chap 7.3.4	Reactive Sulfide
TOC	Lloyd Kahn	Total organic carbon
TOC	9060A / 5310B	Total organic carbon
Turbidimetric	9038 / ASTM 516-02	Sulfate
UV/VIS	350.1 / 4500NH3 H	Ammonia as N
UV/VIS	9251 / 4500Cl E	Chloride
UV/VIS	Chap. 7.3.4	Reactive Cyanide
UV/VIS	376.3	AVS-SEM
UV/VIS	3500Fe D	Ferrous Iron
Cleanup Methods	3630C	Silica Gel
UV/VIS	7196	Chromium VI
UV/VIS	7196A	Chromium VI
UV/VIS	9012B / ILM05.3	Total cyanide
Preparation	**Method**	**Type**
Preparation	1311	Toxicity Characteristic Leaching Procedure
Preparation	1312	Synthetic Precipitation Leaching Procedure
Cleanup Methods	3660B	Sulfur
Cleanup Methods	3620C	Florsil
Cleanup Methods	3630C	Silica Gel
Cleanup Methods	3640A	GPC
Organic Preparation	3540C	Soxhlet Extraction
Organic Preparation	3545A	Pressurized Fluid Extraction
Organic Preparation	3550C	Sonication
Inorganics Preparation	3050B	Hotblock
Inorganics Preparation	3060A	Alkaline Digestion
Volatile Organics Preparation	5035/5035A	Closed System Purge and Trap

Notes:

1) This laboratory offers commercial testing service.

Approved By: _____ Date: November 4, 2009

R. Douglas Leonard
Chief Technical Officer

Issued: 11/04/09

Target List	EPA Method	Aqueous Accuracy % Recovery	Aqueous Precision RPD (1)	Water PQLs	Water MDLs
Volatile Organic Compounds				**ug/L**	**ug/L**
1,1,1-Trichloroethane	8260B	77-129	0-20 (nominal)	1.0	0.20
1,1,2,2-Tetrachloroethane	8260B	79-121	0-20 (nominal)	1.0	0.38
1,1,2-Trichloroethane	8260B	84-115	0-20 (nominal)	1.0	0.33
1,1-Dichloroethane	8260B	76-130	0-20 (nominal)	1.0	0.21
1,1-Dichloroethene	8260B	88-127	0-20 (nominal)	1.0	0.35
1,2,4-Trichlorobenzene	8260B	76-126	0-20 (nominal)	1.0	0.37
1,2-Dichlorobenzene	8260B	86-112	0-20 (nominal)	1.0	0.15
1,2-Dichloroethane	8260B	81-125	0-20 (nominal)	1.0	0.20
1,2-Dichloropropane	8260B	84-118	0-20 (nominal)	1.0	0.25
1,3-Dichlorobenzene	8260B	86-110	0-20 (nominal)	1.0	0.26
1,4-Dichlorobenzene	8260B	86-111	0-20 (nominal)	1.0	0.24
2-Butanone (MEK)	8260B	71-132	0-20 (nominal)	5	1.31
2-Hexanone	8260B	80-124	0-20 (nominal)	5	1.70
4-methyl-2-pentanone	8260B	83-122	0-20 (nominal)	5.0	1.32
Acetone	8260B	62-172	0-20 (nominal)	5.0	2.21
Benzene	8260B	86-116	0-20 (nominal)	1.0	0.26
Bromodichloromethane	8260B	85-122	0-20 (nominal)	1.0	0.33
Bromoform	8260B	86-117	0-20 (nominal)	1.0	0.23
Bromomethane	8260B	57-135	0-20 (nominal)	2.0	0.49
Carbon Disulfide	8260B	71-129	0-20 (nominal)	1.0	0.25
Carbon Tetrachloride	8260B	87-126	0-20 (nominal)	1.0	0.22
Chlorobenzene	8260B	89-113	0-20 (nominal)	1.0	0.22
Chloroethane	8260B	53-157	0-20 (nominal)	2.0	0.55
Chloroform	8260B	78-128	0-20 (nominal)	1.0	0.32
Chloromethane	8260B	59-123	0-20 (nominal)	2.0	0.36
cis-1,2-Dichloroethene	8260B	85-123	0-20 (nominal)	1.0	0.21
cis-1,3-Dichloropropene	8260B	83-119	0-20 (nominal)	1.0	0.19
Cyclohexane	8260B	71-133	0-20 (nominal)	1.0	0.31
Dibromochloromethane	8260B	85-119	0-20 (nominal)	1.0	0.30
Dichlorodifluoromethane	8260B	29-164	0-20 (nominal)	2.0	0.24
Ethylbenzene	8260B	88-113	0-20 (nominal)	1.0	0.21
Isopropylbenzene	8260B	96-136	0-20 (nominal)	1.0	0.23
Methyl Acetate	8260B	70-132	0-20 (nominal)	1.0	0.53
Methylcyclohexane	8260B	73-125	0-20 (nominal)	1.0	0.30
Methylene Chloride	8260B	72-129	0-20 (nominal)	5.0	1.13
Methyl tert-butyl ether	8260B	81-125	0-20 (nominal)	1.0	0.36

