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Severn Trent Services
STL Savannah

Responses to Comments on the STL Savannah Laboratory Quality Manual (LQM)

And

Standard Operating Procedures (SOPs) from USEPA

September 6, 2001

SEVERN TRENT SERVICES

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Mr. Bob Veenstra
URS Corporation
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RE: STL Savannah Response to EPA Region V SOP/QAM Comments
– Sauget Area 2 Site

Dear Bob:

The following response addresses the seven-(7) issues delineated in a letter from Steven D. Smith, Project Coordinator of Solutia Inc. The letter, received on August 24, 2001, contains comments on the STL Savannah Laboratory Quality Manual (LQM) and Standard Operating Procedures (SOP) from US EPA.

Issue 1. Volatile Compounds by GC/MS (8260B) VM20

An uncontrolled copy of the most recent revision of this SOP has been provided in Attachment A. A project-specific addendum has been affixed to this SOP. The Addendum contains the project reporting limits (RL), Method Detection Limits (MDL), accuracy and precision limits, and QC requirements and corrective actions, which are excerpted from the project QAPP.

The project RL for Benzene, cis-1,3-Dichloropropene and Trichloroethene can be achieved using the low concentration analysis for 8260B. The RL for all target compounds are nominally 1.0 mg/l, with higher RL for the water-soluble ketones.

The target 1,2-Dibromo-3-chloropropane (DBCP) has been included in the 8260B target list. This compound is listed as a target in the 8081 compound list but STL Savannah has not performed an initial demonstration of capability nor a Method Detection Limit Study for DBCP by Method 8081 therefore it has been excluded from the 8081 target list.

Issue 2. Semivolatile Compounds by GC/MS (8270C) SM05

An uncontrolled copy of the most recent revision of this SOP has been provided in Attachment B. A project-specific addendum has been affixed to this SOP. The Addendum contains the project reporting limits (RL's), Method Detection Limits (MDL), accuracy and precision limits, and QC requirements and corrective actions, which are excerpted from the project QAPP.

STL Savannah proposes to report the target compounds at the reporting limits listed in the SOP Addendum. To demonstrate that the compounds can be detected at the proposed concentrations, a calibration standard at one half the routine RL (nominally 5ug/mL) will be analyzed in each clock that project samples are analyzed. In addition, target compounds will be evaluated to the method detection limit (MDL). Results above the MDL but below the project RL will be reported and flagged as estimated.

The most recent version of SOPs EX30, EX35, and EX40 are included in Attachment C for review.

Issue 3. Organochlorine Pesticides and PCBs by GC(SG45)

An uncontrolled copy of the most recent revision of this SOP has been provided in Attachment D. A project-specific addendum has been affixed to this SOP. The Addendum contains the project reporting limits (RL), Method Detection Limits (MDL), accuracy and precision limits, and QC requirements and corrective actions, which are excerpted from the project QAPP.

STL Savannah proposes to analyze the following compounds that were previously listed as Method 8081 targets by alternate approved methods:

Compound	Method (SOP)
1,2-Dibromo-3-chloropropane	8260B (VM20)
Diallate	8270C (SM05)
Hexachlorobenzene	8270C (SM05)
Hexachlorocyclopentadiene	8270C (SM05)

The project RL, compound MDL, and accuracy and precision criteria are given in the project-specific addenda for the alternate method.

In order to meet the project RL for alpha-BHC, beta-BHC, delta-BHC, and gamma-BHC, STL Savannah proposes to 1) Include a standard at one half the routine RL (concentration of the calibration level is 0.0025 µg/ml), and 2) To concentrate the extract to one half of the routine volume (5 ml instead of the routine 10 ml).

With respect to the target Toxaphene, the previously listed modifications will result in a project RL of 2.5 µg/l for Toxaphene in water. Toxaphene is a mixture of several compounds. As such, a majority of the peaks in this multi-component compound must be present in order to identify the peaks a Toxaphene. An on-column mass of 0.5 ng is necessary to provide sufficient peak response to properly identify and quantify Toxaphene at the proposed project RL.

The most recent version of SOPs EX30, EX35, and EX40 are included in Attachment C for review.

Issue 4. Chlorinated Herbicides (SG65)

An uncontrolled copy of the most recent revision of this SOP has been provided in Attachment E. A project-specific addendum has been affixed to this SOP. The Addendum contains the project reporting limits (RL's), Method Detection Limits (MDL), accuracy and precision limits, and QC requirements and corrective actions, which are excerpted from the project QAPP.

STL Savannah does not currently analyze for the target 4-Nitrophenol by Method 8151. STL Savannah proposes that this compound be analyzed and reported by Method 8270C.

The RL for Dalapon is elevated due to matrix interference routinely encountered in environmental samples. Dalapon elutes early in the chromatogram near the solvent front and may be obscured by sample matrix interferences.

The most recent version of SOP EX45 has been included in Attachment F.

Issue 5. Polychlorinated Biphenyls (PCBs) by GC/MS (SM07)

An uncontrolled copy of the most recent revision of this SOP has been provided in Attachment G. A project-specific addendum has been affixed to this SOP. The Addendum contains the project reporting limits (RL's), Method Detection Limits (MDL), accuracy and precision limits, and QC requirements and corrective actions, which are excerpted from the project QAPP.

The most recent version of SOPs EX30, EX35, and EX40 are included in Attachment C for review.

Issue 6. Elements by ICP (ME70)

An uncontrolled copy of the most recent revision of this SOP has been provided in Attachment H. A project-specific addendum has been affixed to this SOP. The Addendum contains the project reporting limits (RL's), Method Detection Limits (MDL), accuracy and precision limits and QC requirements and corrective actions, which are excerpted from the project QAPP.

The most recent version of SOPs ME50 and ME51 have been included in Attachment I.

Issue 7. Provide SOP

The most recent version of the requested SOPs has been included in Attachment J. Note that an SOP for Dissolved Oxygen has *not* been included, since this is routinely a field analysis. Note also that Carbon Dioxide is included in the SOP for Alkalinity (SOP BA35).

The SOPs included in Attachment J are:

SOP	Document Number
TCLP – Nonvolatiles	EX15
TCLP - Volatiles	EX16
Oxidation – Reduction Potential	BA72
Ferrous Iron	ME05
Nitrate	GE30
Sulfate	GE97
Alkalinity	BA35
Methane	AR30
Hydrogen ion (pH)	BA70
TOC in Soils	BA09, BA05

Additionally as per your telephone request, STL Savannah has included the following SOPs.

TO4 and TO13	AR15
TO15	LM-AT-TO15

We appreciate the opportunity to provide this supplemental information in response to EPA's request. Should you have any questions or require additional information please contact me at 912-354-7858 extension 3211or via email at jlong@stl-inc.com or Michelle Owens at extension 3007 or via email at rowens@stl-inc.com.

Sincerely,

Janette D. Long

Janette D. Long
Client Services Director

JL/kd

Cc: Mr. Steven D. Smith, Solutia Inc.

Attachments

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STL SAVANNAH

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EPA RESPONSE

ATTACHMENT A

VOLATILE COMPOUNDS BY GC/MS (EPA 8260B)

This documentation has been prepared by Severn Trent Laboratories (STL) solely for STL's own use and the use of STL's customers in evaluating its qualifications and capabilities in connection with a particular project. The user of this document agrees by its acceptance to return it to Severn Trent Laboratories upon request and not to reproduce, copy, lend, or otherwise disclose its contents, directly or indirectly, and not to use if for any other purpose other than that for which it was specifically provided. The user also agrees that where consultants or other outside parties are involved in the evaluation process, access to these documents shall not be given to said parties unless those parties also specifically agree to these conditions.

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Approved by: R. Wayne Robb 3 April 2001
Date

Title: Technical Manager, QA

STL X Savannah __ Tallahassee __ Mobile __ Tampa West

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1.0 SCOPE AND APPLICATION

1.1 This SOP describes the procedures that can be used to determine the concentration of volatile organic compounds (VOC) in water, wastewater, soils/sediments, wastes, oils, sludges, and solids. The attached quantitation report lists the target compounds, an example of the retention time order of each target compound, the quantitation and confirmation ions of the target compounds, and internal standard assignments.

1.2 The reporting limit (RL), the method detection limit (MDL), and the accuracy and precision criteria for each target compound are listed in Section 5 of the current revisions of the STL Laboratories' *Comprehensive Quality Assurance Plan* and *Corporate Quality Assurance Plan.*

2.0 SUMMARY OF METHOD

2.1 Volatile organic compounds (VOC) are purged from the sample matrix with helium. The VOC are transferred from the sample matrix to the vapor phase. The vapor is swept through a sorbent tube where the VOC are trapped. After the purging is completed, the trap is heated and backflushed with helium to desorb the VOCs onto a GC column. The GC is temperature-programmed to separate the VOC, which are then detected by a mass spectrometer. Qualitative identification of the target compounds in the sample is based on the relative retention time and the mass spectra of the characteristic masses (ions) determined from standards analyzed on the same GC/MS under the same conditions. Quantitative analysis is performed using the internal standard technique with a single characteristic ion.

2.2 Aqueous samples may be purged at ambient conditions (recommended) or at 40C (optional). Five to twenty-five milliliter aliquots of the sample may be purged. The calibration standards and the associated QC must be analyzed under the same conditions and volume.

2.3 Low-level (nominally <1mg/kg) soil samples are purged at 40C in a purge and trap instrument designed to add water and internal standards to the vial containing the sample without breaking the seal. The sample is stirred during purging to thoroughly mix the soil and water. The calibration standards are purged under the same conditions.

2.4 High level soils (nominally >1mg/kg) and waste samples are extracted with methanol-1mL of methanol per gram of sample. An aliquot of the methanol extract is injected into reagent water. The methanol extract/reagent water is purged at ambient temperature using the same instrument conditions and calibration used for aqueous samples.

2.5 This method is based on the guidance in SW-846 Methods 8260B and 5035.

3.0 SAFETY

3.1 Use good common sense when working in the lab. Do not perform any procedure that you do not understand or that will put yourself or others in a potentially hazardous situation.

3.2 Each chemical compound should be treated as a potential health hazard. Exposure to these chemicals must be reduced to the lowest level possible. Lab coats, gloves, eye protection, or other equipment should be used. Standards and highly contaminated samples should be handled in a hood.

3.3 Material Safety Data Sheets (MSDS) are available to the analyst at each lab division. These sheets specify the type of hazard that each chemical poses and the procedures that are used to safely handle these materials.

3.4 The exit vent of the split injector must have a carbon trap in-line to collect the volatile compounds that are vented during the injection of the sample. The traps should be changed a minimum of every three months and disposed of in accordance with STL-SL SOP CA70: *Waste Management.*

4.0 INTERFERENCES

4.1 VOCs commonly used in the laboratory are potential sources of contamination. Methylene chloride, acetone, Freon-113, MEK, hexane, toluene, and isopropanol are used in the laboratory and tend to present the most problems.

4.2 The volatiles lab must be kept as free from contamination as possible. Highly contaminated samples must be segregated from routine samples. Contact with sections of the laboratory where solvents are used should be minimized. Refrigerator blanks should be prepared, stored, and analyzed to evaluate the sample storage areas for possible contamination. Guidance is provided in STL-SL SOP AN70: *Segregation of Low and High Concentration Volatile and Semivolatile Samples.*

4.3 Matrix interferences may be overcome by the use of the secondary ions for quantitation. An example of this is the use of mass 82 for quantitation with chlorobenzene-d5 internal standard when a potential co-eluter, 1,1,1,2-terachloroethane, is a target compound. One of the mass fragments of 1,1,1,2-tetrachloroethane is mass 117, which is the recommended quantitation ion for chlorobenzene-d5. The use of the secondary ions should be used for quantitation in such cases when the lab can clearly demonstrate matrix problems. Mass 58 is recommended for quantitation of acetone due to the elution of a hydrocarbon at the same retention time.

4.4 The analysis of highly contaminated samples (>1mg/L or >1mg/kg) can affect succeeding analyses. Carry-over can occur when low concentration samples are analyzed after high concentration samples. Trap replacement and purging of the entire purging system may be necessary when carry-over is suspected. Reagent blanks must be analyzed when carryover is suspected to demonstrate that the system is free from contamination.

4.5 The Teflon seals of the purge and trap device can absorb and outgas many of the compounds that are included in this method. These Teflon fittings should be periodically checked for integrity. If contamination of the fittings is suspected, the fittings may be heated at 105 C for one hour or replaced.

5.0 SAMPLE COLLECTION, HANDLING, AND PRESERVATION

5.1 Liquid samples are collected with no headspace in 40mL vials equipped with Teflon-lined caps. The samples are acidified at the time of collection with about 0.10mL of concentrated HCl per 40mL of sample. The acid prevents the biological degradation of the aromatic compounds and prevents the dehydrohalogenation of some of the chlorinated alkanes. The sample must be iced at the time of collection and refrigerated at 4C (less than 6C with no frozen samples) in the lab until analysis.

Check each sample vial at the time of receipt for the presence of "bubbles". If the bubbles are less than 3mm in diameter, the vial is acceptable. If the bubble is greater than 3mm, use another vial. Notify the department supervisor or project manager if there are no acceptable vials for analysis.

A "sacrificial" vial or the vial used for screening analysis is used to check the sample pH. If the sample pH is greater than 2, notify the department supervisor or project manager. If directed by supervisor or project manager, hydrochloric acid may be added through the septum to bring the pH <2. Do not add more than 400uL (0.40mL) of 1:1 HCl to a VOC vial. If pH cannot be adjusted to <=2 without destroying the integrity of the sample, the sample must be analyzed within 7 days of collection.

The holding time for samples preserved with HCl is 14 days for all target compounds. The holding time for un-preserved samples is 7 days.

5.2 Soils: Soils are routinely collected in duplicate in Encore samplers. A "bulk" sample is also routinely collected in a 125-mL jar fitted with a Teflon-lined cap. The bulk sample can be used for the methanol extraction if the concentration of the sample collected in the Encore exceeds the working range of the analytical system.

Soils collected in Encore samplers must be analyzed within 48 hours of collection or must be transferred within 48 hours of collection to sealed vials containing sodium bisulfate solution or methanol. If the sample contains high levels of carbonates, the sample is preserved with water and frozen until the time of analysis. The procedure for preparing soil samples is given in Section 9.2.

The hold time of the preserved sample is 14 days from the date of collection. The hold time for frozen samples is 14 days from the date of collection.

5.3 High level soil and waste samples are collected in glass containers (usually 125-mL clear glass) equipped with Teflon-lined caps. Soil samples may also be submitted as core samples contained in Encore samplers, metal or plastic "tubes", or in 40-mL VOA vials. The samples are iced at the time of collection and stored at 4C (less than 6C with no frozen samples). The holding time for soil and waste samples subjected to methanol extraction is14 days from date of collection; that is, the extraction and analysis must be completed within 14 days of collection.

5.4 TCLP leachate samples are collected with no headspace in Tedlar bags or syringes. The leachate samples are acidified at the time of collection (after the leaching procedure) with about 0.10mL of concentrated HCl per 40mL of sample and stored at 4C (less than 6C with no frozen samples) from the time leaching is completed until the analysis. The acidified leachate sample must be analyzed within 14 days of the leaching procedure. If the sample is not acidified, the leachate must be analyzed within 7 days of the leaching procedure.

NOTE: Samples that are suspected of having very high concentrations of VOC should be segregated from the "routine" samples and stored in a manner that will minimize sample and laboratory contamination. See STL-SL SOP AN70. If possible, keep the field QC in the same storage refrigerator as the samples.

6.0 APPARATUS AND MATERIALS

The apparatus and materials listed in this section may vary from lab to lab. The items listed are to give guidance and to provide a general overview of the equipment employed in this analysis.

6.1 Mass spectrometer: equipped with a capillary direct interface and a split/splitless injector or molecular jet separator

6.2 Gas chromatograph, compatible with the MS and purge and trap systems. If the GC is equipped with an injector that is operated in the split mode, the exit vent must have a carbon trap in-line to collect the volatile compounds that are vented during the transfer from the purge and trap device. The carbon traps should be changed a minimum of every three months.

6.3 Purge and trap device Tekmar 3000 Liquid Concentrator or equivalent

6.4 Supelco Vocarb 3000 trap or equivalent, Other traps may be used as long as the target compounds can be detected at the required quantitation limit.

6.5 Archon soil analyzer for low level soils, compatible with Tekmar purge and trap instruments. The instrument must be capable of automatically adding water and internal standard to the container while maintaining the septum seal, heating the sample to 40C, and spinning the stir bar to mix the sample during the purging step.

6.5 Data System compatible with the analytical system

6.6 Microsyringes: 10ul, 25ul, 50ul, 100ul, 250ul, 500ul, 2.5mL

6.7 Gastight syringe: 5mL, 25mL with luerlock tip

6.8 Volumetric flasks: 1.0mL, 10mL, 100mL

6.9 Recommended Columns

J&W DB-624: 60m x 0.32mm ID, 1.8um film
J&W DB-624: 20m x 0.18mm ID, 1.8um film

7.0 REAGENTS

Reagents must be tracked in accordance with STL-SL SOP AN44: *Reagent Traceability.*

7.1 Reagent water-free of volatile contaminants (obtained by purging with inert gas or carbon filtration)

7.2 Methanol-Burdich and Jackson, Purge and Trap grade

7.3 Sodium bisulfate-reagent grade. This salt is hydroscopic and should be stored in a dessicator.

7.4 Soil preservation solution- Slowly add, while stirring, 200g of sodium bisulfate to a 1.0-L volumetric containing about 700mL of reagent water. After the salt has dissolved, dilute to volume with reagent water, transfer to a storage container, and store the solution in an area free from VOC-especially water-soluble solvents such as acetone. The reagent should be tested prior to use by the analysis of a blank containing 5mL of the solution. The reagent is acceptable if it meets the same criteria as a method blank.

8.0 STANDARDS

Calibration and spike solutions are prepared from either certified stock solutions purchased from vendors or from stock standards prepared from neat materials. Certificates of analysis or purity must be received with all stock solutions or neat compounds. All preparation steps must be in accordance with STL-SL SOP AN41: *Standard Material Traceability.*

8.1 Preparation of **Stock Standards** from Neat Compounds

The lab should attempt to obtain a certified primary standard or secondary standard before preparing stock standards from neat materials. If primary stock standards must be prepared in-house, the target concentration range is from 2000ug/mL to 10000ug/mL. SL-SOP AN43: *Standard Preparation* gives the general instructions for the preparation of the stock solutions from neat materials.

8.2 Preparation of the **Working Standard** from Stock Standards

The working standard is prepared from the primary stock standards that are either prepared from neat compounds or purchased as certified solutions. The working standard contains one or more of the target compounds at a concentration suitable for preparing the calibration standards, generally 10-200ug/mL. A known volume of the working standard is then added to a known volume of reagent water to make the calibration standard.

The standards and standard concentrations listed in Table 1 are the suggested for routine use. If other "recipes" are used, the lab must document the standard preparation procedures in the standard traceability log.

8.3 Preparation of the **Calibration Standards** from the Working Standards

The calibration standards are the standards that are analyzed on the instrument. The calibration standard is made by adding a known volume of the working standard to a known volume of reagent water. The instrument must be calibrated using a minimum of five calibration standards. The lowest level standard must be at the reporting limit and the rest of the standards will define the working range of the analytical system.

8.3.1 Add 5.0mL of reagent water to a 5mL-glass syringe or 25ml of reagent water to a 25-ml glass syringe.

8.3.2 Add a known volume of the working standard to 5.0mL or 25ml of reagent water.

NOTE: The calibration standards for the low level soils are prepared using the same procedures as for the 5mL water purge except that the standards are purged at 40C. The lab has the option of using blank sand in the calibration standards.

The calibration standards listed in Table 1 are the suggested for routine use. If other "recipes" are used, the lab must document these standard preparation procedures in the standard traceablity log. A 5mL-purge volume may be used for low level (nominal RL of 1ug/L) if the instrument has sufficient sensitivity to detect the targets and the calibration criteria is met.

9.0 SAMPLE PREPARATION

Composite samples can be prepared using the guidance provided in STL-SL-SOP AN70.

9.1 **Aqueous samples** are analyzed directly by purge and trap/GC-MS. No sample preparation is necessary except to homogenize the sample prior to subsampling. The pH of liquid samples is checked and recorded prior to analysis to determine if the sample has been properly preserved.

9.2 Preparation of Soil Samples (5035)

9.2.1 Remove the Encore samples and the bulk sample from the storage area.

9.2.2 Test an aliquot of the bulk sample for the presence of carbonates.

- Transfer 5g of sample from the bulk sample to a 40mL vial..
- Add 5ml of the sodium bisulfate solution and shake the vial .
- If the sample exhibits effervescence, the Encore samples should be preserved as described above using 5mL of volatile-free water in place of the sodium bisulfate solution and placed in a freezer at –10C. The analytical hold time for frozen samples is 14 days from collection.
- If no effervescence is noted, the Encore samples may be preserved with 5mL soil preservation solution.

9.2.3 Add a stir bar to a vial and weigh the vial and record its tare weight(or tare the vial and stir bar weight by pressing the autotare button).

9.2.4 Transfer the sample from the Encore sampler to the tared vial and record the weight of the sample log.

If the sample effervesced during the carbonate test (9.2.2), add 5.0mL of reagent water and freeze at –10C.
The hold time is 14 days from collection.

If not, add 5.0mL of the soil preservation solution, seal the vial, and store the sample at 4C until the time of analysis. The preserved sample must be analyzed within 14 days of collection.

NOTE: A preparation blank is prepared when Encore samples are transferred. The preparation blank contains the same reagents as the samples-either 5mL of reagent water or 5mL of soil preservation solution.

9.3 A methanol extraction is prepared when the concentration of the target compounds (by direct purge) exceeds the working range of the calibration curve. The bulk sample, collected in the 125-mL sample container, can be used to prepare the methanol extraction. Carry out the preparation quickly to minimize the loss of volatiles.

-Mix the sample with a stainless steel spatula and transfer 10g (+/- 0.5g) to a glass vial.

-Add 8uL of the surrogate spiking solution (2500ug/mL) to the sample and quickly add 10mL of purge and trap grade methanol. The theoretical concentration of the surrogates in the sample, assuming a sample weight of 10g and 100% percent solids, is calculated:

$$Ct(ug/kg,dw) = \frac{0.008mL \otimes 2500ug/mL}{0.010g \otimes solids} = 2000ug/kg,dw$$

-Shake the sample for two minutes. Allow the solvent to separate from the solids portion of the sample and transfer a 1-2mL aliquot of the extract to a storage vial. The vial should be sealed with no headspace. Store the methanol extract at 4C until the time of analysis. The extract must be analyzed within 14 days of sample collection.

-For each batch of twenty or fewer samples, prepare a method blank and a lab control standard. Prepare a matrix spike and matrix spike duplicate at a frequency of 5% of all samples.

The method blank is prepared by adding 8uL of the surrogate spiking solution to 10mL of purge and trap grade methanol. Assume a sample weight of 10g. Analyze 125uL of the extract.

The lab control standard is prepared by adding 8uL of the surrogate spiking solution and 8uL of the matrix spiking solution to 10mL of purge and trap grade methanol. Assume a sample weight of 10g. Analyze 125uL of the extract.

The matrix spikes are prepared by adding 8uL of the surrogate spiking solution (2500ug/mL) and 8uL of the matrix spiking solution (2500ug/mL) to 10-g aliquots of the sample selected for the MS/MSD. Quickly add 10mL of purge and trap grade methanol to each sample and shake for two minutes. Analyze 125uL of the extract or a smaller volume if the VOC concentration is high.

-Add 125uL of the extract (or a smaller volume if the VOC concentration exceeds the linear range of the system with 125uL) to 5.0mL of water (or to 25mL if the calibration is based on 25mL). Add the internal standard solution and analyze the sample using the ambient water calibration.

9.4 Methanol Extraction for Wastes

Carry out the preparation quickly to minimize the loss of volatiles.

9.4.1 Mix the sample with a stainless steel spatula and transfer 1g (+/- 0.2g) to a glass vial.

9.4.2 Add 10uL of the surrogate spiking solution (2500ug/mL) to the sample and quickly add 10mL of purge and trap grade methanol. If the sample is completely soluble in the methanol, dilute to a final volume of 10mL. The theoretical concentration of the surrogates in the sample, assuming a sample weight of 1.0g , is calculated:

$$Ct(ug/kg) = \frac{0.010mL \otimes 2500ug/mL}{0.0010g \otimes solids} = 25000ug/kg$$

9.4.2 Shake the sample for one minute. Allow the solvent to separate from the solids portion of the sample and transfer 1mL to 2mL of the extract to a storage vial. The vial should be sealed with no headspace. Store the methanol extract at 4C until the time of analysis. The extract must be analyzed within 14 days of sample collection.

For each batch of twenty or fewer samples, prepare a method blank and a lab control standard. Prepare a matrix spike and matrix spike duplicate at a frequency of 5% of all samples.

The method blank is prepared by adding 8uL of the surrogate spiking solution (2500ug/mL) to 10mL of purge and trap grade methanol. Assume a sample weight of 1.0g. Analyze 100uL of the extract.

The lab control standard is prepared by adding 10uL of the surrogate spiking solution (2500ug/mL) and 10uL of the matrix spiking solution (2500ug/mL) to 5.0mL of purge and trap grade methanol. Assume a sample weight of 5.0g. Analyze 100uL of the extract.

The matrix spikes are prepared by adding 10uL of the surrogate spiking solution (2500ug/mL) and 10uL of the matrix spiking solution (2500ug/mL) to 1g aliquots of the sample selected for the MS/MSD. Quickly add 10mL of purge and trap grade methanol to each sample and shake for one minute.

Add 100uL of the extract (or a smaller volume) to 5.0mL of water (or to 25mL if the calibration is based on 25mL). Add the internal standard solution and analyze the sample using the ambient water calibration.

NOTE: Waste samples may require significant dilution prior to analysis.

10.0 PROCEDURE

The following instrument conditions are recommended. The actual conditions may vary due to differences in instrumentation. The lab must document the instrument conditions in the maintenance log, the data system, or on the analysis log.

10.1 Instrument Conditions

10.1.1 GC Conditions
GC conditions may vary according to the environment and condition of each instrument. The lab must document the instrument conditions to assure consistent results and to aid in trouble-shooting the analytical system. Each lab is responsible for assuring that the conditions necessary to achieve adequate separation and sensitivity of the target analytes are maintained.

10.1.1.1 Example GC temperature program

Initial column temperature: 35 C for 3 minutes
Column temperature program 1: 20C per minute
Intermediate column temperature: 70C for 4 minutes
Column temperature program 2: 10C per minute
Final column temperature: 200C for 5.25 minutes

10.1.1.2 Column flow: Approximately 5-10mL/minute helium with a make-up of 20-25mL/minute helium. Total flow into the jet separator should be about 30mL/minute. The vacuum gauge on the jet separator will read about 0.5Torr.

If no jet separator is used and the column is plumbed directly into the source, the column flow should be adjusted to 0.5-1.0ml/min and a split ratio (desorb to column flow) of about 40:1 established. Smaller bore capillary columns (0.18 to 0.32mm) are required if the column is plumbed directly into the source

10.1.1.3 Mass Spectrometer and interface parameters

Jet separator temperature: 240C
Mass spectrometer interface: 240C
Mass spectrometer source temperature: factory set at 300C
range: 35-300amu, with a minimum scan cycle of 1 scan per second

10.1.2 Purge and Trap Conditions
The purge and trap conditions listed in this section are for guidance. The lab must document the actual conditions used. The purge time must be 11 minutes. Other parameters may be varied to optimize the detection of the target compounds.

10.1.2.1 "Three ring trap"-charcoal, Tenax, silica gel
Purge Time: 11 minutes
Purge temperature: aqueous-ambient; soils-heated 40C
Desorb time: 4 minutes
Desorb temperature: 180C
Bake time: 8 minutes at 225C
Purge flow: Approximately 20-30mL/minute
Valve temperature: 100C
Transfer line: 100C

10.1.2.1 VOCARB 3000 trap
Purge Time: 11 minutes
Purge temperature: aqueous-ambient; soils-heated 40C
Desorb time: 4 minutes
Desorb temperature: 225C
Bake time: 8 minutes at 250C
Purge flow: Approximately 20-30mL/minute
Valve temperature: 100C
Transfer line: 100C

The purge flow must be balanced for adequate sensitivity of the target compounds. If the purge flow is too high, the response of the gases will be low and not reproducible. The SPCC criteria for chloromethane may not be achieved if the purge flow is too high. If the purge flow is too low, the response of the more water-soluble targets-ketones, ethers, bromoform-may be low and the reporting limit may not be achieved on a routine basis.

10.2 BFB Tune Check

10.2.1 Fifty nanograms of 4-BFB must be analyzed at the beginning of each 12-hour clock as a check on the "**tune**" of the mass spectrometer. Meeting the tuning criteria ensures that the instrument is measuring the proper masses in the proper ratios. The 4-BFB analysis takes place under the same instrument conditions as the calibration standards and samples except that a different temperature program can be used to allow for the timely elution of 4-BFB. All other instrument conditions must be identical-the mass range, scan rate, and multiplier voltage. If the instrument is configured for direct injection, 50ng of 4-BFB may be injected directly on to the column. If the purge and trap is used to analyze the 4-BFB, the purge and trap conditions must be the same as for the calibration standards and samples.

10.2.2 Evaluation of the 4-BFB peak.

10.2.2.1 The chromatogram should exhibit acceptable baseline behavior and the 4-BFB peak should be symmetrical. A spectrum of the baseline that shows high abundances of mass 40 (Argon) and mass 44 (carbon dioxide) may indicate a leak or contaminated carrier gas.

10.2.2.2 The spectrum of the 4-BFB must meet the criteria listed in the attached SOP Summary. Background subtraction must be straightforward and designed only to eliminate column bleed or instrumental background. Scans +/- 5 scans from the apex can be evaluated for the 4-BFB criteria. Consecutive scans within this range can be averaged to meet the criteria.

10.2.2.3 The following records must be kept for each 4-BFB analysis that meets the criteria:
- the date, time, and data file of the analysis
- a spectrum of the scan or averaged scans
- a tabulation of the ion abundances of the scan

10.2.2.4 The 4-BFB analysis should be evaluated as to the relative size of the 4-BFB peak under the m/z 95 profile. A benchmark area window should be established for each instrument. Response outside of this window suggests instrumental problems such as a poor purge, clogged jet separator, leak in the Tekmar purging device, reduced or elevated detector sensitivity, improper electron multiplier voltage selection, wrong tune method or tune file selected for this analysis, PFTBA valve left open , or other anomalies.

10.2.2.5 If the 4-BFB fails to meet the acceptance criteria, the instrument may require tuning (manually or automatically with PFTBA). Depending on the nature of the results from the 4-BFB analysis, other corrective measures may include remaking the 4-BFB standard and/or cleaning the mass spectrometer source.

10.3 Initial Calibration

After the 4-BFB criteria has been met, the initial calibration standards are analyzed. Prepare the initial calibration standards according to the example recipes in the SOP appendices or lab-specific recipe. The lab must document the "recipe" used to prepare the calibration standards. The lowest level calibration standard must be at or below the routine RL and the other calibration standards will define the working range of the system.

10.3.1 Remove the plunger from the syringe and fill the barrel to overflowing with reagent water (syringe valve in the "red" position).

10.3.2 Replace the plunger, switch the syringe valve to "green", and force any airspace out of the syringe. Adjust the volume to the syringe volume(5mL or 25mL)

10.3.3 Briefly remove the syringe valve and inject the standards and internal standards into the syringe.

NOTE: Use the internal standard (IST) mix when preparing the calibration standards for analysis. The surrogates are already included in the standard mixes.

10.3.4 Load the standard(s) onto the purge and trap device and begin the analysis. All pertinent information concerning the standards must be recorded on the analysis log. The standards must be clearly identified and traceable to the preparation steps.

NOTE: The standards for low-level soil samples are prepared in the same manner as the 5mL standards. The standards for the low-level soils are purged at 40C. The lab has the option of using blank sand or soil in the calibration standards and the blank in the low level soil analysis.

10.3.5 After the acquisition has taken place, evaluate the calibration standards to ensure that each target compound, surrogate, and internal standard has been correctly identified. The analyst must be careful to complete this step before proceeding.

10.3.6 After each target compound, surrogate, and internal standard has been correctly identified, the relative response factor for each target compound and surrogate is calculated using the data system or using a PC spreadsheet as follows:

$$RRF = \frac{(Ax)(Cis)}{(Ais)(Cx)}$$

where
Ax = area of the characteristic ion for the compound being measured
Ais = area of the characteristic ion for the internal standard associated with the compound being measured (see the attached quantitation report for a list of the compounds that are associated with the various internal standards)
Cx = concentration or mass on-column of the target compound being measured (ug/L or ug/kg OR ng or ug on-column)
Cis = concentration or mass on-column of the internal standard (ug/L or ug/kg OR ng or ug on-column)

The average relative response factor (RRFavg) is calculated for each target compound and each surrogate compound:

$$RRFavg = \frac{RRF1 + RRF2 + ... + RRFn}{n}$$

where n = number of calibration levels

Calculate the standard deviation (SD) for the target compounds and surrogates at all calibration levels:

$$SD = \sqrt{\frac{\sum_{i=1}^{n}(RFi - RFavg)^2}{n-1}}$$

where
Rfi = response factor of a target compound in the individual calibration level
Rfavg = average response factor
n= number of calibration levels

10.3.7 Calculate the relative standard deviation (% RSD) of the calibration levels for each target:

$$\%RSD = \frac{standard\ deviation}{RRFavg} \otimes 100$$

10.3.8 The results of the initial calibration are evaluated against the Calibration Check Compound (CCC) criteria and the System Performance Check Compound (SPCC) criteria, which are listed below. The CCC and SPCC criteria must be met before samples can be analyzed.

Calibration Check Compounds – CCC Vinyl chloride, 1,1-dichloroethene, chloroform, 1,2-dichloropropane, toluene, ethylbenzene

Initial Calibration	Continuing Calibration
<=30% RSD	<=20% difference from initial calibration

System Performance Check Compounds-SPCC

SPCC	Minimum RRF
Chloromethane	0.10
1,1-Dichloroethane	0.10
Chlorobenzene	0.30
Bromoform	>0.10
1,1,2,2-Tetrachloroethane	0.30 (0.10 for 25mL purge volume)

NOTE: The CCC and SPCC criteria must be met even if the calibration curve option is used for quantitation. If the CCC and SPCC criteria do not pass, a new calibration curve must be prepared and analyzed.

10.3.9 After the initial calibration criteria (CCC and SPCC) have been met, each target is evaluated for linearity.

If the %RSD of the target compound is less than or equal to 15%, the average response factor can be used for quantitation of samples.

If the %RSD of the target compound is greater than 15%, a regression curve (linear, quadratic, etc) must be used for the quantitation of samples. A regression curve may also be used for the compounds that have %RSD less than 15%. The results can be used to plot a calibration curve of response ratios-Ax/Ais is plotted on the y-axis; Cx/Cis is plotted on the x-axis where

Ax = area of the characteristic ion for the compound being measured
Ais = area of the characteristic ion for the internal standard associated with the compound being measured (See attached quantitation report for a list of the compounds that are associated with the correct internal standard)
Cx = concentration or mass on-column of the target compound being measured (ug/L or ug/kg OR ng or ug)
Cis = concentration of the internal standard (ug/L or ug/kg OR ng or ug)

If the correlation coefficient of the regression curve is greater than 0.99, the curve can be used to quantify samples.. Regression curves may be forced through zero but it is recommended that the curve be evaluated without forcing through zero first and then with the curve forced through the origin. The analyst must ensure that the type of regression curve selected accurately defines the concentration/response relationship over the entire calibration range

When more calibration levels are analyzed than required, individual compounds may be eliminated from the lowest or highest calibration levels(s) only. If points or levels are eliminated, analyte concentration in samples must fall within the range defined by the resulting curve. In no case should individual points in the middle of the calibration curve be eliminated without eliminating the entire level.

NOTE: Linear regression curves must be used for South Carolina DHEC compliance samples. See pre-project plans and client QAPPs for other exceptions to using non-linear curve fitting.

8000B exception: evaluation of the "grand mean": If the average %RSD of ALL (all targets including CCC and SPCC) compounds in the initial calibration is less than 15%, the average response factor can be used for quantitation of all target compounds. The recommended course is to use regression curves, as described above, to quantify targets where the %RSD criterion (<=15%) is exceeded.

NOTE: If a target compound that passes by the "grand mean exception" is detected (>RL), the PM is notified via an anomaly report or case narrative. If the targets are <RL, no notification is required.

10.3.10 After the initial calibration criteria has been met, the method blank is analyzed. 5.0mL or 25mL of reagent water is spiked with the internal standard/surrogate and analyzed. The concentrations of the target compounds in the method blank are calculated and the results are compared to the reporting limits (RL) in Table 5 of the STL-SL CQAP or other specified QAP.

If the concentrations of all target compounds are below the RL, analysis of client samples can take place. Note that all target compounds must meet the criteria.

If the concentration of any target compound is above the RL in Table 5 of the STL-SL CQAP, the method blank must be reanalyzed. The analytical system must be demonstrated to be free from contamination before the analysis of samples can take place.

If the method blank repeatedly fails to meet the criteria, contact the immediate supervisor to determine the cause of the problem and to determine a course of action. This action may include re-cleaning the sparging tubes (with soap, hot water, and methanol), purging the effected autosampler ports with heated methanol, flushing the purge and trap ALS concentrator with methanol, replacing the trap, changing the transfer line, and changing the column. A method blank is then analyzed after taking the corrective action to demonstrate that the contamination has been eliminated. Once the system is determined to be free from contamination, sample analysis may begin. Method blanks may be required after the analysis of samples that contain very high levels of VOC.

10.4 Continuing Calibration Verification

At the beginning of each 12-hour clock, the tune of the instrument must be checked by the analysis of 50ng of 4-BFB. This criteria must be met before the analysis of the calibration check standards can take place.

10.4.1 After the tune criteria has been met, a continuing calibration check standard(s) is analyzed. The continuing calibration standard should be at a nominal concentration of 50ug/L-kg for 5ml/5g samples and 10ug/L for 25mL with ketones and poor purgeables at higher concentrations. The CCC and SPCC criteria (Section 10.3.8) must be met before the analysis of the method blank and samples can take place. The percent difference (%D) is calculated as follows:

$$\%D = \frac{RRFavg - RRFccv}{RRFavg} \otimes 100$$

where
RRFavg = average response factor from initial calibration
RRFccv = response factor from the check (12-hour) standard-calibration verification

The percent drift (%Drift) may also be used to evaluate the change/deviation of the curve:

$$\%Drift = \frac{Ci - Cccv}{Ci} \otimes 100$$

where
Ci = Calibration Check Compound standard concentration
Cccv = measured concentration using the selected quantitation method

NOTE: The SPCC criteria (10.3.8) must be met even if the regression curve option is used for quantitation. If this criteria is not met, corrective action must be taken. The corrective action may include reanalysis of the calibration check standard or preparation of a new secondary stock standard and reanalysis of the calibration check standard. If subsequent analysis of the standard is still out of criteria, a new initial calibration curve must be analyzed and evaluated.

10.4.2 The calibration standard (CCV) must also be evaluated for internal standard retention time and response.

If the retention time of any internal standard changes by more than 30 seconds from the retention times of the internal standards in the initial calibration, the analytical system must be inspected for problems and corrective action instituted.

If the extracted ion current profile (EICP) area for any of the internal standards changes by more than a factor of two (-50% to +100%) from the last calibration check standard, the analytical system must be inspected for problems and corrective action instituted. If the CCV is the first one after the initial calibration, compare the ISTD response to the corresponding level in the ICAL.

10.4.3 After the continuing calibration criteria has been met, the method blank is analyzed. 5.0mL or 25mL of reagent water is spiked with the internal standard/surrogate and analyzed. The concentrations of the target compounds in the method blank are calculated and the results are compared to the reporting limits (RL) in Table 5 of the STL-SL CQAP.

If the concentrations of all target compounds are below the RL, analysis of client samples can take place. Note that all target compound must meet the criteria.

If the concentration of any target compound is above the RL in Table 5 of the STL-SL CQAP, the method blank must be reanalyzed. The analytical system must be demonstrated to be free from contamination before the analysis of client samples can take place.

10.5 Aqueous Sample Analysis-5.0mL to 25mL

The analyst must use the same volume as was used for the calibration standards-if a 5mL sample is used, it must be quanted off of the 5mL calibration curve; if a 25ml sample is used, it must be quanted off of the 25mL calibration curve. Samples are analyzed only after the tune criteria, the calibration (initial or continuing) criteria has been met, and the method blank criteria has been met. See the SOP Summary for the analytical sequence.

10.5.1 Remove the samples to be analyzed from the refrigerator and allow the samples to come to ambient temperature.

10.5.2 Put on a pair of gloves before transferring the sample from the vial to the syringe. The sample is most likely preserved with acid or may contain toxic or hazardous chemicals or biologically active components that may cause skin irritations. ***Gloves must be worn when handling samples.***

10.5.3 Mix the contents of the vial by inverting the vial several times. Check to see if there are air bubbles present in the sample. If air bubbles are present, use another vial if available. Make a note on the analysis log if the sample used contained bubbles and notify the supervisor and/or the project manager.

10.5.5 Remove the plunger from the glass syringe. Attach a syringe valve to the syringe Luer-tip to prevent sample from spilling out of the syringe when sample is added.

10.5.5 Open the vial of the well-mixed sample and gently pour the sample into the syringe barrel. The sample should fill the barrel of the syringe and overflow to allow trapped air bubbles to escape.

10.5.6 Replace the plunger into the syringe barrel. Try not to let air bubbles get into the barrel. If air bubbles are present, turn the syringe up, open the syringe valve , and expel the air while adjusting the volume to 5.0mL or 25mL. If no air bubbles were trapped, adjust the syringe to volume.

NOTE: For TCLP leachate samples, use 1.25mL of sample (1:4 dilution).

10.5.7 Open the syringe valve and inject the internal standard/surrogate (ISSU) mix into the sample.

10.5.8 Transfer the sample from the syringe to the purge and trap device. Record all of the sample identification information on the analysis log. Check the pH of the sample with pH paper and record the pH on the instrument log or other appropriate log.

10.5.9 Analyze the samples using the purge and trap and GC/MS conditions used for the initial and continuing calibration standards.

10.5.10 Determine the concentration of the samples and QC items. If the concentration of a sample is above the highest calibration standard, the sample must be diluted and reanalyzed.

NOTE: Unless otherwise specified by a client QAPP, results from a single analysis are reported as long as the largest target analyte (when multiple analytes are present) is in the upper half if the calibration range. When reporting results from dilutions, appropriate data flags should be used or qualification in a case narrative provided to the client. For TCLP analyses, every reasonable effort should be made to achieve the regulatory level with out instrument overload.

For clients who require we provide lower detection limits, a general guide would be to report the dilution detailed above and one additional run at a dilution factor 1/10 of the dilution with t the highest target in the upper half of the calibration curve. For example, if samples analyzed at a 1/50 dilution resulted in a target in the upper half of the calibration curve, the sample would be analyzed at a dilution factor of 1/5 to provide lower RLs.

A dilution is made when a volume of the sample is mixed with the reagent water to a final volume of 5.0mL or 25ml,depending on which curve is being used. The dilution factor is calculated by dividing the volume of sample into the volume used for the calibration curve.

$$DF = \frac{final\ volume\ of\ dilution(mL)}{volume\ of\ sample\ used(mL)}$$

For example, if 1.0mL of sample is diluted to final volume of 5.0mL, the dilution factor is 5. (5.0/1.0 = 5). If 1.0mL of sample is diluted to a final volume of 25mL, the dilution factor is 25 (25/1=25).

The following table gives some dilution factors:

Volume of Sample (mL)	Volume of Reagent Water (mL)	Final Volume (mL)	Dilution factor
5.0	0	5.0	1
2.5	2.5	5.0	2
1.0	4.0	5.0	5
0.5	4.5	5.0	10
0.10	4.9	5.0	50
25.0	0	25.0	1
5.0	20.0	25.0	5
2.5	22.5	25.0	10
1.0	24.0	25.0	25
0.50	24.5	25.0	50
0.10	24.9	25.0	250

NOTE: The same volume of internal standard/surrogate mix (ISSU) is added to the dilution as was added to the undiluted sample.

10.6 Low Level Soil Samples by Heated Purge and Trap (Method 5035)

The soil analytical system is calibrated using the same concentrations as the 5mL purge. The tune, initial and continuing calibration criteria, and the method blank criteria must be met before samples are analyzed. Standards and QC items must be analyzed under the same heated purge and trap conditions.

Remove the samples to be analyzed (Section 9.2) from the refrigerator or freezer and allow the sample to come to ambient temperature. Inspect the vial for cracks or obvious breaches in the septum. Load the samples on to the soil-purging unit and analyze according to the sequence described in Appendix B.

Liquid field QC for soils (trip blank, field blank, etc.) should be analyzed with the associated soil samples, using the same preparation and analytical procedures, including the heated purge. Report the results for liquid trip blanks as ug/L.