Target List	EPA Method	Aqueous Accuracy % Recovery	Aqueous Precision RPD (1)	Water PQLs	Water MDLs
Styrene	8260B	88-117	0-20 (nominal)	1.0	0.23
Tetrachloroethene	8260B	47-155	0-20 (nominal)	1.0	0.40
Toluene	8260B	84-118	0-20 (nominal)	1.0	0.27
trans-1,2-Dichloroethene	8260B	78-125	0-20 (nominal)	1.0	0.25
trans-1,3-Dichloropropene	8260B	85-135	0-20 (nominal)	1.0	0.20
Trichloroethene	8260B	79-121	0-20 (nominal)	1.0	0.28
Trichlorofluoromethane	8260B	70-149	0-20 (nominal)	2.0	0.24
Vinyl Chloride	8260B	64-131	0-20 (nominal)	2.0	0.25
Xylenes (Total)	8260B	89-116	0-20 (nominal)	3.0	0.25
Surrogates:					
DBFM	8260B	68-128	--	--	--
1,2-DCA-d4	8260B	67-135	--	--	--
Toluene-d8	8260B	65-128	--	--	--
BFB	8260B	56-133	--	--	--
Semivolatile Organic SIM Compounds				**ug/L**	**ug/L**
2-Methylnaphthalene	8270C SIM	51-114	0-30 (nominal)	0.20	0.077
Acenaphthene	8270C SIM	53-90	0-30 (nominal)	0.20	0.064
Acenaphthylene	8270C SIM	55-105	0-30 (nominal)	0.20	0.054
Anthracene	8270C SIM	70-95	0-30 (nominal)	0.20	0.044
Benzo(a)anthracene	8270C SIM	70-110	0-30 (nominal)	0.20	0.046
Benzo(a)pyrene	8270C SIM	63-98	0-30 (nominal)	0.20	0.066
Benzo(b)fluoranthene	8270C SIM	67-102	0-30 (nominal)	0.20	0.089
Benzo(g,h,i)perylene	8270C SIM	62-106	0-30 (nominal)	0.20	0.065
Benzo(k)fluoranthene	8270C SIM	68-103	0-30 (nominal)	0.20	0.049
Chrysene	8270C SIM	70-95	0-30 (nominal)	0.20	0.036
Dibenzo(a,h)anthracene	8270C SIM	66-108	0-30 (nominal)	0.20	0.070
Fluoranthene	8270C SIM	81-109	0-30 (nominal)	0.20	0.073
Fluorene	8270C SIM	53-95	0-30 (nominal)	0.20	0.061
Indeno(1,2,3-cd)pyrene	8270C SIM	61-112	0-30 (nominal)	0.20	0.052
Naphthalene	8270C SIM	46-84	0-30 (nominal)	0.20	0.064
Phenanthrene	8270C SIM	73-100	0-30 (nominal)	0.20	0.051
Pyrene	8270C SIM	71-104	0-30 (nominal)	0.20	0.059
Surrogates:					
2-Methylnaphthalene-D10	8270C SIM	43-92	---	---	---
Fluorene-D10	8270C SIM	29-101	---	---	---
Pyrene-D10	8270C SIM	53-166	---	---	---
Polychorinated Biphenyls				**ug/L**	**ug/L**