10.7 Analysis of Methanol Extracts of Soils and Wastes

The methanol extraction is used when the concentration of one or more target compounds exceeds the linear range of the low-level purge technique (>1000ug/kg). or if the concentration of VOC in the soil or waste samples is high. Samples are analyzed only after the 4-BFB criteria, the calibration criteria (initial and continuing), and the method blank criteria has been met. Medium level soil extracts are quanted using the ambient purge calibration curve. Sample preparation steps are included in Section 9.

10.7.1 Remove the plunger from the 5.0-mL syringe and fill the barrel to overflowing with reagent water(syringe valve in the "red" position). Replace the plunger, switch the syringe valve to "green", and force any airspace out of the syringe. Adjust the volume to the syringe volume(5mL)

10.7.2 Briefly remove the syringe valve and inject the sample extract and 5uL of the internal standard (IST) solution into the syringe. Use 125ul of the extract for soils and 100uL of the extract for wastes. Smaller aliquots are used if the concentration of target analytes exceed the working range of the system.

NOTE: Use the internal standard (IST) mix when preparing the medium level samples. Recall that the surrogates have already been added to the sample during the methanol extraction step (Section 9).

10.7.3 Load the sample on to the purge and trap device and begin the analysis. All pertinent information concerning the samples must be recorded on the analysis log. The samples must be clearly identified and traceable to the extraction log. These conditions must be the same as was used for the initial and continuing calibration standards-ambient purge for aqueous samples.

10.7.4 Determine the concentration of the samples and QC items using the procedures of Section 11. If the concentration of a sample is above the highest calibration standard, a smaller aliquot of the methanol extract is reanalyzed to bring the highest target within the upper half of the calibration curve. Follow the guidelines in Section 10.4.10 for reporting dilutions.

NOTE: It is possible to dilute the surrogates in the sample extract below the linear range of the calibration curve. The minimum extract aliquot that can be used to provide a quantifiable result for the surrogates and matrix spikes is 0.0025mL (2.5uL).

SOIL: 10g to 10mL MeOH	WASTES: 1g to 10mL MeOH	Surrogates- Theoretical ng on-column
125uL(0.125mL)	100uL (0.100mL)	250
62.5uL(0.0625mL)	50uL(0.050mL)	125
25uL(0.025mL)	25uL(0.020mL)	50
12.5uL(0.0125mL)	10ul(0.010mL)	25
2.5uL(0.0025mL)	2.0uL(0.0020mL)	5.0-quantiation limit
<2.5uL(0.025mL)	<2.0uL(0.0020mL)	<5.0ng- below the quantitation limit-diluted out

NOTE: Some instrument quantitation limits may be higher than the limit listed in the table. The volume of extract should be adjusted accordingly.

11.0 DATA ANALYSIS/CALCULATIONS

11.1 Qualitative Analysis of Target Compounds

A target compound is identified by the visual comparison of the sample mass spectrum with the mass spectrum of the target compound from a reference spectrum of the target compound stored in a library generated on the same instrument or a standard spectral library such as the NIST/NBS.

11.1.1 Two criteria must be met in order to identify a target compound.

1) elution of the sample component within +/-0.06 RRT (relative retention time) units of the daily standard containing that compound.

$$RRT = \frac{\textit{retention time of the target compound}}{\textit{retention time of the associated internal standard}}$$

2) correspondence of the target compound spectrum and the standard component mass spectrum

11.1.2 All ions present in the standard component mass spectrum at a relative intensity greater than 10% (most abundant ion = 100%) should be present in the sample component mass spectrum. Other ions may be present in the sample component. Coelution of a non-target compound with a target compound will make the identification of the target compound more difficult. These ions due to the non-target compound should be subtracted from the sample component spectrum as part of the background to account for the discrepancy between the sample spectrum and the standard spectrum.

11.1.3 The relative intensities of the ions present in the sample component spectrum should agree within +/- 30% of the relative intensities of the ions in the standard reference spectrum. For example, an ion with an abundance of 50% in the reference spectrum should have a corresponding abundance between 20% and 80% in the sample component spectrum.

11.1.4 If the above criteria are not met exactly, the analyst should seek help from a senior analyst or supervisor. If there is sufficient evidence to support the identification of the component, then the component is identified, quantified, and reported.

11.2 Tentatively Identified Compounds

For samples containing components not associated with the calibration standards, a library search on a reference library, such as the NIST/NBS, may be conducted in order to identify the non-target compounds. Only after visual comparison between the sample spectra and the library-generated reference spectra will the mass spectral analyst assign tentative identification. Tentative identifications of non-targets will be made only by analysts having completed the training specified in the training schedule.

11.2.1 Relative intensities of the major ions (masses) in the reference spectra (ions >10% of the most abundant ion) should be present in the sample spectrum.

11.2.2 The relative intensities of the major ions should agree within +/-30%.

11.2.3 Molecular ions present in the spectrum should be present in the sample spectrum.

11.2.4 Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible subtraction from the sample spectrum because of over-lapping or co-eluting peaks.

11.2.5 Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of coeluting peaks.

11.2.6 If, in the opinion of the analyst, there is enough evidence to support the tentative identification of a compound even though the above criteria is not met exactly, the peak may be considered tentatively identified. The analyst should consult other analysts or the mass spectral interpretation specialist if there are any questions concerning an interpretation of spectra.

11.2.7 The estimated concentration of the tentatively identified compound (TIC) is calculated using the total ion area of the tentatively identified peak and total ion area of the nearest internal standard that has no interferences. The calculation is

Aqueous

$$TIC(ug/L) = \frac{Cis}{AREAis} \otimes AREAtic \otimes DF$$

where
Cis = concentration of the internal standard, ug/L
AREAis = total ion peak area of the internal standard
AREAtic= total ion peak area of the TIC
DF = dilution factor

Soils by Heated P/T

$$TIC\,(ug/kg,dw) = \frac{Cis}{AREAis} \otimes AREAtic \otimes \frac{5.0g}{(W)(solids)}$$

where
Cis = concentration of the internal standard, ug/kg
AREAis = total ion peak area of the internal standard
AREAtic= total ion peak area of the TIC
W = weight of sample analyzed, g
solids = decimal equivalent of percent solids

Soils by Methanol Extraction

$$TIC\,(ug/kg,dw) = \frac{Cis}{AREAis} \otimes AREAtic \otimes \frac{Vcal}{(W)(solids)}$$

where
Cis = concentration of the internal standard, ug/kg
AREAis = total ion peak area of the internal standard
AREAtic= total ion peak area of the TIC
Vcal = volume that calibration curve is based on (5mL or 25mL)
solids = decimal equivalent of the percent solids(percent solids/100)
W = weight of sample added to the reagent water (g)

This weight is determined using the following equation:

$$W = \frac{Wext(g)}{Vf(mL)} \otimes Vext(mL)$$

where
Wext = weight of sample extracted (g)
Vf = final volume of the extract (mL)
Vext = volume of extract added to the water (mL)

11.3 Calculations for Samples-Internal Standard Technique

Aqueous Samples- relative response factor :

$$concentration(ug/L) = \frac{Ax}{Ais} \otimes \frac{Cis}{RRFavg} \otimes DF$$

where
Ax = area of the characteristic ion of the compound being measured
Ais = area of the characteristic ion of the internal standard
Cis = concentration of the internal standard (ug/L)
RRFavg = average response factor of the compound being measured
DF = dilution factor

Aqueous Samples: regression curve

$$concentration(ug/L) = concentration(curve) \otimes DF$$

where
DF = dilution factor

The reporting limit (RL) is calculated:

$$RL(ug/L) = RLqap \otimes DF$$

where
DF = dilution factor. The SL CQAP Table 5 RL(RLqap) assumes a DF of 1.

Soils by Heated P/T- relative response factor :

$$concentration(ug/kg,dw) = \frac{Ax}{Ais} \otimes \frac{Cis}{RRFavg} \otimes \frac{5.0g}{(W)(solids)}$$

where
Ax = area of the characteristic ion of the compound being measured
Ais = area of the characteristic ion of the internal standard
Cis = concentration of the internal standard (ug/kg)
RRFavg = average response factor of the compound being measured
W = weight of sample added to the sparging vessel (g)
solids = (percent solids)/100)

Soils by Heated P/T: regression curve

$$conc(ug/kg,dw) = Ccurve(ug/kg) \otimes \frac{5.0g}{(W)(solids)}$$

where
Ccurve = concentration from curve(ug/kg)
W = weight of sample added to the sparging vessel (g)
solids = (percent solids)/100)

The reporting limit (RL) is calculated:

$$RL = RLqap \otimes \frac{5.0g}{(W)(solids)}$$

where
W = weight of sample added to the sparging vessel (g)
solids = (percent solids)/100)

The STL-SL CQAP assumes W= 5.0g and solids = 1.

Methanol Extraction Soils and Wastes- relative response factor

$$concentration(ug/kg,dw) = \frac{Ax}{Ais} \otimes \frac{Cis}{RRFavg} \otimes \frac{Vcal}{(W)(solids)}$$

where
Ax = area of the characteristic ion of the compound being measured
Ais = area of the characteristic ion of the internal standard
Cis = concentration of the internal standard (ug/L)
RRFavg = average response factor of the compound being measured
Vcal = volume that calibration curve is based on (5mL or 25mL)
solids = (percent solids)/100)
W = weight of sample added to the reagent water (g)

This weight is determined using the following equation:

$$W = \frac{Wext(g)}{Vf(mL)} \otimes Vext(mL)$$

Wext = weight of sample extracted (g)
Vf = final volume of the extract (mL)
Vext = volume of extract added to the water (mL)

Methanol Extraction of Soils and Solids- regression curve:

$$conc(ug,kg,dw) = Ccurve(ug/L) \otimes \frac{Vcal}{(W)(solids)}$$

where
Vcal = volume that calibration curve is based on (0.005L or 0.025L)
W = weight of sample added to the reagent water (g)-defined above

The reporting limit (RL)is calculated:

$$RL = RLqap \otimes \frac{5.0g}{(W)(solids)}$$

where
W = weight of sample added to the reagent water (g)
solids = (percent solids)/100)

The STL-SL CQAP assumes W= 5.0g and solids = 1.

12.0 QUALITY ASSURANCE /QUALITY CONTROL

12.1 The analytical batch consists of up to twenty client samples and the associated QC items that are analyzed together. The matrix spike and LCS frequency is defined in Section 3.1.3 of STL-SL SOP AN02: *Analytical Batching*. Note that the method blank for liquid samples and low-level soils is clock-specific and that the method blank for medium level soil samples is extraction batch-specific.

STL-SLSOP AN02: *Analytical Batching* describes the procedure for evaluating batch-specific QC. This criteria is summarized in the attached 8260 SOP Summary.

STL-SL SOP AN02 also contains the calculations for accuracy and precision and the calculations for the theoretical concentrations of surrogates, lab spikes, and matrix spikes.

12.2 Initial Demonstration of Capability (IDOC) to Generate Acceptable Accuracy and Precision

Each analyst must demonstrate competence in the analysis of samples by this procedure. The minimum criteria for this demonstration is the preparation and analysis of spiked reagent water. Section 8.3 of EPA Method 8260A gives the general procedure for the performance of the IDOC and Table 6 of EPA Method 8260A gives the acceptance criteria for the accuracy and precision.

12.3 Method Detection Limit

The method detection limit is determined in accordance with STL-SL SOP CA90.

13.0 PREVENTIVE MAINTENANCE

Preventive maintenance items will be added at a later date. Section 10 of the STL-SL QAPs provide guidance on preventive maintenance.

14.0 TROUBLE-SHOOTING

Trouble-shooting items will be added at a later time. See instrument manufacturers' manuals for guidance on locating and repairing instrument problems.

15.0 REFERENCES

1. *Savannah Laboratories' Comprehensive Quality Assurance Plan* and *Savannah Laboratories' Corporate Quality Assurance Plan*, current revisions.
2. Method s 5035, 8000B, and 8260B. *Test Methods for Evaluating Solid Wastes, Third Edition, SW-846.including Update III.* U.S. EPA Office of Solid Waste and Emergency Response: Washington, DC.

Appendix A

VOLATILES BY GC/MS WORKING STANDARDS -EXAMPLE

These standards can be used to prepare the working standards for EPA Method 8260 to report the TCL (target compound list) compounds and the extended list of target compounds generally associated with EPA 8260. The standards are prepared in purge and trap grade methanol and are stored at 4C with minimum headspace.

Working Standard 1 (TCL WS-1)

STOCK STANDARD	CONC (ug/mL)	microliters of stock to final volume of 1.0mL	STD CONC (ug/mL)
VOA Cal #2	2000	12.5	25
VOA Cal #3	2000	12.5	25
VOA Cal #4	2000	12.5	25
1,2,-DCB	5000	5.0	25
1,3-DCB	5000	5.0	25
1,4-DCB	5000	5.0	25
2-CEVE	1000	125	125

Working Standard 2 (TCL WS-2)

STOCK STANDARD	CONC (ug/mL)	microliters of stock to final volume of 1.0mL	STD CONC (ug/mL)
VOA Cal #1	5000	25	125
8260 Surrogates	2500	10	25

Working Standard for GASES (TCL GASES)

STOCK STANDARD	CONC (ug/mL)	microliters of stock to final volume of 1.0mL	STD CONC (ug/mL)
502.2 Cal 1	2000	12.5	25

Appendix A

Working Standard 3 (8260 WS-3)

STOCK STANDARD	CONC (ug/mL)	microliters of stock to final volume of 1.0mL	STD CONC (ug/mL)
8260 Custom Mix #1	200	125	25
8260 Custom Mix #2	200	125	25
1,1,2,2-Tetrachloroethane	2000	12.5	25

Appendix A

Internal Standard (8260 ISTD)

STOCK STANDARD	CONC (ug/mL)	microliters of stock to final volume of 1.0mL	STD CONC. ug/mL
VOA ISTD	2500	20	50
1,2-DCE-d4	2000	25	50

Internal Standard/Surrogate (8260 ISSU)

STOCK STANDARD	CONC (ug/mL)	microliters of stock to final volume of 1.0mL	STD CONC (ug/mL)
VOA ISTD	2500	20	50
1,2-DCE-d4	2000	25	50
8260 Surrogate	2500	20	50

Tune Evaluation Standard (4-BFB)

STOCK STANDARD	CONC (ug/mL)	microliters of stock to final volume of 1.0mL	STD CONC. ug/mL
4-BFB	5000	10	50

Matrix Spike Standard (5-component subset)

STOCK STANDARD	CONC (ug/mL)	microliters of stock to final volume of 1.0mL	STD CONC. ug/mL
Matrix Spiking Solution	2500	20	50

TCLP matrix Spike Standard (5-component subset)

STOCK STANDARD	CONC (ug/mL)	microliters of stock to final volume of 1.0mL	STD CONC. ug/mL
TCLP Spiking Solution	2000	16	125

Appendix A

VOLATILES BY GC/MS CALIBRATION STANDARDS - EXAMPLES

The following calibration standards are prepared to define the working range of the EPA 8260 analysis for the target compound list (TCL) and the extended list of compounds generally associated with EPA 8260. The lowest level standard is at the reporting limit and the other standards define the working range. Samples with target analytes above the concentration of the highest calibration standard must be diluted and reanalyzed.

TARGET COMPOUND LIST

Working Level standards	Conc (ug/mL)	TCL-1 *	TCL-2 *	TCL-3 *	TCL-4 *	TCL-5 *	TCL-6 *
TCL WS-1	25/125	1.0	2.0	5.0	10.0	20.	40
TCL WS-2	125	1.0	2.0	5.0	10	20	40
TCL GASES	25	1.0	2.0	5.0	10	20	40
TCL ISTD	50	5.0	5.0	5.0	5.0	5.0	5.0

*uL of the working standard added to 5.0mL of reagent water or to 5.0g of blank sand.

8260 EXTENDED LIST (TCL+ADDITIONAL COMPOUNDS)

Working Level standards	Conc (ug/mL)	8260-1 *	8260-2 *	8260-3 *	8260-4 *	8260-5 *	8260-6 *
TCL WS-1	25/125	1.0	2.0	5.0	10.0	20.	40
TCL WS-2	125	1.0	2.0	5.0	10	20	40
8260 WS-3	25	1.0	2.0	5.0	10	20	40
TCL GASES	25	1.0	2.0	5.0	10	20	40
TCL ISTD	50	5.0	5.0	5.0	5.0	5.0	5.0

*uL of the working standard added to 5.0mL of reagent water or to 5.0g of blank sand.

CONCENTRATIONS OF THE CALIBRATION STANDARDS-5.0mL OR 5.0g

Cal Std	all targets except ketones, 2-CEVE	ketones, 2-CEVE
TCL-1,8260-1	5ug/l-kg	25ug/l-kg
TCL-2,8260-2	10ug/l-kg	50ug/l-kg
TCL-3,8260-3	25ug/l-kg	125ug/l-kg
TCL-4,8260-4	50ug/l-kg	250ug/l-kg
TCL-5,8260-5	100ug/l-kg	500ug/l-kg
TCL-6,8260-6	200ug/l-kg	1000ug/l-kg

Appendix A

VOLATILES BY GC/MS CALIBRATION STANDARDS-25mL Purge Volume-EXAMPLES

These calibration standards are prepared to define the working range of the EPA 8260 analysis for the target compound list (TCL) and the extended list of compounds generally associated with EPA 8260. The standards are based on a volume of 25mL to achieve lower quantitation limits for the target compounds. The lowest level standard is at the reporting limit and the other standards define the working range. Samples with target analytes above the concentration of the highest calibration standard must be diluted and reanalyzed.

TARGET COMPOUND LIST

Working Level standards	Conc (ug/mL)	25TCL -1*	25TCL-2*	25TCL-3*	25TCL-4*	25TCL-5*	25TCL-6*
TCL WS-1	25/125	1.0	2.0	5.0	10.0	20.	40
TCL WS-2	125	1.0	2.0	5.0	10	20	40
TCL GASES	25	1.0	2.0	5.0	10	20	40
TCL ISTD	50	5.0	5.0	5.0	5.0	5.0	5.0

*uL of the working standard added to 25mL of reagent water.

8260 EXTENDED LIST (TCL+ADDITIONAL COMPOUNDS)

Working Level standards	Conc (ug/mL)	258260-1*	258260 -2*	258260-3*	258260-4*	258260-5*	258260-6*
TCL WS-1	25/125	1.0	2.0	5.0	10.0	20.	40
TCL WS-2	125	1.0	2.0	5.0	10	20	40
8260 WS-3	25	1.0	2.0	5.0	10	20	40
TCL GASES	25	1.0	2.0	5.0	10	20	40
TCL ISTD	50	5.0	5.0	5.0	5.0	5.0	5.0

*uL of the working standard added to 25mL of reagent water.

CONCENTRATIONS OF THE CALIBRATION STANDARDS

Cal Std	all targets except ketones, 2-CEVE	ketones, 2-CEVE
25TCL-1,25-8260-1	1.0ug/l	5.0ug/l
25TCL-2,25-8260-2	2.0ug/l	10ug/l
25TCL-3,25-8260-3	5.0ug/l	25ug/l
25TCL-4,25-8260-4	10ug/l	50ug/l
25TCL-5,25-8260-5	20ug/l	100ug/l
25TCL-6,25-8260-6	40ug/l	200ug/l

Appendix B
8260 SOP SUMMARY

HOLD TIMES

MATRIX	Preservative/ Storage*	Container	Hold Time
Aqueous	None; 4C	40mL no headspace	7 days
	HCl pH<2; 4C	40mL-no headspace	14 days
Soil/solid(low level)	Iced at collection; 5mL sodium bisulfate added upon arrival in lab; store at 4C	5-g Encore Sampler	14 days
Soil/solid(low level) -high carbonates	Iced at collection; 5mL water added upon arrival in lab; store at –10C	5-g Encore Sampler	14 days
Soil/solid(high level)	None; 4C	Glass 125mL	14 days
TCLP	HCl pH<2; 4C	Tedlar bag or syringe	14 days

*storage temperature is 4C with a control criteria of less than 6C with no frozen samples

ANALYSIS SEQUENCE

INITIAL CALIBRATION	CONTINUING CALIBRATION
4-BFB 50ng on column Clock starts at injection	4-BFB 50ng on column Clock starts at injection
Calibration standards- minimum of five cal levels	Mid point calibration verification (50ug/L or 50ug/kg)) RL Standard-low point on cal curve (if necessary)
Method blank	Method blank
Samples analyzed until the 12-hour clock expires	Samples analyzed until 12-hour clock expires

See SL SOP AN02, Section 3.1.3, for the batch/clock options for LCS and MS/MSD.

Recommended Internal Standards:
1,2-dichloroethane-d4; 1,4-difluorobenzene; chlorobenzene-d5; 1,4-dichlorobenzene-d4

Surrogates/System Monitoring Compounds:
dibromofluoromethane; toluene-d8; 4-bromofluorobenzene

LCS/MS: CQAP Subset:
1,1-dichloroethene; benzene; trichloroethene; toluene; chlorobenzene

Appendix B
8260 SOP SUMMARY

VOLATILE ORGANIC GC/MS TUNING AND MASS CALIBRATION BROMOFLUOROBENZENE (BFB)	
m/e	**Abundance Criteria**
50	8.0-40.0% of mass 95
75	30.0-66.0% of mass 95
95	Base peak, 100% relative abundance
96	5.0-9.0% of mass 95
173	< 2.0% of mass 174
174	50-120%% of mass 95
175	4.0-9.0% of mass 174
176	93.0-101.0% of mass 174
177	5.0-9.0% of mass 176

(1) *8260 criteria taken from CLP OLMO4.0 (January 1998)

CALIBRATION ACCEPTANCE CRITERIA

Calibration Check Compounds - CCC
Vinyl chloride, 1,1-dichloroethene, chloroform, 1,2-dichloropropane, toluene, ethylbenzene

Initial Calibration	**Continuing Calibration**
Less than or equal to 30% RSD	Less than or equal to 20% difference or drift from initial calibration

System Performance Check Compounds-SPCC

SPCC	Minimum RRF
Chloromethane	0.10
1,1-Dichloroethane	0.10
Chlorobenzene	0.30
Bromoform	>0.10
1,1,2,2-Tetrachloroethane	0.30 (0.10 for 25mL purge volume)

See Sections 10.3 and 10.4 for ICAL and CCV linearity checks and criteria.

Appendix B

QC Check	Frequency	Acceptance Criteria	Corrective Action
MS Tune Check - 50ng 4-BFB	Before initial and continuing calibration standards - every 12 hours	Mass abundances within method acceptance criteria	-Evaluate chromatogram and spectrum - Reanalyze - Retune MS and reanalyze - Remake standard and reanalyze - Perform instrument maintenance and reanalyze
Initial Calibration – minimum five point curve with lowest point at or below the Reporting Limit (RL)	Initially; after major instrument maintenance; whenever continuing calibration check fails. Prior to analysis of method blank and samples	Method criteria for CCC/SPCC (see -Calibration Acceptance Criteria – Table presented earlier in this document)	- Evaluate chromatograms, spectra, and integrations - Reanalyze standard(s) - Remake and reanalyze standard(s) - Perform instrument maintenance and recalibrate
Continuing Calibration check - midpoint standard	Every 12 hours before analysis of method blank and samples	Method criteria for CCC/SPCC (see Calibration Acceptance Criteria - Table presented earlier in this document)	- Evaluate chromatogram, spectra, integrations - Reanalyze standard - Remake and reanalyze standard - Recalibrate - Perform instrument maintenance and recalibrate
Method Blank	Every 12 hours (per clock) before sample analyses	All reported targets <RL	-Evaluate chromatogram and integrations. Check calculations. -Reanalyze - Follow guidance in STL-SL SOP AN02 and Table 13.1 in CQAP -Perform instrument or column maintenance, recalibrate, and reanalyze

Appendix B

QC Check	Frequency	Acceptance Criteria	Corrective Action
Lab Control Sample (LCS) -subset of target compounds unless full target spike specified by client	Each batch	STL-SL CQAP Section 5	-Evaluate chromatogram and integrations. Check calculations. -Follow guidance in STL-SL SOP AN02 and Table 13.1 in CQAP -Perform instrument or column maintenance, recalibrate, and reanalyze
Matrix Spike/Matrix Spike Duplicate (MS/MSD) -subset of target compounds unless full target spike specified by client	Each batch	STL-SL CQAP Section 5	-Evaluate chromatogram and integrations. Check calculations. -Follow guidance in STL-SL SOP AN02 and Table 13.1 in CQAP -Perform instrument or column maintenance, recalibrate, and reanalyze
Surrogates	All samples, blanks, LCS, MS	STL-SL CQAP Section 5	-Evaluate chromatogram and integrations. Check calculations. -Reanalyze - Follow guidance in STL-SL SOP AN02 and Table 13.1 in CQAP -Perform instrument or column maintenance, recalibrate, and reanalyze
Internal Standard Area	Evaluate all standards and samples	-Areas in continuing calibration verification must be 50% to +200% of previous initial calibration sequence -Retention time of internal standard must be +/-30 seconds from internal standard in initial calibration -Areas in samples should be evaluated for gross error . Consult supervisor.	-Evaluate chromatogram and integrations. Check calculations. -Reanalyze

Appendix B

QC Check	Frequency	Acceptance Criteria	Corrective Action
Reporting Limit Standard -1x to 2x the RL	(Optional) Daily. Required for Florida DEP	Detected with reasonable response	-Evaluate chromatogram, spectra, and integrations -Reanalyze -Remake standard and reanalyze -Retune and recalibrate -Perform instrument maintenance and recalibrate
Initial Demonstration of Capability	Per analyst	Method criteria	-Reanalyze targets that do not meet criteria
Method Detection Limit (MDL)	See STL-SL SOP CA90	See STL-SL SOP CA90	-Reanalyze and re-evaluate

Appendix C
EXAMPLE QUANTITATION REPORT

-quantitation ions
-internal standard and target compound association

SEVERN TRENT SERVICES

CHANGE -IN-PROGRESS ATTACHMENT

SOP Document No: VM20:11.12.99:4

SOP Description: Volatile Compounds by GC/MS (8260)

Approval Signature: R. Wayne Robbs 6 Sept 2001
Date

Title: Technical Manager, QA

STL: X Savannah __ Tallahassee __ Mobile __ Tampa West

The following revisions or additions have been made to the referenced SOP.

The following attachments are for a specific project and will be effective from the date of approval until the date that the project is completed. The purpose of this CIPA is to document changes or additions to the standard operating procedures requested for the Sauget Area 2 Sites Group and EPA Region V.

The attachments are tables of the project RLs and MDLs, including the QC limits, and an excerpt from the Sauget Area 2 Sites Group QAPP.

SEVERN TRENT SERVICES

Target Compounds-Volatiles by GC/MS (8260) Water

PARAMETER	METHOD	%REC	%RPD	MDL(ug/L)	RL(ug/L)
Acetone	8260(5030)(low level)	32-174	<=52	10	25
Benzene (MS)	8260(5030)(low level)	62-135	<=37	0.18	1.0
Bromodichloromethane	8260(5030)(low level)	65-125	<=28	0.14	1.0
Bromoform	8260(5030)(low level)	52-148	<=31	0.16	1.0
Bromomethane	8260(5030)(low level)	40-141	<=32	0.14	1.0
2-Butanone (MEK)	8260(5030)(low level)	42-167	<=31	1.4	10
Carbon disulfide	8260(5030)(low level)	28-152	<=23	0.28	1.0
Carbon tetrachloride	8260(5030)(low level)	57-128	<=38	0.11	1.0
Chlorobenzene (MS)	8260(5030)(low level)	72-127	<=22	0.37	1.0
Chloroethane	8260(5030)(low level)	47-148	<=34	0.28	1.0
Chloroform	8260(5030)(low level)	62-130	<=20	0.17	1.0
Chloromethane	8260(5030)(low level)	34-145	<=44	0.18	1.0
Dibromochloromethane	8260(5030)(low level)	68-126	<=31	0.14	1.0
1,2-Dibromo-3-chloropropane	**8260(5030)(low level)**	**70-130**	**<=30**	**0.21**	**1.0**
1,1-Dichloroethane	8260(5030)(low level)	51-140	<=47	0.21	1.0
1,2-Dichloroethane	8260(5030)(low level)	65-131	<=23	0.13	1.0
1,2-Dichloroethenes (Total)	8260(5030)(low level)	43-136	<=22	0.48	2.0
1,1-Dichloroethene	8260(5030)(low level)	46-147	<=30	0.29	1.0
1,2-Dichloropropane	8260(5030)(low level)	67-128	<=24	0.068	1.0
cis-1,3-Dichloropropene	8260(5030)(low level)	66-125	<=21	0.21	1.0
trans-1,3-Dichloropropene	8260(5030)(low level)	49-136	<=24	0.12	1.0
Ethylbenzene	8260(5030)(low level)	74-122	<=18	0.30	1.0
2-Hexanone	8260(5030)(low level)	48-155	<=36	0.31	10
Methylene chloride	8260(5030)(low level)	47-140	<=50	1.0	5
4-Methyl-2-pentanone (MIBK)	8260(5030)(low level)	50-150	<=42	0.51	10
Styrene	8260(5030)(low level)	66-130	<=28	0.22	1.0
1,1,2,2-Tetrachloroethane	8260(5030)(low level)	67-133	<=22	0.14	1.0
Tetrachloroethene	8260(5030)(low level)	60-148	<=24	0.30	1.0
Toluene (MS)	8260(5030)(low level)	68-131	<=33	0.29	1.0
1,1,1-Trichloroethane	8260(5030)(low level)	69-120	<=27	0.13	1.0
1,1,2-Trichloroethane	8260(5030)(low level)	63-133	<=21	0.13	1.0
Trichloroethene(MS)	8260(5030)(low level)	56-143	<=35	0.38	1.0
Vinyl chloride	8260(5030)(low level)	43-142	<=21	0.26	1.0
Xylenes (total)	8260(5030) (low level)	73-135	<=26	0.84	2.0
Surrogate					
Toluene-d8	8260(5030)	77-122	NA	NA	NA
p-Bromofluorobenzene	8260(5030)	74-126	NA	NA	NA
Dibromofluoromethane	8260(5030)	70-130	NA	NA	NA

SEVERN TRENT SERVICES

Target Compounds-Volatiles by GC/MS (8260) Soils and Solids

PARAMETER	METHOD	%REC	%RPD	MDL(ug/kg)	RL(ug/kg)
Acetone	8260(5035)	43-154	<=28	5	50
	8260(5035ext)	43-154	<=28	200	2000
Benzene (MS)	8260(5035)	49-142	<=42	0.4	5
	8260(5035ext)	49-142	<=42	16	200
Bromodichloromethane	8260(5035)	32-149	<=33	0.16	5
	8260(5035ext)	32-149	<=33	6.4	200
Bromoform	8260(5035)	41-138	<=24	0.36	5
	8260(5035ext)	41-138	<=24	14	200
Bromomethane	8260(5035)	23-173	<=79	1.2	10
	8260(5035ext)	23-173	<=79	48	400
2-Butanone (MEK)	8260(5035)	45-154	<=39	1.1	25
	8260(5035ext)	45-154	<=39	44	1000
Carbon disulfide	8260(5035)	40-135	<=68	0.41	5
	8260(5035ext)	40-135	<=68	16	200
Carbon tetrachloride	8260(5035)	40-135	<=59	0.17	5
	8260(5035ext)	40-135	<=59	6.8	200
Chlorobenzene (MS)	8260(5035)	66-135	<=34	0.19	5
	8260(5035ext)	66-135	<=34	7.6	200
Chloroethane	8260(5035)	30-135	<=51	0.71	10
	8260(5035ext)	30-135	<=51	28	400
Chloroform	8260(5035)	50-133	<=38	0.36	5
	8260(5035ext)	50-133	<=38	14	200
Chloromethane	8260(5035)	32-142	<=53	0.39	10
	8260(5035ext)	32-142	<=53	16	400
Dibromochloromethane	8260(5035)	47-135	<=22	0.16	5
	8260(5035ext)	47-135	<=22	6.4	200
1,2-Dibomo-3-chloropropane	**8260(5035)**	**28-148**	**<=36**	**0.36**	**10**
	8260(5035ext)	**28-148**	**<=36**	**144**	**400**
1,1-Dichloroethane	8260(5035)	51-129	<=38	0.38	5
	8260(5035ext)	51-129	<=38	15	200
1,2-Dichloroethane	8260(5035)	49-136	<=25	0.3	5
	8260(5035ext)	49-136	<=25	12	200
1,2-Dichloroehtenes (total)	8260(5035)	37-142	<=56	0.88	10
	8260(5035ext)	37-142	<=56	36	400
1,1-Dichloroethene (MS)	8260(5035)	40-164	<=46	0.4	5
	8260(5035ext)	40-146	<=46	16	200
1,2-Dichloropropane	8260(5035)	52-124	<=27	0.43	5
	8260(5035ext)	52-124	<=27	17	200
cis-1,3-Dichloropropene	8260(5035)	40-133	<=34	0.27	5
	8260(5035ext)	40-133	<=34	11	200
trans-1,3-Dichloropropene	8260(5035)	45-131	<=50	0.2	5
	8260(5035ext)	45-131	<=50	8	200
Ethylbenzene	8260(5035)	51-135	<=44	0.13	5
	8260(5035ext)	51-135	<=44	5.2	200
2-Hexanone	8260(5035)	45-127	<=32	1.2	25
	8260(5035ext)	45-127	<=32	48	1000
Methylene chloride	8260(5035)	44-142	<=32	2.2	5
	8260(5035ext)	44-142	<=32	88	200
4-Methyl-2-pentanone (MIBK)	8260(5035)	34-159	<=37	0.56	25
	8260(5035ext)	34-159	<=37	22	1000
Styrene	8260(5035)	43-140	<=45	0.2	5
	8260(5035ext)	43-140	<=45	8	200
1,1,2,2-Tetrachloroethane	8260(5035)	49-144	<=28	0.37	5
	8260(5035ext)	49-144	<=28	15	200
Tetrachloroethene	8260(5035)	71-146	<=44	0.26	5
	8260(5035ext)	71-146	<=44	10	200
Toluene (MS)	8260(5035)	38-158	<=32	0.34	5
	8260(5035ext)	38-158	<=32	14	200

SEVERN TRENT SERVICES

Target Compounds-Volatiles by GC/MS (8260) Soils and Solids

PARAMETER	METHOD	%REC	%RPD	MDL(ug/kg)	RL(ug/kg)
1,1,1-Trichloroethane	8260(5035)	41-134	<=54	0.33	5
	8260(5035ext)	41-134	<=54	13	200
1,1,2-Trichloroethane	8260(5035)	34-148	<=27	0.4	5
	8260(5035ext)	34-148	<=27	16	200
Trichloroethene (MS)	8260(5035)	51-146	<=34	0.26	5
	8260(5035ext)	51-146	<=34	10	200
Vinyl chloride	8260(5035)	33-142	<=65	0.3	10
	8260(5035ext)	33-142	<=65	12	400
Xylenes (total)	8260(5035)	37-133	<=43	0.57	10
	8260(5035ext)	37-133	<=43	23	400
Surrogates					
Toluene-d8	8260(5035)	64-136	NA	NA	NA
	8260(5035ext)	64-136	NA	NA	NA
p-Bromofluorobenzene	8260(5035)	63-135	NA	NA	NA
	8260(5035ext)	63-135	NA	NA	NA
Dibromofluoromethane	8260(5035)	58-142	NA	NA	NA
	8260(5035ext)	58-142	NA	NA	NA
(ext) = methanol extraction; 1mL methanol per gram of sample					

SEVERN TRENT SERVICES

Table 7A. *Volatile organic compounds using USEPA Method 8260B Quality Control Requirements and Corrective Actions.**

Audit	Frequency	Control Limits	Corrective Action
Holding times	Samples must be extracted and analyzed within holding time.	VOCs: Analyze within 14 days from collection.	If holding times are exceeded for initial or any re-analyses required due to QC excursions, notify QAO* immediately since re-sampling may be required. Document corrective action in the case narrative.
MS Tuning	Once every 12 hours prior to initial calibration and calibration verifications.	1. BFB key ions and abundance criteria listed in the method must be met for all 9 ions and analyses must be performed within 12 hours of injection of the BFB. 2. Part of the BFB peak will not be background subtracted to meet tune criteria. 3. Documentation of all BFB analyses and evaluation must be included in the data packages.	1. Tune the mass spectrometer. 2. Document corrective action in the case narrative –samples cannot be analyzed until control limit criteria have been met.
Initial Calibration	Prior to sample analysis and when calibration verifications criteria are not met. Initial calibration will contain all target analytes in each standard.	1. Five concentrations bracketing expected concentration range for all compounds of interest; one std must be near the PQL. 2. CCC compounds <30% RSD, remaining compounds ≤50% RSD. 3. SPCC RF as listed in method, non-SPCC ≥ 0.050 RF except for ketones and 2-chloroethyl vinyl ether with RF ≥ 0.010. 4. For compound with %RSD >15, quantitation must be performed using a separate calibration curve and the COD must be > 0.99.	1. Identify and correct problem. 2. If criteria are still not met, recalibrate. 3. Document corrective action in the case narrative – samples cannot be analyzed until calibration control limit criteria are met. Contact QAO* to discuss problem target analytes such as 2-chloroethyl vinyl ether before proceeding with analysis.

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Audit	Frequency	Control Limits	Corrective Action
Internal Standards	All samples and blanks (including MS/MSD)	1. Response –50% - +100% of internal standards from continuing calibration of the day. 2. RT must be ± 30 sec. From associated calibration verification standard of that sequence.	1. Reanalyze. 2. If still outside of the limits, report both analyses, and contact the QAO*. 3. Document corrective action in the case narrative. Special Circumstances: If matrix interferences is present (as demonstrated by the lab and documented in the case narrative): 1. Reanalyze (may be at a higher dilution) 2. If internal standard is >10%, report both runs. 3. In internal standard is <10%, report both runs and contact QAO*.
Surrogate Spike	All samples and blanks (including MS/MSD)	Recovery within laboratory control limits.	1. Reanalyze any environmental or QC sample with surrogates that exceed control limits. 2. If still outside of the limits, report both analyses and contact the QAO*. 4. Document corrective action in the case narrative. Special Circumstances: If matrix interferences is present (as demonstrated by the lab and documented in the case narrative): 1. Reanalyze (may be at a higher dilution) 2. If surrogate standard is >10%, report both runs. 3. In surrogate standard is <10%, report both runs and contact QAO*.
Matrix Spike/Matrix Spike Dup. (MS/MSD) Analysis	1 per group of similar concentration and matrix, 1 per case of samples, or 1 in 20, whichever is greater.	Recovery and RPD within laboratory control limits. Spike must contain target analysis.	1. Reanalyze if <10%. 2. If reanalysis is still <10%, report both analyses and document in the case narrative. 3. If >10% and LCS criteria are met, document in case narrative; no additional corrective action required. 4. If LCS criteria are exceeded also, examine other QC data for source of problem; *i.e.*, surrogate recoveries for extraction efficiency and calibration data for instrument performance issues, and contact QAO*. Re-extract or reanalyze samples and associated MS/MSD and LCSs as required.
Field Dup. Analysis	Collected 1 per matrix; every 10 samples of similar matrix	50% RPD for waters and 100% RPD for soil	If these criteria are not met, sample results will be evaluated on a case by case basis.

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Audit	Frequency	Control Limits	Corrective Action
Percent solids	For soil samples, the percent solids will be determined and sample results will be corrective for percent solids.	Not applicable	Not applicable
Continuing Calibration	Every 12 hours. Calibration verification will contain target analytes at a concentration that is representative of the midpoint of the initial calibration.	1. Within method specified criteria, percent drift or percent difference (%D) $\leq$ 20 for CCC and $\leq$ 50 for remaining compounds. SPCC RF as listed in method; non SPCC RF $\geq$ 0.050 except for Ketones and 2-CEVE with RF of $\geq$ 0.010. 2. The internal standards areas and retention times must meet the method criteria.	1. Re-analyze 2. If criteria are still not met, identify and correct problems, recalibrate and notify QAO. 3. Document corrective action in the case narrative- samples cannot be analyzed until calibration control limit criteria are met. If the laboratory chooses to apply the grand mean exception (average % drift or % difference is less than 15 %) the QAO will be contacted prior to proceeding with analysis.

Notes:

* Indicates that data validation will be performed in accordance with QA/QC criteria established in these tables and the analytical methods. Excursions from QA/QC criteria will be qualified based on guidance provided in Section 9.2.2 of this QAPP.

QAO* indicates that communications with the QAO will be documented and included in the data packages.

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EPA RESPONSE

ATTACHMENT B

SEMI-VOLATILE COMPOUNDS BY GC/MS (8270C)

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Approved by: R. Wayne Robbins 3 April 2001
Date

Title: Technical Manager, QA

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1.0 SCOPE AND APPLICATION

1.1 This method can be used to determine the concentration of various semi-volatile organic compounds (SVOC) in groundwater, TCLP and SPLP leachates, soils, sediments, waste, and solid sample extracts. The attached quantitation report (Appendix B) lists the routine target compounds, the retention times of the target compounds, the characteristic ions of the target compounds, and the internal standard association of each target compound.

1.2 The reporting limit (RL), the method detection limit (MDL), and the accuracy and precision limits for the target compounds are given in Section 5 of the current revision of the STL Savannah Laboratories' *Laboratory Quality Plan.*

2.0 SUMMARY OF METHOD

2.1 A measured volume or weight of sample is extracted using an appropriate extraction procedure. The extract is dried, concentrated to a volume of 1.0mL, and analyzed by GC/MS. Qualitative identification of the target compounds in the extract is based on the retention time and the mass spectra determined from standards analyzed on the same GC/MS under the same conditions. Quantitative analysis is performed using the internal standard technique with a single characteristic ion.

2.2 This procedure is based on the guidance provided in SW-846 Method 8270C.

3.0 SAFETY

3.1 Use good common sense when working in the lab. Do not perform any procedures that you do not understand or that will put you or others in potentially dangerous situations.

3.2 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined. Each chemical compound should be treated as a potential health hazard. Exposure to these chemicals must be reduced to the lowest level possible. Lab coats, gloves, and lab glasses or face shield should be worn while handling extracts and standards. Standard preparation, addition of the internal standard solution, and sample extract dilution should be performed in a hood or well ventilated area.

3.3 Material Safety Data Sheets (MSDS) are available to the analyst at each lab division. These sheets specify the type of hazard that each chemical poses and the procedures that are used to handle these materials safely.

3.4 The exit vent of the splitless injector must have a carbon trap in-line to collect the semivolatile compounds that are vented during the injection of the extract. The traps should be changed every three months and disposed of in accordance with SOP CA70: *Waste Management.*

4.0 INTERFERENCES

4.1 Method interferences may be caused by contaminants in solvents, reagents, or glassware. Glassware and/or extraction vessels that have not been properly cleaned may contribute artifacts that make identification and quantification of the target compounds difficult. Elevated baselines may be due to oils, greases, or other hydrocarbons that may be extracted from improperly cleaned glassware or extraction vessels.

4.2 Matrix interferences may be caused by contaminants that are extracted from the sample matrix. The sample may require cleanup or dilution prior to analysis to reduce or eliminate the interferences. Sample extracts that contain high concentrations of non-volatile material such as lipids and high molecular weight resins and polymers may require the optional GPC cleanup prior to analysis. The GPC cleanup is generally not effective in removing non-target material that is associated with common petroleum products such as diesel or waste oil.

4.3 Secondary ions may be used for quantification if there is interference with the primary quantitation ion. If a secondary ion is used for quantification, the concentration/response relationship of the secondary ion must be established. The secondary ion must meet the same calibration criteria as the primary ion.

5.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

MATRIX	Preservative/ Storage	Routine Container	Sample Hold Time	Extract Hold Time
Aqueous	none; 4C	1-L amber	7 days	40 days
Soil/ Sediment	none; 4C	500-mL	14 days	40 days
Waste	none; 4C	Glass	14 days	40 days
TCLP	none; 4C	1-L amber	7 days from TCLP leaching procedure	40 days

Refrigerator temperature acceptance criterion is less than 6C with no frozen samples.

6.0 APPARATUS AND MATERIALS

6.1 Gas chromatograph- Hewlett-Packard (HP) 5890 or equivalent with compatible autosampler, splitless injector, and direct capillary interface. The exit vent of the splitless injector must have a carbon trip in-line to collect the semivolatile compounds that are vented during the injection of extracts. The carbon traps should be changed every three months.

6.2 Mass spectrometer- HP5971, HP5972, HP5973 or equivalent

6.3 Recommended Capillary column-HP-5MS, 30m x 0.25mm ID x 0.25um film thickness or equivalent column.

6.4 Data system- compatible with GC/MS system

6.5 Microsyringes- appropriate volumes

6.6 Volumetric flasks, Class A-appropriate volumes

6.7 Autosampler vials and crimper, compatible with autosampler

7.0 REAGENTS

Reagents must be tracked in accordance with SOP AN44: *Reagent Traceability.*

7.1 Methylene chloride-pesticide residue grade, for preparation of standards

7.2 Acetone-pesticide residue grade, for preparation of standards

8.0 STANDARDS

The preparation of the calibration standards must be tracked in accordance with SOP AN41: *Standard Material Traceability*. General guidance on the preparation of standards is given in SOP AN43: *Standard Preparation.*

The lab should purchase certified solutions from STL approved vendors, if available. The lab should prepare standards from neat materials only if a certified solution is not available. See SOP AN43 for guidance for standard preparation from neat materials.