Target List	EPA Method	Aqueous Accuracy % Recovery	Aqueous Precision RPD (1)	Water PQLs	Water MDLs
Aroclor 1016	8082	65-112	0-30 (nominal)	0.50	0.15
Aroclor 1221	8082	---	---	0.50	0.20
Aroclor 1232	8082	---	---	0.50	0.089
Aroclor 1242	8082	---	---	0.50	0.18
Aroclor 1248	8082	---	---	0.50	0.200
Aroclor 1254	8082	---	---	0.50	0.082
Aroclor 1260	8082	62-104	0-30 (nominal)	0.50	0.17
Surrogates:					
Tetrachloro-m-xylene	8082	62-111	---	---	---
Decachlorobiphenyl	8082	44-135	---	---	---
Pesticides				**ug/L**	**ug/L**
4,4'-DDD	8081	64-108	0-30 (nominal)	0.10	0.0090
4,4'-DDE	8081	64-105	0-30 (nominal)	0.10	0.0049
4,4'-DDT	8081	51-103	0-30 (nominal)	0.10	0.0089
Aldrin	8081	58-98	0-30 (nominal)	0.05	0.0074
Alpha-BHC	8081	66-104	0-30 (nominal)	0.05	0.0069
Alpha-Chlordane	8081	73-100	0-30 (nominal)	0.05	0.0076
Beta-BHC	8081	68-115	0-30 (nominal)	0.05	0.0063
Delta-BHC	8081	61-117	0-30 (nominal)	0.05	0.013
Dieldrin	8081	72-97	0-30 (nominal)	0.10	0.0065
Endosulfan I	8081	40-70	0-30 (nominal)	0.05	0.0064
Endosulfan II	8081	50-79	0-30 (nominal)	0.10	0.0057
Endosulfan Sulfate	8081	61-113	0-30 (nominal)	0.10	0.0067
Endrin	8081	70-103	0-30 (nominal)	0.10	0.0084
Endrin Aldehyde	8081	64-103	0-30 (nominal)	0.10	0.0062
Endrin Ketone	8081	65-114	0-30 (nominal)	0.10	0.0078
Gamma-BHC(Lindane)	8081	67-105	0-30 (nominal)	0.05	0.0072
Gamma-Chlordane	8081	72-101	0-30 (nominal)	0.05	0.0060
Heptachlor	8081	55-110	0-30 (nominal)	0.05	0.0080
Heptachlor Epoxide	8081	73-98	0-30 (nominal)	0.05	0.0074
Methoxychlor	8081	54-118	0-30 (nominal)	0.50	0.0084
Toxaphene	8081	---	0-30 (nominal)	1.0	0.17
Surrogates:					
Tetrachloro-m-xylene	8081	48-112	---	---	---
Decachlorobiphenyl	8081	41-131	---	---	---
1,2-Dinitrobenzene	8330	78-120	---	---	---

Target List	EPA Method	Aqueous Accuracy % Recovery	Aqueous Precision RPD (1)	Water PQLs	Water MDLs

LCS and Surrogate limits are updated annually

MDL's are updated annually

1. Represented as Relative Percent Difference
2. Accuracy is determined by Laboratory Control Samples and Matrix Spike/Matrix Spike Duplicates.
3. Accuracy for metals for MS/MSD only applies when the spike is > 4X the native analyte concentration.
4. Practical Quantitation Limits (PQLs) can increase based on percent water content and/or dilution factors.
5. The MDL and PQL for method 6020 include a dilution factor of 5 due to the matrix interference of Hydrochloric acid.
6. LCS limits are based on the manufacturer's limits for the SRM sample. Limits for MS/MSD are nominal (75-125%)
7. MDL's are determined annually therefore the MDLs listed on this table may change.
8. DoD QSM Version 4.1 limits