8.1 Preparation of the Stocks from Neat Standards

The steps for the preparation of primary stock standards from neat materials are given in SOP *AN43: Standard Preparation.* The standards should be prepared in methylene chloride but may require other solvents to dissolve the material.

8.2 Preparation the calibration standards from the stock standards

A minimum of five calibration standards are prepared. The concentrations of the stock standards are in the 1000-10000ug/mL range. The recommended standards are listed in Section 10.2. The lowest level standard should be at the equivalent of the reporting limit and the rest of the standards should define the working range of the detector. Note that six calibration levels are required for a second order regression curve and seven calibration points are required for a polynomial regression curve (see SW-846 Method 8000B). Internal standards should be added to each standard to give a final concentration of 40 ug/mL.

Each lab should develop controlled recipes that can be posted or maintained in appropriate logbooks.

9.0 SAMPLE PREPARATION

9.1 The sample extraction procedures are given in the following SOPs:

Matrix	SOP	Extraction Technique
Aqueous, TCLP leachates	EX30	Continuous Liquid-liquid Extraction
Aqueous, TCLP leachates	EX35	Separatory Funnel
Soils/Sediments	EX40	Sonication
Wastes	EX42	Waste dilution

9.2 The sample concentration procedures are given in SOP EX 50: Zymark Nitrogen Concentration.

9.3 Gel permeation chromatography (GPC- SOP EX61) may help to eliminate or minimize matrix interferences in a limited number of samples. The GPC cleanup is generally not effective on samples containing petroleum products.

10.0 PROCEDURE

10.1 Instrument Conditions

Instrument conditions may vary according to the sensitivity of each instrument. The following conditions are provided for guidance. The lab must optimize and document the conditions used for the analysis of SVOC by GC/MS.

Recommended Column:

HP-5MS 30m x 0.25mm ID x 0.25um film thickness or equivalent

Column flow: Approximately 1mL/min helium

GC Oven temperatures:

Initial column temperature: 45 C for 3 minutes
Column temperature program: 10C per minute
Final column temperature: 300C (until at least one minute past the elution time of Benzo (g,h,i) perylene).

GC injector parameters

Injector temperature: 250-270EC
Injection type: split, approximately 1:10 or splitless injection
Injector liner: 4mm ID quartz or 4mm glass, deactivated (single "Gooseneck")
Sample injection volume: 1-2uL

Mass Spectrometer and interface parameters

Mass spectrometer interface: 300C
Mass spectrometer source temperature: Factory Set
Mass range: 35-500amu, with a scan time of 1.0 scans per second or greater

10.2 Calibration

A minimum of five calibration standards are prepared and analyzed. The recommended TCL standards are 10, 50, 80, 100, 200, and 350ug/mL. The recommended Appendix IX concentrations are 10, 20, 50, 80, 100, 120, and 160ug/mL. The lowest level standard should be at or below the equivalent of the reporting limit and the rest of the standards should define the working range of the detector. Note that six calibration levels are required for a second order regression curve and seven calibration points are required for a polynomial regression curve (see SW-846 Method 8000B).

10.2.1 Fifty nanograms of DFTPP must be analyzed at the beginning of each 12-hour clock as a check on the "tune" of the mass spectrometer. Meeting the tuning criteria demonstrates that the instrument is measuring the proper masses in the proper ratios. The DFTPP analysis takes place under the same instrument conditions as the calibration standards and samples except that a different temperature program can be used to allow for the timely elution of DFTPP. All other instrument conditions must be identical-the mass range, scan rate, and multiplier voltage.

10.2.1.1 Prepare a 50 ng/uL solution of tune/ column evaluation standard containing each of the following compounds at 50 ug/mL in methylene chloride: DFTPP, pentachlorophenol, p,p'-DDT, and benzidine.

10.2.1.2 Analyze a 1uL aliquot of the tune/column evaluation solution.

10.2.1.3 Evaluate the DFTPP peak.

-The chromatogram should exhibit acceptable baseline behavior and the DFTPP peak should be symmetrical.

-The spectrum of the DFTPP must meet the criteria listed in the SOP Summary (Appendix A). Background subtraction must be straightforward and designed only to eliminate column bleed or instrumental background. Scans +/- 2 scans from the apex can be evaluated for the DFTPP criteria. Consecutive scans within this range may be averaged to meet the criteria.

NOTE: The DFTPP analysis should be evaluated as to the relative size of the DFTPP peak under the m/z 198 profile. A benchmark area window should be established for each instrument and data system. Area outside of this window suggests instrumental problems such as a bad injection, clogged autosampler syringe, leaking injector, reduced or elevated detector sensitivity, improper electron multiplier voltage selection, wrong tune method or tune file selected for this analysis, PFTBA valve left open, etc.

If the DFTPP fails to meet the criteria, the instrument may require tuning (manually or automatically with PFTBA). Depending on the nature of the results from the DFTPP analysis, other corrective measures may include remaking the DFTPP standard, cleaning the mass spectrometer source, etc.

10.2.1.4 Benzidine and pentachlorophenol should be present at their normal responses with no peak tailing visible. This is a good check on the system: if pentachlorophenol (a CCC) does not respond well, the calibration standard should not be analyzed. Perform injector port and column maintenance and reanalyze the tune/column evaluation standard.

The percent breakdown of p,p'- DDT is calculated using the following equation. The percent breakdown should not exceed 20%.

$$\%Breakdown = \frac{(areaDDE + areaDDD)}{(areaDDT + areaDDE + areaDDD)} x\ 100$$

Areas from the total ion chromatogram are used to calculate DDT breakdown.

10.2.2 After the DFTPP criteria and column evaluation criteria have been met, the initial calibration standards are analyzed

10.2.2.1 Prepare the initial calibration standards. The lowest calibration standard should be at the RL and the rest of the standards will define the working range. See section 10.2 for guidance regarding calibration levels.

10.2.2.2 Set up a sequence and analyze the calibration standards. The injection volume must be the same for the calibration standards and all sample extracts.

10.2.3 Identify the internal standards, surrogates, and the target compounds. The data system must be updated with the proper retention times and ion data.

10.2.4 Calculate the relative response factor for each compound as follows:

$$RRF = \frac{(Ax)(Cis)}{(Ais)(Cx)}$$

where

Ax = area of the characteristic ion for the compound being measured
Ais = area of the characteristic ion for the internal standard associated with the compound being measured
(See the attached quantitation report for a list of the compounds that are associated with the correct internal standard)
Cx = concentration of the compound being measured (ug/mL)
Cis = concentration of the internal standard (40ug/mL)

Secondary ions may be used for quantification if there is interference with the primary quantitation ion. If a secondary ion is used for quantification, the concentration/response relationship of the secondary ion must be established. The secondary ion must meet the same calibration criteria as the primary ion.

10.2.5 Calculate the average relative response factor (RRF_{avg}) for each target compound and each surrogate compound:

$$RRF_{avg} = \frac{RRF1 + RRF2 + RRF3.... + RRFn}{n}$$

RRF1 = relative response factor of the first standard
RRFn = relative response factor of the last standard
n = number of calibration standards

NOTE: As noted previously, some target compounds may have fewer than five calibration standard levels.

10.2.6 Calculate the standard deviation (SD) for the initial calibration standards:

$$SD = \sqrt{\frac{\sum_{i-1}^{n_1} (RRF_i - RRF_{avg})^2}{n-1}}$$

10.2.7 Calculate the relative standard deviation (%RSD) of the target compounds in the calibration standards.

$$\%RSD = \frac{SD}{RRF_{avg}} x\ 100$$

10.2.8 Evaluation of the Initial Calibration

The initial calibration is evaluated specifically for the calibration check compounds (CCC) and the system performance check compounds (SPCC). The CCC and SPCC criteria are given in the SOP Summary (Appendix A). The %RSD criteria for CCC and minimum RRF for SPCC must be met before the analysis of sample extracts can begin.

If the CCC and SPCC criteria are not met, action must be taken to bring the analytical system into compliance with the criteria. This action may include injection port maintenance, source cleaning, changing the column, or replacement of injection port lines and assembly. In any case, if the criteria are not met, the initial calibration must be repeated. The analyst must be aware of the 12-hour clock for the DFTPP analysis. The DFTPP criteria must be met prior to the analysis of the calibration standards.

10.2.8 After the initial calibration criteria (CCC/SPCC) have been met, each target is evaluated for linearity.

If the %RSD of the target compound is less than or equal to 15%, the average response factor can be used for quantitation of samples.

If the %RSD of the target compound is greater than 15%, a regression curve (linear, quadratic, etc) must be used for the quantitation of samples. A regression curve may also be used for the compounds that have %RSD less than 15%. The results can be used to plot a calibration curve of response ratios-Ax/Ais is plotted on the y-axis; Cx/Cis is plotted on the x-axis where

Ax = area of the characteristic ion for the compound being measured
Ais = area of the characteristic ion for the internal standard associated with the compound being measured (See attached quantitation report for a list of the compounds that are associated with the correct internal standard)
Cx = concentration of the target compound being measured (ug/mL)
Cis = concentration of the internal standard (ug/mL)

A linear, quadratic, or higher order regression fit may be used to define the concentration/response relationship. If the correlation coefficient of the regression curve is greater than 0.99, the curve can be used to quantify samples. Regression curves may be forced through zero but it is recommended that the curve be evaluated without forcing through zero first and then with the curve forced through the origin. The analyst must ensure that the type of regression curve selected accurately defines the concentration/response relationship over the entire concentration range.

NOTE: Linear regression curves must be used for South Carolina DHEC compliance samples. See pre-project plans and client QAPPs for other exceptions to using non-linear curve fitting.

When more calibration levels are analyzed than required, individual compounds may be eliminated from the lowest or highest calibration levels(s) only. If points or levels are eliminated, analyte concentration in samples must fall within the range defined by the resulting curve. In no case should individual points in the middle of the calibration curve be eliminated without eliminating the entire level.

8000B exception: evaluation of the "grand mean": If the average %RSD of ALL (all targets including CCC and SPCC) compounds in the initial calibration is less than 15%, the average response factor can be used for quantitation of all target compounds. The recommended course is to use regression curves, as described above, to quantify targets where the %RSD criterion (<=15%) is exceeded.

NOTE: If a target compound that passes by the "grand mean exception" is detected (>RL), the PM is notified via an anomaly report or case narrative. If the targets are <RL, no notification is required.

10.3 Continuing Calibration Verification

At the beginning of each 12-hour clock, the tune of the instrument must be checked by the analysis of the tune/column evaluation solution (10.2.1.1). The tune and column evaluation criteria (10.2.1.3 and 10.2.1.4) must be met before the analysis of the calibration check standards can take place.

10.3.1 After the tune and column evaluation criteria have been met, a continuing calibration check standard(s) is analyzed. The continuing calibration standard should be at a mid level concentration. The CCC and SPCC criteria (SOP Summary, Appendix A) must be met before the analysis of samples can take place. The percent difference (%D) is calculated as follows:

$$\%D = \frac{RRFavg - RRFccv}{RRFavg} \otimes 100$$

where
RRFavg = average response factor from initial calibration
RRFccv = response factor from the check (12-hour) standard-calibration verification

The percent drift (%Drift) may also be used to evaluate the change/deviation of the curve:

$$\%Drift = \frac{Ci - Cccv}{Ci} \otimes 100$$

where
Ci = Calibration Check Compound standard concentration (ug/mL)
Cccv = measured concentration using the selected quantitation method (ug/mL)

NOTE: The SPCC criteria (10.3.8) must be met even if the regression curve option is used for quantitation. If these criteria are not met, corrective action must be taken. The corrective action may include reanalysis of the calibration check standard or preparation of a new secondary stock standard and reanalysis of the calibration check standard. If subsequent analysis of the standard is still out of criteria, a new initial calibration curve must be analyzed and evaluated.

10.3.2 The continuing calibration verification standard (CCV) must also be evaluated for internal standard retention time and response.

If the retention time of any internal standard changes by more than 30 seconds from the last 12-hour calibration check, the analytical system must be inspected for problems and corrective action instituted.

If the extracted ion current profile (EICP) area for any of the internal standards in the CCV changes by more than a factor of two (-50% to +100%) from the last initial calibration sequence, the analytical system must be inspected for problems and corrective action instituted.

10.4 Samples are analyzed only after the DFTPP criteria, column evaluation criteria and the calibration verification criteria have been met. The analytical system must be evaluated every 12 hours by the analysis and evaluation of the tune/column evaluation standard and a mid-level calibration standard.

ANALYSIS SEQUENCE

INITIAL CALIBRATION	CONTINUING CALIBRATION
Tune/Column Evaluation Standard Clock starts at injection	Tune/Column Evaluation Standard Clock starts at injection
Calibration standards- Minimum of five cal levels	Mid point calibration verification Optional RL: Standard-low point on cal curve
Samples analyzed until the 12-hour clock expires	Samples analyzed until 12-hour clock expires

10.4.1 Remove the sample extracts to be analyzed from the refrigerator and allow the sample to come to ambient temperature.

10.4.2 Add 20-uL of the internal standard mix (2000 ug/mL) to each 1.0 mL aliquot of the sample extract. The concentration of the internal standard in the extract is 40 ug/mL.

10.4.3 Mix the contents of the autosampler vial by inverting several times.

10.4.4 Analyze the samples using the same analytical conditions used for the initial and continuing calibration standard. Determine the concentration of the samples and QC items using the procedures of Section 11. If the concentration of a sample is above the highest calibration standard, the sample must be diluted and reanalyzed.

NOTE: Unless otherwise specified by a client QAPP, results from a single analysis are reported as long as the largest target analyte (when multiple analytes are present) is in the upper half if the calibration range. When reporting results from dilutions, appropriate data flags should be used or qualification in a case narrative provided to the client. For TCLP analyses, every reasonable effort should be made to achieve the regulatory level with out instrument overload.

For clients who require we provide lower detection limits, a general guide would be to report the dilution detailed above and one additional run at a dilution factor 1/10 of the dilution with t the highest target in the upper half of the calibration curve. For example, if samples analyzed at a 1/50 dilution resulted in a target in the upper half of the calibration curve, the sample would be analyzed at a dilution factor of 1/5 to provide lower RLs.

10.4.5 The dilution factor is calculated by dividing the volume of sample extract in microliters into 1000. For example, if 100uL of a sample extract are diluted to final volume of 1.0mL, the dilution factor is 10. (1000/100 = 10). The following table gives some dilution factors:

Dilution Preparation

uL extract-Vext	uL MeCl2	volume of dilution (Vdil-uL)	uL ISTD (2000ug/mL)-Vistd	DF
1000	0	1000	20	1
500	500	1000	10*	2
200	800	1000	16*	5
100	900	1000	18*	10
50	950	1000	19*	20
20	980	1000	20*	50

*assumes dilution of a 1.0mL extract or 1mL aliquot of an extract that has been spiked with the internal standard at 40ug/mL using 20ul of a 2000ug/mL internal standard solution

The concentration of internal standards must remain constant for all extracts and extract dilutions at 40ug/mL. The following equation can be used to determine the volume of the 2000ug/mL internal standard solution to add to an extract when a dilution is prepared from an extract that has already been spiked with the internal standard solution:

$$Vistd(uL) = 20uL - \left(\frac{Vext}{Vdil} \otimes 20ul\right)$$

Vistd = volume of 2000ug/mL internal standard to add to the diluted extract (uL)
Vext = volume of extract used to prepare the dilution (uL)
Vdil = final volume of the dilution (uL)-1000uL (1.0mL)

11.0 DATA ANALYSIS/CALCULATIONS

11.1 Qualitative Analysis

11.1.1 Target Compounds

A target compound is identified by the visual comparison of the sample mass spectrum with the mass spectrum of the target compound from the daily calibration standard or a reference spectrum of the target compound stored in a library generated on the same instrument or a standard spectral library such as the NIST/NBS.

11.1.1.1 Two criteria must be met in order to positively identify a compound.

1) elution of the sample component within +/-0.06 RRT (relative retention time) units of the daily standard containing that compound.

$$RRT = \frac{\textit{retention time of the target compound}}{\textit{retention time of the associated internal standard}}$$

2) correspondence of the target compound spectrum and the standard component mass spectrum

11.1.1.2 All ions present in the standard component mass spectrum at a relative intensity greater than 10% (most abundant ion = 100%) should be present in the sample component mass spectrum. Other ions may be present in the sample component. Coelution of a non-target compound with a target compound will make the identification of the target compound more difficult. Ions due to the non-target compound should be subtracted from the sample component spectrum as part of the background to account for the discrepancy between the sample spectrum and the standard spectrum.

11.1.1.3 The relative intensities of the ions present in the sample component spectrum should agree within +/- 30% of the relative intensities of the ions in the standard reference spectrum. For example, an ion with an abundance of 50% in the reference spectrum should have a corresponding abundance between 20% and 80% in the sample component spectrum.

11.1.1.4 If the above criteria are not met exactly, the analyst should seek help from a senior analyst or supervisor. If there is sufficient evidence to support the identification of the component, then the component is identified, quantified, and reported.

11.1.2 Tentatively Identified Compounds

For samples containing components not associated with the calibration standards, a library search on a reference library, such as the NIST/NBS, may be conducted in order to identify the non-target compounds. Only after visual comparison between the sample spectra and the library-generated reference spectra will the mass spectral analyst assign tentative identification..

11.1.2.1 Relative intensities of the major ions (masses) in the reference spectra (ions >10% of the most abundant ion) should be present in the sample spectrum.

11.1.2.2 The relative intensities of the major ions should agree within +/-30%.

11.1.2.3 Molecular ions present in the spectrum should be present in the sample spectrum.

11.1.2.4 Ions present in the sample spectrum, but not in the reference spectrum, should be reviewed for possible subtraction from the sample spectrum because of over-lapping or co-eluting peaks.

11.1.2.5 Ions present in the reference spectrum, but not in the sample spectrum, should be reviewed for possible subtraction from the sample spectrum because of coeluting peaks.

11.1.2.6 If, in the opinion of the analyst, there is enough evidence to support the tentative identification of a compound even though the above criteria is not met exactly, the peak may be considered tentatively identified. The analyst should consult senior analysts or the mass spectral interpretation specialist if there are any questions concerning an interpretation of spectra.

11.1.2.7 The estimated concentration of the tentatively identified compound (TIC) is calculated using the total ion area of the tentatively identified peak and total ion area of the nearest internal standard that has no interferences. The calculations assume that the same volume is injected for standards and samples.

Aqueous

$$TIC(ug/L) = \frac{Cis}{AREAis} \otimes AREAtic \otimes \frac{F}{V} \otimes DF$$

where

Cis =	concentration of the internal standard (ug/mL)
AREAis =	total ion peak area of the internal standard
AREAtic=	total ion peak area of the TIC
F =	final volume of extract (mL)
V =	volume of sample extract (L)
DF =	dilution factor

Soils

$$TIC\ (ug/kg, dw) = \frac{Cis}{AREAis} \otimes AREAtic \otimes \frac{F}{(W)(solids)} \otimes DF$$

where

Cis =	concentration of the internal standard, ug/mL
AREAis =	total ion peak area of the internal standard
AREAtic=	total ion peak area of the TIC
F =	final volume of extract mL
W =	weight of sample analyzed (kg)
solids =	decimal equivalent of percent solids

11.2 Calculations for Samples-Internal Standard Technique
These calculations assume that the same volume is injected for standards and samples and that the standards and samples have the same concentration of internal standard.

11.2.1 Aqueous Samples

11.2.1.1 If the relative response factor is used, the calculation for samples is :

$$concentration(ug/L) = \frac{Ax}{Ais} \otimes \frac{Cis}{RRFavg} \otimes \frac{F}{V} \otimes DF$$

where

Ax =	area of the characteristic ion of the compound being measured
Ais =	area of the characteristic ion of the internal standard
Cis =	concentration of the internal standard (ug/mL)
RRFavg =	average response factor of the compound being measured
F =	final volume of extract (mL)
V =	volume of sample extracted (L)
DF =	dilution factor

11.2.1.2 If a regression curve is used, the concentration is given:

$$concentration(ug/L) = Ccurve \otimes \frac{F}{V} \otimes DF$$

where

C_{curve} =	concentration from curve (ug/mL)
F =	final volume of extract (mL)
V =	volume of sample extracted (L)
DF =	dilution factor

11.2.1.3 The reporting limit (RL) for each sample is given:

$$RL(ug/L) = RLqap \otimes \frac{F}{Fqap} \otimes \frac{Vqap}{V} \otimes DF$$

where

F =	final volume of extract (mL)
Fqap =	1.0mL
Vqap =	1.0L
V =	volume of sample extracted
DF =	dilution factor. The SL CQAP Table 5 RL(RLqap) assumes a DF of 1.

NOTE: If V = 800mL to 1200mL, assume that Vqap/ V = 1 in the calculation of the reporting limit.

11.2.2 Soils

11.2.2.1 If the relative response factor is used, the calculation for samples is :

$$concentration(ug/kg,dw) = \frac{Ax}{Ais} \otimes \frac{Cis}{RRFavg} \otimes \frac{F}{(W)(solids)} \otimes DF$$

where

Ax =	area of the characteristic ion of the compound being measured
Ais =	area of the characteristic ion of the internal standard
Cis =	concentration of the internal standard (ug/mL)
RRFavg =	average response factor of the compound being measured
F =	final volume of extract (mL)
W =	weight of sample extracted (kg)
solids =	(percent solids)/100
DF =	dilution factor

11.2.2.2 If the regression curve is used, the concentration is given:

$$conc(ug/kg,dw) = Ccurve \otimes \frac{F}{(W)(solids)} \otimes DF$$

where

Ccurve =	concentration from curve(ug/mL)
W =	weight of sample extracted (kg)
F =	final volume of extract (mL)
solids =	(percent solids)/100)
DF =	dilution factor

11.2.2.3 The reporting limit (RL) for each sample is given:

$$RL = RLqap \otimes \frac{F}{Fqap} \otimes \frac{Wqap}{(W)(solids)} \otimes DF$$

where

F =	final volume of extract (mL)
W =	weight of sample extracted (kg)
solids =	(percent solids)/100

The SL CQAP assumes Wqap = 30g, solids = 1, Fqap = 1.0mL, and DF = 1.

12.0 QUALITY ASSURANCE /QUALITY CONTROL

12.1 The analytical batch consists of up to twenty client samples and the associated QC items that are analyzed together. The matrix spike and LCS frequency is defined in AN02: *Analytical Batching*. SOP AN02 also describes the procedure for evaluating batch-specific QC. The QA/QC criteria are summarized in the SOP Summary (Appendix A).

12.2 Initial Demonstration of Capability (IDOC) to Generate Acceptable Accuracy and Precision

Each analyst must participate in the analysis of samples by this procedure in accordance with SOP CA92: *Evaluation of IDOCs.*

12.3 Method Detection Limit

The method detection limit is determined in accordance with SOP CA90.

13.0 PREVENTIVE MAINTENANCE

Preventive maintenance items will be added at a later date. See Section 10 of the current Laboratory Quality Manual.

14.0 TROUBLE-SHOOTING

Trouble-shooting items will be added at a later time.

15.0 REFERENCES

15.1 *STL Savannah Laboratories' Laboratory Quality Manual* current revisions.

15.2 Method 8270C:*Test Methods for Evaluating Solid Wastes, Third Edition, SW-846;* U.S. EPA Office of Solid Waste and Emergency Response: Washington, DC.

APPENDIX A
8270C SOP SUMMARY

HOLD TIMES

MATRIX	Preservative/ Storage	Routine Container	Sample Hold Time	Extract Hold Time
Aqueous	none; 4C	1-L amber	7 days	40 days
Soil/ Sediment	none; 4C	500-mL	14 days	40 days
Waste	none; 4C	Glass	14 days	40 days
TCLP	none; 4C	1-L amber	7 days	40 days

ANALYSIS SEQUENCE

INITIAL CALIBRATION	CONTINUING CALIBRATION
Tune/Column Evaluation Standard Clock starts at injection	Tune/Column Evaluation Standard Clock starts at injection
Calibration standards- minimum of five cal levels	Mid point calibration verification standard RL Standard (lowest point on calibration curve if required by client or state-specific QAP)
Samples analyzed until the 12-hour clock expires	Samples analyzed until 12-hour clock expires

SEMIVOLATILE ORGANIC GC/MS TUNING AND MASS CALIBRATION (DFTPP)	
m/e	**Ion Abundance Criteria (1)**
51	30-80% of mass 442
68	Less than 2.0% of mass 69
69	Present
70	Less than 2.0% of mass 69
127	25-75% of mass 198
197	Less than 1% of mass 198
198	Base peak, 100% relative abundance
199	5.0-9.0% of mass 198
275	10-30% of mass 198
365	Greater than 0.75% of mass 198
441	Present but less than mass 443
442	40-110% of mass 198
443	15.0-24.0% of mass 442

(1) 8270 criteria taken from CLP OLMO4.0 (January 1998). The use of alternate criteria is expressly allowed in SW-846 Method 8270C.

APPENDIX A
8270C SOP SUMMARY

CALIBRATION ACCEPTANCE CRITERIA

Calibration Check Compounds - CCC
Phenol, 1,4-Dichlorobenzene, 2-Nitrophenol, 2,4-Dichlorophenol, Hexachlorobutadiene, 4-Chloro-3-methylphenol, 2,4,6-Trichlorophenol, Acenapthene, N-Nitrosodiphenylamine, Pentachlorophenol, Fluoranthene, Di-n-octylphthalate, Benzo(a) pyrene

System Performance Check Compounds-SPCC
N-Nitrosodi-n-propylamine, Hexachlorocyclopentadiene, 2,4-Dinitrophenol, 4-Nitrophenol

Initial Calibration	Continuing Calibration*
CCC: <= 30% RSD	CCC: <= 20% difference from initial calibration
SPCC: RRFavg >= 0.050	SPCC: RRF>= 0.050

*If CCC and/or SPCC do not meet the stated criteria, all targets that are reported must meet the CCC criteria.

NOTE: The CCC and SPCC criteria must be met even if the calibration curve option is used for quantitation. If the CCC and SPCC criteria do not pass, a new calibration curve must be prepared and analyzed.

The results for all target compounds are evaluated for linearity. If the %RSD is less than 15%, the calibration is assumed linear through the origin and the average response factor can be used for quantitation. If the average response factor for the target exceeds 15% (including any CCC), the analyst must use the calibration curve option.

NOTE: The lab has the option of using a regression curve for all analytes.

A linear, quadratic, or higher order regression fit may be used to define the concentration/response relationship. If the correlation coefficient of the linear regression curve or the coefficient of determination of a higher order fit is greater than 0.99, the curve can be used to quantify samples. The analyst must ensure that the type of regression curve selected accurately defines the concentration/response relationship over the entire calibration range. The minimum number of calibration standards required for a regression curve are given in the following table:

Type of curve	Minimum Number of Calibration Points
Linear (first order)	5
Quadratic (second order)	6
Polynomial(third)	7

QC Item	Frequency	Acceptance Criteria	Corrective Action
Tune/Column Evaluation Standard DFTPP 50ng Pentachlorophenol - 50ng Benzidine – 50ng p,p'-DDT 50ng	Prior to analysis of calibration standards every 12 hours	DFTPP - within criteria	-Evaluate alternative scans -Reanalyze and evaluate -Retune and reanalyze -Clean source, retune, reanalyze
		Pentachlorophenol and benzidine - present at usual response with no peak tailing visible p,p'-DDT - %breakdown <20%	-Reanalyze -Perform injector port maintenance and reanalyze -Cut more than usual length of column and reanalyze -Replace column
Initial Calibration	After Tune Check and when calibration verification standard fails acceptance criteria. All initial calibration standards	CCC: %RSD < 30% SPCC: RRFavg > 0.050 Use regression curve for quantitation if %RSD for any target compound exceeds 15%	-Reanalyze standard(s) -Prepare new standard(s) and reanalyze -Perform injector port maintenance and reanalyze standards -Retune and reanalyze standards -Replace column and reanalyze standards -Clean source and reanalyze standards
Continuing Calibration Verification	After tune check; every 12 hours prior to analysis of samples	CCC: %Difference <= 20% Or %Drift <= 20% SPCC: RRF >= 0.050	-Reanalyze standard -Prepare new standard and reanalyze -Recalibrate
Internal Standard Areas	Evaluate all standards and samples	Areas in continuing calibration verification must be 50% to +200% of previous initial calibration sequence Areas in samples should be evaluated for gross error . Consult supervisor Retention time of internal standard must be +/-30 seconds from internal standard in previous CCV.	-Evaluate chromatogram, spectra, and integrations -Reanalyze extract -Perform instrument maintenance and reanalyze extract -Re-extract and reanalyze if sufficient sample available -Recalibrate

QC Item	Frequency	Acceptance Criteria	Corrective Action
Surrogate recovery	Evaluate for all samples and QC items if extract is not diluted OR If diluted, where >RL	Within LQM Control Limits	-Evaluate chromatogram, spectra, and integrations -Reanalyze extract(s) -Re-extract and reanalyze if sufficient sample available
Method Blank	Per batch	All targets < RL in LQM	-Evaluate chromatogram, spectra, and integrations -Reanalyze extract -Follow guidance in SOP AN02
Lab Control Standard (LCS) - QAP subset	Per batch See STL SOP AN02	Within LQM Control Limits	-Evaluate chromatogram, spectra, and integrations -Reanalyze extract -Follow guidance in SOP AN02
Matrix spike (MS) Matrix spike duplicate (MSD)	Per batch if sufficient sample volume/weight supplied See AN02	Within LQM Control Limits	-Evaluate chromatogram, spectra, and integrations -Reanalyze extract -Follow guidance in SOP AN02
RL Standard (reporting limit)	Daily (optional)-lowest point on calibration curve if required by client or state-specific QAP	Detected at reasonable sensitivity	-Evaluate integrations and spectra; -Reanalyze -Prepare new standard and reanalyze
Initial Demonstration of Capability (IDOC)	Each work group	Accuracy and precision within method specified criteria	-Evaluate data -Reanalyze extracts if warranted -Re-extract and reanalyze for targets that fail criteria
Method Detection Limit (MDL)	Annually for each routine matrix See STL SL SOP CA90	Evaluate according to SOP CA90	Evaluate according to SOP CA90

APPENDIX B- EXAMPLE QUANTITATION REPORT

SEVERN TRENT SERVICES

CHANGE -IN-PROGRESS ATTACHMENT

SOP Document No: SM05:01.07.00:6

SOP Description: Semivolatile Compounds by GC/MS (8270C)

Approval Signature:

R. Wayne Robbins 6 Sept 2001

Date

Title: Technical Manager, QA

STL X Savannah __ Tallahassee __ Mobile __ Tampa West

The following revisions or additions have been made to the referenced SOP.

The following attachments are for a specific project and will be effective from the date of approval until the date that the project is completed. The purpose of this CIPA is to document changes or additions to the standard operating procedures requested for the Sauget Area 2 Sites Group and EPA Region V.

The attachments are tables of the project RLs and MDLs, including the QC limits, and an excerpt from the Sauget Area 2 Sites Group QAPP.

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Semivolatile Compounds by GC/MS (8270) Water

PARAMETER	METHOD	%REC	%RPD	MDL (ug/L)	RL (ug/L)
Acenaphthene (MS)	8270(3510/3520)	36-121	<=35	1.4	10
Acenaphthylene	8270(3510/3520)	41-121	<=28	1.4	10
Anthracene	8270(3510/3520)	45-126	<=21	0.60	10
Benzo(a)anthracene	8270(3510/3520)	33-136	<=34	0.79	10
Benzo(b)fluoranthene	8270(3510/3520)	33-132	<=32	0.97	10
Benzo(k)fluoranthene	8270(3510/3520)	33-150	<=34	0.63	10
Benzo(g,h,i)perylene	8270(3510/3520)	28-146	<=39	0.65	10
Benzo(a)pyrene	8270(3510/3520)	45-120	<=24	1.3	10
Bis(2-chloroethoxy) methane	8270(3510/3520)	47-110	<=20	1.2	10
Bis(2-chloroethyl) ether	8270(3510/3520)	34-114	<=58	1.0	10
2,2-Oxybis(1-chloropropane)	8270(3510/3520)	15-144	<=23	1.2	10
Bis(2-ethylhexyl) phthalate	8270(3510/3520)	34-160	<=26	0.84	10
4-Bromophenyl phenyl ether	8270(3510/3520)	36-124	<=26	0.94	**5.0**
Butyl benzyl phthalate	8270(3510/3520)	38-141	<=41	0.60	10
Carbazole	8270(3510/3520)	48-127	<=23	0.99	**5.0**
4-Chloroaniline	8270(3510/3520)	10-130	<=67	1.1	20
4-Chloro-3-methyl-phenol (MS)	8270(3510/3520)	34-126	<=31	0.89	10
2-Chloronaphthalene	8270(3510/3520)	45-107	<=22	1.4	10
2-Chlorophenol (MS)	8270(3510/3520)	38-115	<=34	1.4	10
4-Chlorophenylphenyl ether	8270(3510/3520)	22-140	<=26	1.4	10
Chrysene	8270(3510/3520)	44-128	<=31	0.54	10
Diallate	**8270(3510/3520)**	**10-150**	**<=50**	**0.76**	**10**
Dibenz(a,h)anthracene	8270(3510/3520)	33-143	<=35	0.56	10
Dibenzofuran	8270(3510/3520)	50-119	<=20	1.3	10
Di-n-butyl phthalate	8270(3510/3520)	43-145	<=29	0.92	10
1,2-Dichlorobenzene	8270(3510/3520)	34-130	<=30	1.1	10
1,3-Dichlorobenzene	8270(3510/3520)	28-130	<=26	1.4	10
1,4-Dichlorobenzene(MS)	8270(3510/3520)	27-130	<=31	1.2	10
3,3'-Dichlorobenzidine	8270(3510/3520)	10-144	<=72	1.7	20
2,4-Dichlorophenol	8270(3510/3520)	25-134	<=30	1.0	10
Diethyl phthalate	8270(3510/3520)	46-134	<=49	1.2	10
2,4-Dimethylphenol	8270(3510/3520)	28-130	<=43	1.0	10
Dimethylphthalate	8270(3510/3520)	22-141	<=31	0.97	10
4,6-Dinitro-2-methylphenol	8270(3510/3520)	10-173	<=33	1.6	**25**
2,4-Dinitrophenol	8270(3510/3520)	10-209	<=63	11	50
2,4-Dinitrotoluene (MS)	8270(3510/3520)	37-129	<=32	1.0	10
2,6-Dinitrotoluene	8270(3510/3520)	24-139	<=24	1.1	10
Di-n-octyl phthalate	8270(3510/3520)	24-152	<=33	0.66	10
Fluoranthene	8270(3510/3520)	41-129	<=24	1.1	10
Fluorene	8270(3510/3520)	50-124	<=23	1.6	**5.0**
Hexachlorobenzene	8270(3510/3520)	49-121	<=31	0.96	10
Hexachlorobutadiene	8270(3510/3520)	27-130	<=30	1.2	10
Hexachlorocyclopentadiene	8270(3510/3520)	D-130	<=67	5.4	10
Hexachloroethane	8270(3510/3520)	26-130	<=35	1.2	**5.0**
Indeno(1,2,3-cd)pyrene	8270(3510/3520)	37-140	<=38	0.62	10
Isophorone	8270(3510/3520)	29-130	<=33	1.1	10
2-Methylnaphthalene	8270(3510/3520)	43-130	<=30	1.2	10
2-Methyl phenol(o-cresol)	8270(3510/3520)	31-119	<=33	1.2	10
3 and 4-Methyl phenol	8270(3510/3520)	24-136	<=27	1.1	10
Naphthalene	8270(3510/3520)	41-130	<=33	1.4	10
2-Nitroaniline	8270(3510/3520)	26-130	<=49	0.85	50
3-Nitroaniline	8270(3510/3520)	10-130	<=57	0.84	50
4-Nitroaniline	8270(3510/3520)	10-140	<=39	0.89	50
Nitrobenzene	8270(3510/3520)	50-111	<=21	1.2	**5.0**
2-Nitrophenol	8270(3510/3520)	35-125	<=24	1.4	10
4-Nitrophenol (MS)	8270(3510/3520)	12-143	<=44	0.72	50
N-Nitrosodi-n-propylamine(MS)	8270(3510/3520)	31-138	<=30	1.0	10
Nitrosodiphenylamine	8270(3510/3520)	24-146	<=25	0.84	10

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Semivolatile Compounds by GC/MS (8270) Water

PARAMETER	METHOD	%REC	%RPD	MDL (ug/L)	RL (ug/L)
Pentachlorophenol (MS)	8270(3510/3520)	19-148	<=33	5.6	**25**
Phenanthrene	8270(3510/3520)	50-121	<=20	0.80	10
Phenol (MS)	8270(3510/3520)	33-122	<=36	1.0	10
Pyrene(MS)	8270(3510/3520)	31-139	<=42	0.88	10
1,2,4-Trichlorobenzene (MS)	8270(3510/3520)	28-110	<=28	1.3	10
2,4,5-Trichlorophenol	8270(3510/3520)	38-127	<=28	1.4	10
2,4,6-Trichlorophenol	8270(3510/3520)	36-126	<=22	1.0	**5.0**
Surrogates					
Nitrobenzene-d5	8270(3510/3520)	34-130	NA	NA	NA
2-Fluorobiphenyl	8270(3510/3520)	36-124	NA	NA	NA
Terphenyl-d14	8270(3510/3520)	14-148	NA	NA	NA
Phenol-d5	8270(3510/3520)	25-128	NA	NA	NA
2-Fluorophenol	8270(3510/3520)	29-121	NA	NA	NA
2,4,6-Tribromophenol	8270(3510/3520)	29-143	NA	NA	NA

Semivolatile Compounds by GC/MS (8270) Soils and Solids

PARAMETER	METHOD	%REC	%RPD	MDL(ug/kg)	RL(ug/kg)
Acenaphthene (MS)	8270(3550)	18-123	<=49	17	170
Acenaphthylene	8270(3550)	42-119	<=48	36	170
Anthracene	8270(3550)	40-148	<=27	42	170
Benzo(a)anthracene	8270(3550)	54-137	<=43	17	170
Benzo(b)fluoranthene	8270(3550)	43-134	<=51	22	170
Benzo(k)fluoranthene	8270(3550)	25-182	<=48	20	170
Benzo(g,h,i)perylene	8270(3550)	10-148	<=50	17	170
Benzo(a)pyrene	8270(3550)	41-142	<=55	18	170
Bis(2-chloroethoxy) methane	8270(3550)	34-108	<=52	19	170
Bis(2-chloroethyl) ether	8270(3550)	18-122	<=50	25	170
Bis(2-chloroisopropyl) ether	8270(3550)	10-135	<=28	25	170
Bis(2-ethylhexyl) phthalate	8270(3550)	47-143	<=22	19	170
4-Bromophenyl phenyl ether	8270(3550)	31-157	<=19	43	170
Butyl benzyl phthalate	8270(3550)	58-122	<=27	18	170
Carbazole	8270(3550)	10-158	<=50	36	170
4-Chloroaniline	8270(3550)	10-130	<=85	24	330
4-Chloro-3-methylphenol (MS)	8270(3550)	24-114	<=32	30	170
2-Chloronaphthalene	8270(3550)	39-107	<=47	22	170
2-Chlorophenol (MS)	8270(3550)	15-111	<=38	21	170
4-Chlorophenylphenyl ether	8270(3550)	36-149	<=62	17	170
Chrysene	8270(3550)	56-133	<=41	17	170
Diallate	**8270(3550)**	**10-150**	**<=60**	**33**	170
Dibenz(a,h)anthracene	8270(3550)	31-129	<=24	41	170
Dibenzofuran	8270(3550)	36-132	<=42	17	170
Di-n-butylphthalate	8270(3550)	42-161	<=59	28	170
1,2-Dichlorobenzene	8270(3550)	25-115	<=24	18	170
1,3-Dichlorobenzene	8270(3550)	26-108	<=28	17	170
1,4-Dichlorobenzene (MS)	8270(3550)	10-105	<=31	17	170
3,3'-Dichlorobenzidine	8270(3550)	10-115	<=39	36	170
2,4-Dichlorophenol	8270(3550)	32-130	<=60	22	170
Diethylphthalate	8270(3550)	31-130	<=40	22	170
2,4-Dimethylphenol	8270(3550)	33-84	<=54	22	170
Dimethylphthalate	8270(3550)	49-130	<=45	17	170
4,6-Dinitro-2-methylphenol	8270(3550)	10-117	<=57	150	850
2,4-Dinitrophenol	8270(3550)	10-125	<=84	160	850
2,4-Dinitrotoluene (MS)	8270(3550)	11-120	<=37	18	170
2,6-Dinitrotoluene	8270(3550)	10-112	<=45	40	170
Di-n-octylphthalate	8270(3550)	22-181	<=43	22	170
Fluoranthene	8270(3550)	39-157	<=50	25	170
Fluorene	8270(3550)	27-151	<=50	24	170

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Semivolatile Compounds by GC/MS (8270) Soils and Solids

PARAMETER	METHOD	%REC	%RPD	MDL(ug/kg)	RL(ug/kg)
Hexachlorobenzene	8270(3550)	19-155	<=33	21	170
Hexachlorobutadiene	8270(3550)	33-114	<=55	18	170
Hexachlorocyclopentadiene	8270(3550)	D-132	<=50	130	170
Hexachloroethane	8270(3550)	10-109	<=30	17	170
Indeno(1,2,3-cd)pyrene	8270(3550)	24-136	<=28	21	170
Isophorone	8270(3550)	15-115	<=50	17	170
2-Methylnaphthalene	8270(3550)	30-133	<=63	20	170
2-Methyl phenol (o-Cresol)	8270(3550)	33-108	<=53	25	170
3- and 4-Methyl phenol	8270(3550)	24-114	<=42	41	170
Naphthalene	8270(3550)	25-131	<=34	25	170
2-Nitroaniline	8270(3550)	17-130	<=48	20	850
3-Nitroanline	8270(3550)	14-130	<=28	30	850
4-Nitroaniline	8270(3550)	10-130	<=55	140	850
Nitrobenzene	8270(3550)	19-120	<=30	17	330
2-Nitrophenol	8270(3550)	30-130	<=50	32	170
4-Nitrophenol(MS)	8270(3550)	15-118	<=57	150	850
N-Nitrosodiphenylamine	8270(3550)	51-132	<=44	18	170
N-Nitrosos-di-N-propylamine (MS)	8270(3550)	11-122	<=37	27	170
Pentachlorophenol (MS)	8270(3550)	10-140	<=55	150	850
Phenanthrene	8270(3550)	39-152	<=30	17	170
Phenol (MS)	8270(3550)	13-115	<=39	22	170
Pyrene (MS)	8270(3550)	10-133	<=42	31	170
1,2,4-Trichlorobenzene (MS)	8270(3550)	10-112	<=22	17	170
2,4,5-Trichlorophenol	8270(3550)	25-130	<=36	23	170
2,4,6-Trichlorophenol	8270(3550)	41-130	<=30	20	170
Surrogates					
Nitrobenzene-d5	8270(3550)	20-120	NA	NA	NA
2-Fluorobiphenyl	8270(3550)	30-120	NA	NA	NA
p-Terphenyl-d14	8270(3550)	30-131	NA	NA	NA
Phenol-d5	8270(3550)	19-114	NA	NA	NA
2-Fluorophenol	8270(3550)	16-113	NA	NA	NA
2,4,6- Tribromophenol	8270(3550)	23-129	NA	NA	NA

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Table 7B. *Semivolatile organic compounds using USEPA Method 8270C Quality Control Requirements and Corrective Actions.**

Audit	Frequency	Control Limits	Corrective Action
Holding Times	Samples must be extracted and analyzed within holding time.	SVOCs: Extract within 7 days for aqueous and 14 days for soil samples from collection. Analyze extracts within 40 days of extraction.	If holding times are exceeded for initial or any re-analyses required due to QC excursions, notify the QAO* immediately since re-sampling may be required.
MS Tuning	Once every 12 hours prior to initial calibration and calibration verification.	1. DFTPP key ions and abundance criteria listed in the method must be met for all 13 ions and analyses must be performed within 12 hours of injection of the DFTPP. 2. Part of the DFTPP peak will not be background subtracted to meet tune criteria. 3. Documentation of all DFTPP analyses and evaluations must be included in the data packages.	1. Tune the mass spectrometer. 2. Document corrective action in the case narrative – samples cannot be analyzed until control limit criteria have been met.
Initial Calibration	Prior to sample analysis and when calibration verification criteria are not met. Initial calibration will contain all target analytes in each standard.	6. Five concentrations bracketing expected concentration range for all compounds of interest; one standard must be near the PQL. 7. CCC compounds meet method RSD, remaining compounds ≤50% RSD. 8. SPCC RF as listed in method, non-SPCC ≥0.050 RF. 9. For compounds with %RSD >15, quantification must be performed using a separate calibration curve and the COD must be ≥0.99.	1. Identify and correct problem. 2. If criteria are still not met, recalibrate. 3. Document corrective action in the case narrative – samples cannot be analyzed until calibration control limit criteria are met. Contact QAO* to discuss problem target analytes such as 2-chloroethyl vinyl ether before proceeding with analysis.
Calibration Verification	Every 12 hours, following DFTPP. Calibration verification will contain all target analytes in each standard at a concentration that is representative of the midpoint of the initial calibration.	1. Within method specified criteria, percent drift or percent difference (%D) ≤ 20 for CCC compounds and ≤ 50%D for remaining compounds, SPCC RF as listed in method, non-SPCC ≥ 0.050. 2. The internal standards areas and retention times must meet the method criteria.	1. Reanalyze. 2. If criteria are still not met, identify and correct problem, recalibrate and notify QAO*. 3. Document corrective action in the case narrative – samples cannot be analyzed until calibration control limit criteria are met. If the laboratory chooses to apply the grand mean exception (average % drift or % difference is less than 15%), the QAO* will be contacted prior to proceeding with analysis.

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Table 7B. *Semivolatile organic compounds using USEPA Method 8270C Quality Control Requirements and Corrective Actions.**

Audit	Frequency	Control Limits	Corrective Action
Surrogate Spike	All samples and blanks (including MS/MDS)	Recovery within laboratory control limits.	1. Reanalyze if more than 1 AE or 1 BS fails, or if any one surrogate %R is < 10%. 2. If recovery is still outside control limits and if the recovery is < 10%, re-extract if still in holding time. 3. If recovery is still outside control limits, and if recovery is >10%, report both analyses. 4. Document corrective action in the case narrative. Special Circumstances: If matrix interference is present (as demonstrated by the lab and documented in the case narrative): 1. Reanalyze (may be at a higher dilution). 2. If surrogate recovery is >10%, report both runs. 3. If surrogate recovery is <10%, report both runs and contact QAO*.
Matrix Spike/Matrix Spike Dup. (MS/MSD) Analysis	1 per group of similar concentration and matrix, 1 per case of samples, or 1 in 20, whichever is greater.	Recovery and RPD within laboratory control limits. Spike must contain target analysis.	1. Reanalyze if <10%. 2. If reanalysis is still <10%, report both analyses and document in the case narrative. 3. If >10% and LCS criteria are met, document in case narrative. 4. If LCS criteria are exceeded also, examine other QC data for source of problem; *i.e.*, surrogate recoveries for extraction efficiency and calibration data for instrument performance issues, and contact QAO* and re-extract or reanalyze samples and associated MS/MSD and LCSs as required.
Field Dup. Analysis Internal Standard	Collected 1 per matrix; every 10 samples of similar matrix All samples and blanks (including MS/MSD).	50% RPD for waters and 100% RPD for soil 1. Response –50% to + 100% of internal standards from continuing calibration of the day. 2. RT must be ± 30 sec. From associated calibration verification standard of that sequence.	If these criteria are not met, sample results will be evaluated on a case by case basis. 1. Re-analyze 2. If still outside of the limits, report both analyses and contact the QAO. 3. Document corrective action in the case narrative. Special Circumstances: If matrix interferences are present (as demonstrated by the lab and documented in the case narrative): Re-analyze (may be at a higher dilution) If internal standard in >10%, report both runs. If internal standard is <10%, report both runs and contact QAO.

Notes:

* Indicates that data validation will be performed in accordance with QA/QC criteria established in these tables and the analytical methods. Excursions from QA/QC criteria will be qualified based on guidance provided in Section 9.2.2 of this QAPP.

QAO* indicates that communications with the QAO will be documented and included in the data packages.

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EPA RESPONSE

ATTACHMENT C

CONTINUOUS LIQUID-LIQUID EXTRACTION

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Approved by: _____ 3 April 2001
Date

Title: Technical Manager, QA
STL __ Savannah __ Tallahassee __ Mobile __ Tampa West

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1.0 SCOPE AND APPLICATION

This SOP describes the general procedures for the extraction of semivolatile organic compounds (SVOC) from aqueous samples using continuous liquid-liquid extraction. This procedure is applicable to a wide range of aqueous matrices including monitoring wells, industrial wastewater, saline waters, and TCLP or EP leachates.

2.0 SUMMARY OF METHOD

2.1 A known volume of sample is adjusted to a specific pH if required, transferred to a continuous liquid-liquid extractor, and extracted using the solvent and conditions specified in Table 2. The extract is concentrated to an appropriate final volume using either the Zymark nitrogen blow-down concentrator (SL-SOP EX50) or the Kuderna Danish concentration procedure (SL-SOP EX51).

2.2 This SOP is based on the guidance in SW-846 Method 3520C and the extraction sections of the EPA 600-series methods.

3.0 SAFETY

3.1 Use good common sense when working in the lab. Do not perform any procedure that you do not understand or that will put you or others in potentially hazardous situations.

3.2 This SOP contains procedures that are designed to reduce the exposure of lab personnel to solvent vapors and to minimize the amount of solvent introduced into the lab air. All solvent transfer steps should be performed quickly and under a hood, if possible. Use the minimum amount of solvent to get the job done. Do not allow open containers of solvent or extracts to evaporate into the lab.

3.3 A lab coat or apron should be worn to protect clothing and skin from acids, bases, and solvents. Gloves must be worn to protect hands and eye protection (goggles or safety glasses) must be worn at all times in the lab. An analyst must not work alone in an isolated area.

3.4 A solvent such as methylene chloride can cause a burning sensation if it contacts the skin. The rapid evaporation of the solvent causes a rapid heat loss in the skin similar to frost bite. If solvent contracts the skin, wash the exposed skin in cold water to reduce the solvent evaporation.

3.5 The analyst should become familiar with the Material Safety Data Sheets (MSDS) for each reagent and standard used in the extraction lab.

4.0 INTERFERENCES

4.1 Improperly cleaned glassware can contribute interferences to the sample extract. Material that is left inside the extractor after cleaning may show up in the next extraction. The glassware must be properly cleaned according to SL SOP AN60. After cleaning, inspect the glassware for the presence of water, especially in the small tubing of the extractor. This water can block the solvent return tube and prevent efficient extraction of the sample. A thorough acetone rinsing will help to eliminate or minimize this problem.

4.2 Sample with large amounts of sediments or particulate may clog the solvent return line. A layer of glass wool, placed in the bottom of the extractor, may be helpful when sediments or particulate are present.

5.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

Aqueous samples are routinely collected in 1-L amber glass containers equipped with Teflon-lined caps. No preservative is required and an orange dot is affixed to the container to indicate this. The sample is stored at 4°C± 2°C in the lab. The sample must be extracted within seven (7) days of collection and the extract must be analyzed within forty (40) days of extraction.

6.0 APPARATUS AND MATERIALS

6.1 Continuous liquid-liquid extractor with compatible condenser, extractor body, and receiving flask.

6.2 Heating mantle and adjustable support. The heating mantle must be connected to a rheostat to control the temperature.

6.3 Rheostat or variable transformer

6.4 Teflon stoppers to fit the receiving flask

6.5 Filter paper-grade 414, 18.5cm diameter (VWR 28320-143)

6.6 Glass funnels

6.7 Pyrex glass wool - purified by Soxhlet extraction with methylene chloride.

6.8 Disposable volumetric pipettes - 1.0-mL and 10-mL

6.9 Boiling stones-Soxhlet extracted with methylene chloride

6.10 Wide range pH paper

7.0 REAGENTS

7.1 Reagent water - lab generated deionized water

7.2 Methylene chloride - residue grade or better

7.3 Acetone - residue grade or better

7.4 Sodium hydroxide (NaOH) - reagent grade

7.5 Sodium hydroxide solution (10N): Dissolve 400g of NaOH pellets into about 500mL of reagent water contained in a 2-L beaker on a magnetic stirrer. Add the NaOH in small portions, with constant stirring, to minimize the time it takes to dissolve the pellets. A good deal of heat will be generated as the NaOH dissolves. After all 400g has been added, carefully dilute to 1000mL with reagent water. Mix the solution thoroughly and transfer to a storage container. Do not store sodium hydroxide solution in volumetric glassware or in containers with ground glass joints.

7.6 Sulfuric acid (H_2SO_4) - concentrated reagent grade

7.7 Sulfuric acid solution (1:1 v/v): Slowly and carefully add 550mL of concentrated H_2SO_4 to 500mL of reagent water contained in a 2-L beaker on a magnetic stirrer. Add the acid in small portions

with constant stirring to reduce the heat evolved when the acid and water are combined. Cool and transfer the solution to a labeled storage container.

7.9 Sodium sulfate-anhydrous, granular, purified by heating for 4 hours at 400C in a shallow tray. Store in glass containers

8.0 STANDARDS

The preparation of the surrogate and matrix spiking solutions are described in SL SOP EX70: *Preparation of Semivolatile Surrogates and Matrix Spiking Solutions.* Table 1 is a summary of the spiking solutions used for the various analytical extraction methods. All preparation steps must be tracked in accordance with SL SOP AN41:*Standard Material Traceability.*

The tables included in SOP EX70 describe "recipes" that can be used to prepare the spiking solutions. The lab can prepare larger or smaller volumes if desired. The recipe used by the lab may be prepared as a "controlled posting" to prompt the analyst in the preparation of the spiking solutions. The controlled posting can be posted in the lab or placed in the extraction lab tracking log.

9.0 SAMPLE PREPARATION

The samples and QC items must be clearly and unambiguously labeled during each step of the extraction and analysis process. Labeling tape should be used to identify the glassware associated with each sample. Solvents will erase grease pens and "Sharpies". Use of different colored labeling tape will aid the analyst in keeping up with the extracts during each step of the extraction and concentration.

9.1 Sample Evaluation

9.1.1 Remove the samples to be extracted from the storage refrigerator. Allow the samples to equilibrate to room temperature while the appropriate glassware is gathered and prepared for the extraction. Fill out as much of the extraction log as possible prior to initiating the extraction.

9.1.2 Inspect the samples. Determine if the samples have multiple layers such as sediment or an oil layer. Consult with the supervisor or technical manager if the sample matrix is unusual or is difficult to categorize or handle.

9.1.3 Mark the level of the sample on the outside of the container. After the sample has been added to the extractor body, fill the empty container with water to the mark. Pour the water into a graduated cylinder and determine the volume. Record the volume in the extraction log to the nearest 5mL..

NOTE: If a reduced volume of sample must be extracted in order to provide sufficient sample volume to meet state or other program QC requirements, the sample is thoroughly mixed and an aliquot is measured with a graduated cylinder and poured into the extractor body. The following volumes are utilized for TCLP samples for BNA and pesticides:

TCLP PARAMETER	Volume of Sample Extracted(mL)	Final Volume (mL)
BNA by GC/MS (8270)	200	1.0
Pesticides by GC (8081)	20	10

9.2 Glassware Preparation

Process glassware and samples (Sections 9.2 through 9.4) in batches not greater than 20 field samples and QC in order to minimize the evaporation of methylene chloride into the lab.

9.2.1 Prepare the continuous liquid-liquid extraction apparatus by rinsing the extractor body, receiving

flask, and condenser with acetone. Pay particular attention to the solvent return line for the presence of water drops or solids.

9.2.2 Set the extractor body on the holder. Add methylene chloride (50-100ml) to the extractor body in order to fill the drain tube and ensure that a continuous flow of solvent from the extractor body to the receiving flask is maintained.

NOTE: Inspect the solvent layer when the sample is added. Large quantities of sediment may plug the tube and extraction will not occur. The newest extractor bodies have been re-designed to reduce the amount of solvent necessary to ensure a continuous flow of solvent. Use the amount of solvent-50mL or 100mL- necessary to allow the extractor to function properly.

9.2.3 In a fume hood, add 100mL to 175mL of methylene chloride to the receiving flask and add a few boiling stones to the flask. Add the same volume to each flask in the batch. Leave the receiving flask with the methylene chloride under the hood until ready to attach it to the extractor or cover tightly with aluminum foil.

9.3 Attach the receiving flask to the extractor body and secure the heating mantle around the flask.

9.4 As soon as possible after the methylene chloride is added to the extractor, gently pour the entire sample into the extractor body, trying not to let the sample leak into the sidearm. The extractor body will be approximately ½ to 2/3 full and the methylene chloride in the solvent return should be about 3/4 of the way to the receiving flask.

NOTE: The lab has the option of using an aliquot of sample if the final volume of the extract is adjusted to compensate for the reduced volume of sample. In some cases, the volume of sample must be reduced in order to have sufficient sample to extract matrix spikes as required by a state or other program quality assurance plan or regulation. In this case, the volume of surrogate and matrix spiking solution added to the sample should also be reduced proportionately .

9.5 Add 1.0L aliquots of reagent water to each of two separate extractors to serve as the method blank and lab control sample (LCS).

EXTRACTION BATCH: An extraction bath consists of up to twenty (20) field samples and the following QC items: method blank, LCS, MS, and MSD. If insufficient sample is available to perform the MS and MSD, the LCS is extracted in duplicate(LCSD) and the extraction log is stamped: INSUFFICIENT SAMPLE AVAILABLE TO PERFORM MS/MSD.

9.6 Addition of Surrogates and Matrix Spikes
The surrogate and matrix spiking solutions are set up so that 1.0ml of the solution will be added . Be sure to use the correct solutions for the extraction of concern. The addition of the surrogates and matrix spikes should be witnessed by another analyst to ensure that the proper volume of the spiking solution is added to each sample.

9.6.1 Add 1.0ml of the surrogate spiking solution to each sample and QC item.

NOTE: If the volume of sample extracted must be reduced to provide sufficient sample to meet state or other program requirements, the volume of surrogate spiking solution must be reduced proportionately.

9.6.2 Add 1.0ml of the matrix spiking solution to each LCS, MS, and MSD.

NOTE: If the volume of sample extracted must be reduced to provide sufficient sample to meet state or other program requirements, the volume of matrix spiking solution must be reduced proportionately.

9.6.3 Adjust the pH of the samples to the range specified in Table 2. The pH should be adjusted by adding small aliquots of 10N sulfuric acid or 10N sodium hydroxide directly to the sample extraction body. Stir the sample with a glass rod or Teflon rod. Check the pH after each addition with wide range paper. Do not dip the paper into the sample. Use a glass rod or pipette to remove a small aliquot of sample and touch the liquid to the pH paper.

NOTE: Sulfuric acid will cause the pH of the sample to decrease; sodium hydroxide will cause the pH of the sample to increase.

9.7 Slowly add reagent water to the extractor body until the level of the liquid causes the methylene chloride to just flow over to the receiving flask.

9.8 Place the condenser securely on the extractor body. Make sure that water is flowing through the condenser and turn the heating mantle on. Observe the extraction for the first hour or so to ensure that the solvent is being boiled, condensed, and returned to the receiving flask. Extract the samples for the time listed in Table 2. The batch is labeled with the start time and the scheduled stop time. I f a single pH extraction is performed, go to 9.11; if a two-pH extraction must be performed, continue at 9.9.

9.9 If a dual pH extraction is required, turn the heating mantle "off" to stop the extraction at the appropriate time and allow the extraction vessel to cool. Adjust the pH of the sample by adding small aliquots of 10N sulfuric acid or 10N sodium hydroxide. Stir the sample with a glass rod or pipette and check the pH after each addition . Do not dip the pH paper into the sample but use a glass rod or pipette to remove a small aliquot of the sample and touch the liquid to the pH paper.

NOTE: Sulfuric acid will cause the pH of the sample to decrease; sodium hydroxide will cause the pH of the sample to increase.

9.10 Turn the heating mantle "on" and extract the sample at the second pH for the time listed in Table 2. The batch is labeled with the start time and the scheduled stop time

9.11 After the samples have extracted for the required time, turn the heating mantle "off" and allow the extraction vessel to cool to room temperature. It is important to allow the receiving flask to cool before it is removed from the extractor.

9.12 Remove the receiving flask from the extractor body and cover it with a Teflon stopper. The extract is stored under near a hood until the filtration and concentration step is performed.

9.13 Working under a hood, place a piece of filter paper into a glass funnel and add a small amount of purified sodium sulfate. Filter the extract through the glass funnel and collect the extract directly into a labeled Zymark tube. Discard the filter paper and sodium sulfate into a waste container which is kept under the hood until removed from the laboratory. The extract is now ready for concentration using the Zymark instrument(SL SOP EX50) and should be kept under a hood tightly covered with aluminum foil until the concentration step. The extract may also be concentrated using the Kuderna-Danish extract evaporation(SL SOP EX51).

NOTE: Perform the extract filtration and drying steps in batches to minimize the loss of solvent into the lab. Cover the remaining containers tightly with aluminum foil and leave under or near a hood.

After the extracts have been dried and filtered, dispose of the filter paper and sodium sulfate by putting them in a chlorinated solvent waste container that is kept under the hood.

NOTE: If the volume of sample extracted has been reduced to provide sufficient sample to meet state or other program QC requirements, the final volume of the extract must be reduced

proportionately.

9.14 Rinse the ground-glass joint of the condenser with acetone and wrap in aluminum foil before placing the condenser in the rack. Collect the acetone rinsate in a separate container for disposal.

9.15 After the receiving flask has been removed from the extractor body, the methylene chloride remaining in the extractor body must be properly disposed. The extractor should be handled with minimum agitation to minimize the amount of solvent allowed to evaporate into the lab and stored in the chlorinated solvent waste container. Place the receiving flask side-arm over the chlorinated waste container. Add tap water to the extractor body to displace the methylene chloride into the waste container

The liquid remaining in the extractor body should be poured carefully down the sink and flushed continuously with water.

10.0 PROCEDURES

No items in this revision.

11.0 DATA ANALYSIS/CALCULATIONS

No items in this revision.

12.0 QUALITY CONTROL/QUALITY ASSURANCE

12.1 The analytical batch consists of up to twenty (20) client samples and the associated quality control items. The quality control items consist of a method (reagent) blank, a lab control standard (LCS), a matrix spike (MS), and a matrix spike duplicate (MSD). If insufficient sample is available for the MS/MSD, the LCS is prepared in duplicate.

SL SOP AN02: *Analytical Batching* contains guidance for evaluating the QC in an analytical batch.

12.2 The lab must perform a method detection limit (MDL) study annually in each matrix in accordance with SL SOP CA90: *Procedure for the Determination of Method Detection Limit (MDL).*

13.0 PREVENTIVE MAINTENANCE

No items in this revision.

14.0 TROUBLESHOOTING

No items in this revision.

15.0 REFERENCES

15.1 *Savannah Laboratories Comprehensive Quality Assurance Plan* and *Savannah Laboratories Corporate Quality Assurance Plan*, current revisions.

15.2 *Test Methods for Evaluating Solid Waste*, Third Edition, SW-846; vs. EPA Office of Solid Waste and Emergency Response: Washington, DC.

Table 1 -Surrogate and Matrix Spiking Solutions

METHODS	TYPES OF COMPOUNDS	SURROGATE SPIKING SOLUTION	MATRIX SPIKING SOLUTION
604	Phenols by GC-FID	SG ACID	604
8041	Phenols by GC-FID	SG ACID	8040
606,8061	Phthalate esters by GC-FID	SG BASE	606/8060
607,8070	Nitroaromatics by GC-FID	8141	target compounds
608	Chlorinated pesticides and PCBs	PEST	608
8081,8082	Chlorinated pesticides and PCBs	PEST	8080
8081,8082	PCBs	PEST	PCB
8081, 8082	Chlorinated pesticides-TCLP	PEST	TCLP-PEST
609,8090	Nitrosamines by GC-FID	SG BASE	target compounds
610	PAH by GC-FID	SG BASE	610
8100	PAH by GC-FID	SG BASE	8100
611,8110	Halogenated ethers by GC/EC	PEST	target compunds
612,8120	Chlorinated hydrocarbons	PEST	target compunds
614,614.1,622, 622.1	Phosphorous and nitrogen containing pesticides	8141	target compunds
8141	Phosphorous and nitrogen containing pesticides	8141	8141
617	Chlorinated pesticides	PEST	target compunds
619/620	Phosphorous and nitrogen containing pesticides	8141	target compunds
627	Chlorinated pesticides	PEST	target compunds
625	BNA	625/8270	625
8270-TCL	BNA	625/8270	8270
8270-K001	BNA	625/8270	K001(8270)
8270-TCLP, AP9	BNA	625/8270	TCLP-8270
8015-EXT	Petroleum products	SG BASE	Diesel-8015-mod Mineral spirits-8015-mod
613/8280	Chlorinated Dioxins & Furans	INT A and INT B	Octa and TH
625-OCPSF	BNA	62518270	625
FL-PRO	Petroleum products	FL-PRO	FL-PRO
8310	PAHs by LC	8310	8310

Table 2 -Extraction Conditions

METHODS	EXTRACTION CONDITIONS	EXTRACTION TIME(hr.)	SOLVENT	FINAL SOLVENT	FINAL VOLUME(mL)
604,8041	Single pH < 2	>12	MeCl2	MeCl2	1.0
606,8061	Single pH as received or at pH<2	>12	Mecl2	MeCl2	1.0
607,8070	Single pH as received or at pH<2	>12	MeCl2	MeCl2	1.0
608,8080,8081 ,8082	Single pH at neutral pH (5-9). pH range is critical for good recovery of some target compounds	>12	MeCl2	Hexane	10
609,8090	Single pH as received or at pH<2	>12	MeCl2	MeCl2	1.0
610,8100	Single pH as received or at pH<2	>12	MeCl2	MeCl2	1.0
611,8110	Single pH as received or at pH<2	>12	MeCl2	MeCl2	1.0
612,8120	Single pH as received or at pH<2	>12	MeCl2	Hexane	10
614,614.1,622, 622.1,8141	Single pH at neutral pH (5-9). pH range is critical for good recovery of some target compounds	>12	MeCl2	Hexane	10
617	Single pH at neutral pH (5-9). pH range is critical for good recovery of some target compounds	>12	MeCl2	Hexane	10
619	Single pH at neutral pH (5-9). pH range is critical for good recovery of some target compounds	>12	MeCl2	Hexane	5.0 or 10
627	Single pH at neutral pH (5-9). pH range is critical for good recovery of some target compounds	>12	MeCl2	Hexane	10
8270-TCL,K001	Single pH <2	>12	MeCl2	MeCl2	1.0
625, 8270-TCLP	Dual pH at pH<2 followed by pH>12	18/18	MeCl2	MeCl2	1.0
8270-AP9	Dual pH at pH<2 followed by pH>12	>12/>12	MeCl2	MeCl2	1.0
8015-EXT	Single pH as received or at pH<2	>12	MeCl2	MeCl2	1.0
6131/8280	Single pH at neutral pH (5-9)	>12	MeCl2	Dodecane	0.2
625-OCPSF	Dual pH at pH>12 followed by pH<2. Extracts are kept separate.	18/18	MeCl2	MeCl2	1.0 Acid 1.0 Base
FL-PRO	Received at pH<2. Adjust to pH<2 if not received at ph<2.	>12	MeCl2	MeCl2/CS2	2.0
8310	Single pH at neutral pH (5-9)	>12	MeCl2	Acetonitrile	1.0

Approval Signature: R. Wayne Robbins	
Title: Corporate QA Officer	Date: 7/13/99

SEPARATORY FUNNEL EXTRACTION

1.0 SCOPE AND APPLICATION

This SOP describes the general procedure for the extraction of semivolatile organic compounds (SVOC) from aqueous samples using separatory funnel extraction. This procedure is applicable to a wide range of aqueous matrices including monitoring wells, industrial wastewater, saline waters, and leachates; however, this procedure should be used only when requested by a client or when turn-around-time requirements prevent the use of the continuous liquid-liquid extractor prorcedure(SL SOP EX30).

2.0 SUMMARY OF METHOD

2.1 A known volume of sample is placed into a separatory funnel, adjusted to a specified pH if required, and extracted using the solvent and conditions specified in Table 1. The extract is concentrated to an appropriate final volume using either the Zymark nitrogen blow-down concentrator (SL-SOP EX50) or the Kuderna Danish concentration procedure (SL-SOP EX51).

2.2 This SOP is based on SW-846 Method 3510 and the extraction sections of the EPA 600-series methods.

3.0 SAFETY

3.1 Use good common sense when working in the laboratory. Do not perform any procedure that you do not understand or that will put you or others in potentially hazardous situations.

3.2 This SOP contains procedures that are designed to reduce the exposure of lab personnel to solvent vapors and to minimize the amount of solvent introduced into the lab air. All solvent transfer steps should be performed quickly and under a hood, if possible. Use the minimum amount of solvent to get the job done. Do not allow open containers of solvent or extracts to evaporate into the lab.

3.3 A lab coat or apron should be worn to protect clothing and skin from acids, bases, and solvents. Gloves must be worn to protect hands and eye protection (goggles or safety glasses) must be worn at all times in the lab. An analyst should not work alone in an isolated area.

3.4 A solvent such as methylene chloride can cause a burning sensation if it contacts the skin. The rapid evaporation of the solvent causes a rapid heat loss in the skin similar to frost bite. If solvent contacts the skin, wash the exposed skin in cold water to reduce the solvent evaporation.

3.5 The analyst should become familiar with the Material Safety Data Sheets (MSDS) for each reagent and standard used in the extraction lab.

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4.0 INTERFERENCES

4.1 Improperly cleaned glassware can contribute interferences to the sample extract. Material that is left inside the extractor after cleaning may show up in the next extraction. The glassware must be properly cleaned according to SL SOP AN60.

4.2 Samples with high levels of organic material (oils, particulates, etc.) may cause the formation of emulsions during the extraction. Emulsions will occur most readily if the sample is adjusted to a basic pH. The extract may be filtered or stirred to remove the emulsion. If the emulsion cannot be broken, the sample and extract should be transferred to a continuous liquid-liquid extractor (SL SOP EX30).

5.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

Aqueous samples are routinely collected in 1-L amber glass containers equipped with Teflon-lined caps. No preservative is required and an orange dot is affixed to the container to indicate this. The sample is stored at 4°C (less than 6°C with no frozen samples) in the lab. The sample must be extracted within seven (7) days of collection and the extract must be analyzed within forty (40) days of extraction.

6.0 MATERIALS AND APPARATUS

6.1 Separatory funnels - 1-L and 2-L, glass with Teflon stopcocks or Teflon

6.2 Filter paper

6.3 Small funnels

6.4 Pyrex glass wool - purified by Soxhlet extraction with methylene chloride.

6.5 Disposable volumetric pipets - 1.0-mL and 10-mL

6.6 Glass or Teflon rods

6.7 Wide range pH paper

6.8 Mechanical shaking device

7.0 REAGENTS

Reagents must be tracked in accordance with SL SOP AN44:*Reagent Traceability*.

7.1 Reagent water - lab generated deionized water

7.2 Methylene chloride - residue grade or better

7.3 Acetone - residue grade or better

7.4 Sodium hydroxide (NaOH) - reagent grade

7.5 Sodium hydroxide solution (10N): Dissolve 400g of NaOH pellets into about 500mL of reagent water contained in a 2-L beaker on a magnetic stirrer. Add the NaOH in small portions, with constant stirring, to minimize the time it takes to dissolve the pellets. A good deal of heat will be generated as the NaOH dissolves. After all 400g has been added, carefully dilute to 1000mL with reagent water. Mix the solution thoroughly and transfer to a storage container. Do not store sodium hydroxide solution in volumetric glassware or in containers with ground glass joints.

7.5 Sulfuric acid (H_2SO_4) - concentrated reagent grade

7.7 Sulfuric acid solution (1:1 v/v): Slowly and carefully add 500mL of concentrated H_2SO_4 to 500mL of reagent water contained in a 2-L beaker on a magnetic stirrer. Add the acid in small portions with constant stirring to reduce the heat evolved when the acid and water are combined. Cool and transfer the solution to a labeled storage container.

7.7 Sodium sulfate-anhydrous, granular, purified by heating for 4 hours at 400C in a shallow tray. Store in glass containers

8.0 STANDARDS

The preparation of the surrogate and matrix spiking solutions are described in SL SOP EX70: *Preparation of Semivolatile Surrogates and Matrix Spiking Solutions.* Table 1 is a summary of the spiking solutions used for the various analytical extraction methods. All preparation steps must be tracked in accordance with SL SOP AN41:*Standard Material Traceability.*

The tables included in SOP EX70 describe "recipes" that can be used to prepare the spiking solutions. The lab can prepare larger or smaller volumes if desired. The recipe used by the lab may be prepared as a "controlled posting" to prompt the analyst in the preparation of the spiking solutions. The controlled posting can be posted in the lab or placed in the extraction lab tracking log.

9.0 SAMPLE PREPARATION

The samples and QC items must be clearly and unambiguously labeled during each step of the extraction and analysis process. Labeling tape should be used to identify the glassware associated with each sample. Solvents will erase grease pens and "Sharpies." Use of different colored labeling tape will aid the analyst in keeping up with the extracts during each step of the extraction and concentration.

9.1 Sample Evaluation

9.1.1 Remove the samples to be extracted from the storage refrigerator. Allow the samples to equilibrate to room temperature while the appropriate glassware is gathered and prepared for the extraction. Fill out as much of the extraction log as possible prior to initiating the extraction.

9.1.2 Inspect the samples. Determine if the samples have multiple layers such as sediment or an oil layer. Consult with the supervisor or technical manager if the sample matrix is unusual or is difficult to categorize or handle.

9.1.3 Mark the level of the sample on the outside of the container. After the sample has been added to the separatory funnel, fill the empty container with water to the mark. Pour the water into a graduated cylinder and determine the volume. Record the volume in the extraction log to the nearest 5mL..

NOTE: If a reduced volume of sample must be extracted in order to provide sufficient sample volume to meet state or other program QC requirements, the sample is thoroughly mixed and an aliquot is measured with a graduated cylinder, transferred to the separatory funnel, and diluted to 500mL or 1L with reagent water. The following volumes are used for TCLP samples for BNA and pesticides:

TCLP PARAMETER	Volume of Sample Extracted(mL)	Final Volume (mL)
BNA by GC/MS (8270)	200	1.0
Pesticides by GC (8080)	20	10

9.2 Prepare the separatory funnels and receiving flasks or beakers by rinsing with acetone. Use a separatory funnel that will hold about 2X the volume of sample being extracted. For example, if 1L of sample is extracted, use a 2-L separatory funnel; if 500mL of sample is being extracted, use a 1-L separatory funnel.

9.3 Gently pour the entire sample into the separatory funnel.

NOTE: The lab has the option of using an aliquot of sample if the final volume of the extract is adjusted to compensate for the reduced volume of sample or if the reduced volume will meet the required reporting limits. In some cases, the volume of sample may be reduced in order to have sufficient sample to extract matrix spikes as required by a state or other program quality assurance plan or regulation.

9.4 Add 1.0L aliquots of reagent water to each of two separate separatory funnels to serve as the method blank and lab control sample (LCS)

EXTRACTION BATCH: An extraction bath consists of up to twenty (20) field samples and the following QC items: method blank, LCS, MS, and MSD. If insufficient sample is available to perform the MS and MSD, the LCS is extracted in duplicate(LCSD) and the extraction log is stamped: INSUFFICIENT SAMPLE AVAILABLE TO PERFORM MS/MSD.

9.5 Addition of Surrogates and Matrix Spikes
The surrogate and matrix spiking solutions are set up so that 1.0mL of the solution will be added . Be sure to use the correct solutions for the extraction of concern. The addition of the surrogates and matrix spikes should be witnessed by another analyst to ensure that the proper volume of the spiking solution is added to each sample. If the final volume of the extract must be reduced to achieve the required reporting limits, the amount of surrogate and matrix spiking solutions should be reduced proportionately.

9.5.1 Add 1.0mL of the surrogate spiking solution to each sample and QC item and gently swirl the separatory funnel to mix.

9.5.2 Add 1.0mL of the matrix spiking solution to each LCS, MS, and MSD and gently swirl the separatory funnel to mix.

9.6 Adjust the pH of the samples to the range specified in Table 2. The pH should be adjusted by adding small aliquots of 10N sulfuric acid or 10N sodium hydroxide directly to the sample container. Shake the separatory funnel to mix the sample with the acid or base. Check the pH after each addition with wide range paper. Do not dip the paper into the sample. Use a glass rod or pipette to remove a small aliquot of sample and touch the liquid to the pH paper.

NOTE: Sulfuric acid will cause the pH of the sample to decrease; sodium hydroxide will cause the pH of the sample to increase.

9.7 Add 50mL of methylene chloride to each separatory funnel.

9.8 Shake each separatory funnel for three minutes with periodic venting (under a hood) to release any excess pressure. If a mechanical shaker is used, extract the sample for five minutes. The extraction should be performed under or near a hood to minimize the solvent vapors released into the laboratory. Allow ten minutes for complete separation between the lower organic and upper water phase.

NOTE: The separatory funnel must be vented under a hood to remove the methylene chloride fumes from the lab.

9.9 Working under a hood, place a piece of filter paper into a glass funnel and add a small amount of purified sodium sulfate. Filter the extract through the glass funnel and collect the extract directly into a labeled Zymark tube. Repeat the extraction two more times with fresh 50mL aliquots of methylene chloride, combining each extract into the same vessel.

9.10 If a dual pH extraction is required, adjust the pH of the sample by adding small aliquots of 10N ulfuric acid or 10N sodium hydroxide. Gently swirl the flask to mix the acid or base and the sample. Check the pH after each addition . Do not dip the pH paper into the sample but use a glass rod or pipette to remove a small aliquot of the sample and touch the liquid to the pH paper.

NOTE: Sulfuric acid will cause the pH of the sample to decrease; sodium hydroxide will cause the pH of the sample to increase.

9.11 Add 50mL of methylene chloride to each separatory funnel.

9.12 Shake each separatory funnel for three minutes with periodic venting to release any excess pressure. The extraction should be performed under or near a hood to minimize the solvent vapors released into the laboratory. Allow ten minutes for complete separation between the lower organic and upper water phase.

NOTE: The separatory funnel must be vented under a hood to remove the methylene chloride fumes from the lab.

9.13 Working under a hood, place a piece of filter paper into a glass funnel and add a small amount of purified sodium sulfate. Filter the extract through the glass funnel and collect the extract directly into a labeled Zymark tube. Repeat the extraction two more times with fresh 50mL aliquots of methylene chloride, combining each extract into the same vessel.

NOTE: The "acid" and "base" extracts are collected in separate Zymark tubes. The volume of solvent used to extract the sample (300mL total) will not fit into a single tube. The two fractions are routinely concentrated and combined prior to analysis, but may be concentrated separately and analyzed separately if desired. The default procedure will be to combine the acid and base fraction prior to analysis.

9.14 The extract (or extracts if the acid and base fractions were separated) is now ready for concentration using the Zymark instrument(SL SOP EX50). The extract may also be concentrated using the Kuderna-Danish extract evaporation(SL SOP EX51).

Perform the extract filtration and drying steps in batches to minimize the loss of solvent into the lab. Cover the remaining containers tightly with aluminum foil and leave under or near a hood.

9.15 If required, the solvent is exchanged into the appropriate solvent; e.g., hexane for pesticides and PCBs by GC/EC (608, 8081, 8082) or acetonitrile for PAHs by HPLC (8310). See Table 2 for the routine final volumes and solvent.

9.16 Pour the liquid remaining in the separatory funnel carefully down the sink and flush continuously with cold tap water.

10.0 PROCEDURE

No items for this section in this revision.

11.0 CALCULATIONS

No items for this section in this revision.

12.0 QUALITY CONTROL/QUALITY ASSURANCE

12.1 The analytical batch consists of up to twenty (20) client samples and the associated quality control items. The quality control items consist of a method (reagent) blank, a lab control standard (LCS), a matrix spike (MS), and a matrix spike duplicate (MSD). If insufficient sample is available for the MS/MSD, the LCS is prepared in duplicate.

SL SOP AN02: *Analytical Batching* contains guidance for evaluating the QC in an analytical batch.

12.2 The lab must perform a method detection limit (MDL) study annually in each matrix in accordance with SL SOP CA90: *Procedure for the Determination of Method Detection Limit (MDL).*

13.0 PREVENTIVE MAINTENANCE

No items in this revision.

14.0 TROUBLESHOOTING

No items in this revision.

15.0 REFERENCES

15.1 *Savannah Laboratories Comprehensive Quality Assurance Plan* and *Savannah Laboratories Corporate Quality Assurance Plan*, current revisions.

15.2 *Test Methods for Evaluating Solid Waste*, Third Edition, SW-846; vs. EPA Office of Solid Waste and Emergency Response: Washington, DC.

Table 1 -Surrogate and Matrix Spiking Solutions

METHODS	TYPES OF COMPOUNDS	SURROGATE SPIKING SOLUTION	MATRIX SPIKING SOLUTION
604	Phenols by GC-FID	SG ACID	604
8040/8041	Phenols by GC-FID	SG ACID	8040
606,8060,8061	Phthalate esters by GC-FID	SG BASE	606/8060
608	Chlorinated pesticides and PCBs	PEST	608
8081, 8082	Chlorinated pesticides and PCBs	PEST	8080
608, 8082	PCBs	PEST	PCB
8081	Chlorinated pesticides-TCLP	PEST	TCLP-PEST
610	PAH by GC-FID	SG BASE	610
8100	PAH by GC-FID	SG BASE	8100
8140,8141	Phosphorous and nitrogen containing pesticides	8141	8141
625	BNA	625/8270	625
8270-TCL	BNA	625/8270	8270
8270-K001	BNA	625/8270	K001(8270)
8270-TCLP, AP9	BNA	625/8270	TCLP-8270
8015-EXT	Petroleum products	SG BASE	Diesel-8015-mod Mineral spirits-8015-mod
FL-PRO	Petroleum products	FL-PRO	FL-PRO
8310	PAHs by LC	8310	8310

Table 2 -Extraction Conditions

METHODS	TYPES OF COMPOUNDS	EXTRACTION CONDITIONS	SOLVENT	FINAL SOLVENT	FINAL VOLUME(mL)
604,8041	Phenols by GC-FID	Single pH < 2	MeCl2	MeCl2	1.0
606,8061	Phthalate esters by GC-FID	Single pH as received or at pH<2	Mecl2	MeCl2	1.0
608,8081,8082	Chlorinated pesticides and PCBs	Single pH at neutral pH (5-9). pH range is critical for good recovery of some target compounds	MeCl2	Hexane	10
610,8100	PAH by GC-FID	Single pH as received or at pH<2	MeCl2	MeCl2	1.0
625	BNA	Dual pH at >12 followed by pH<2	MeCl2	MeCl2	1.0
8270-TCL,K001	BNA	Single pH <2	MeCl2	MeCl2	1.0
8270-TCLP, AP9	BNA	Dual pH at pH<2 followed by pH>12	MeCl2	MeCl2	1.0
8015-EXT	Petroleum products	Single pH as received or at pH<2	MeCl2	MeCl2	1.0
FL-PRO	Petroleum products	Received at pH<2. Adjust to pH<2 if not received at pH<2.	MeCl2	MeCl2/CS2	2.0
8310	PAHs by LC	Single pH at neutral pH (5-9)	MeCl2	Acetonitrile	1.0

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1.0 SCOPE AND APPLICATION

This SOP describes the process for extracting semivolatile organic compounds (SVOC) from solid matrices by ultrasonic (sonication) extraction. This procedure is applicable to soils, sediments, sludges, and wastes.

2.0 SUMMARY OF METHOD

2.1 A known weight of a sample (approximately 30g wet weight) is combined with anhydrous, purified sodium sulfate to form a free flowing, sandy mixture. A solvent, usually 1:1 acetone/methylene chloride, is added to the dried sample and the sample is extracted using an ultrasonic disrupter for three (3) minutes. The solvent is decanted and the extraction is repeated two more times. The extract is filtered and concentrated to an appropriate final volume.
Table 1 defines the extraction conditions.

NOTE: The lab has the option of extracting a sample aliquot equal to 30g on a dry weight basis.

2.2 This procedure is based on SW-846 Method 3550B.

3.0 SAFETY

3.1 Use good common sense when working in the lab. Do not perform any procedures that you do not understand or that will put you or others in potentially dangerous situations.

3.2 This SOP contains procedures that are designed to reduce the exposure of lab personnel to solvent vapors and to minimize the amount of solvent introduced into the lab air. All solvent transfer steps should be performed quickly and under a hood, if possible. Use the minimum amount of solvent to get the job done. Do not allow open containers of solvent or extracts to evaporate into the lab.

3.3 A lab coat or apron should be worn to protect clothing and skin from acids, bases, and solvents. Gloves must be worn to protect hands and eye protection (safety glasses, goggles) must be worn at all times in the lab. An analyst should not work alone in an isolated area.

3.4 A solvent such as methylene chloride can cause a burning sensation when it contacts the skin. The rapid evaporation of the solvent causes a rapid heat loss in the skin which is similar to frost bite. If this occurs, was the exposed skin in cold water to reduce the solvent evaporation.

3.5 The analyst should become familiar with the Material Safety Data Sheets (MSDS) for each reagent used in the extraction lab.

4.0 INTERFERENCES

Improperly cleaned glassware or equipment can contribute interferences to the sample extract. A thorough acetone rinsing will help to eliminate or minimize this problem.

5.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

Soils, sediments, sludges, and wastes are collected in glass containers equipped with Teflon-lined caps. The normal container is 500-mL glass. Larger or smaller containers may be supplied. The sample is

not preserved and should have an orange dot affixed to indicate this. The samples are stored at 4C ± 2C in the lab. The hold time for SVOC in solid matrices is 14 days from the date of collection. The extract must be analyzed within 40 days of extraction.

6.0 APPARATUS AND MATERIALS

6.1 Ultrasonic disrupter: Tekmar Model or equivalent with ¾ inch horn-type titanium-tipped sonication probe. The sonicator should be capable of operating in the pulse mode at full power.

6.2 Sonabox - the sonicator should be placed in the sonabox to reduce noise. The sonabox must be placed under a fume hood.

6.3 Pre-cleaned 500ml extraction bottles (P/N SAV-145). Discard the bottles after use.

6.4 Large glass funnels

6.5 Filter paper-18.5cm

6.6 Pyrex glass wool - purchased purified or extracted with methylene chloride for a minimum of four (4) hours.

6.7 Stainless steel spatulas

6.8 Small cups or beakers for optional pH measurement.

6.9 wide range pH paper

6.10 Disposable volumetric pipets

6.11 Top-loading balance - capable of weighing to 0.1g. The balance calibration must be verified according to SL SOP AN10 each time the balance is used.

7.0 REAGENTS

7.1 Sodium sulfate, powdered and granular, anhydrous - purified by heating at 400C for four (hours) in a shallow tray.

7.2 Methylene chloride - residue grade or better

7.3 Acetone - residue grade or better

7.4 1:1 acetone/methylene chloride: Mix equal volumes of acetone and methylene chloride in an appropriate glass container.

8.0 STANDARDS

The preparation of the surrogate and matrix spiking solutions are described in SL SOP EX70: *Preparation of Semivolatile Surrogates and Matrix Spiking Solutions.* Table 2 is a summary of the spiking solutions used for the various analytical extraction methods. All preparation steps must be tracked in accordance with SL SOP AN41:*Standard Material Traceability.*

The tables included in SOP EX70 describe "recipes" that can be used to prepare the spiking solutions. The lab can prepare larger or smaller volumes if desired. The recipe used by the lab may be prepared as a "controlled posting" to prompt the analyst in the preparation of the spiking solutions. The controlled posting can be posted in the lab or placed in the extraction lab tracking log.

9.0 SAMPLE PREPARATION

9.1 Extraction Glassware Set-up

9.1.1 Remove samples to be extracted from the storage refrigerator and allow the samples to come to room temperature while the extraction glassware is being prepared.

9.1.2 Collect the appropriate glassware and rinse with acetone prior to use. Use the minimum amount of solvent to rinse the glassware.

9.1.3 Fit a filter pad into a large funnel and rinse the filter paper/funnel with acetone.

9.2 Sample Extraction

Record as much information on the extraction log as possible before beginning the extraction to minimize the number of entries required during the extraction. The extraction steps from weighing to the sonication should be carried out quickly to minimize the loss of SVOC through evaporation.

9.2.1 Open the sample container and inspect the sample. Remove any materials such as rocks, sticks, leaves, etc. Using a stainless steel spatula , thoroughly homogenize the sample, mixing in any water that may be present on top of the sediment or soil. Use a separate spatula for each sample to prevent cross-contamination of the samples.

NOTE: If it is difficult to homogenize the sample or if the sample matrix is difficult to characterize, contact the supervisor before preceding with the extraction. A careful inspection of the sample at this point can save time and effort later on in the analysis.

9.2.2 Weigh 30.0 - 30.5g of the homogenized sample into a pre-cleaned, labeled 500-mL extraction bottle. Record the weight for all samples in this batch.

NOTE: The lab has the option of weighing an aliquot of sample equal to 30g on a dry weight basis.

Weight 30g of powdered, purified sodium sulfate into each of two separate extraction vessels to serve as the method blank and lab control spike (LCS).

Weigh two additional 30g portions of a sample in the batch selected as the matrix spike (MS) and matrix spike duplicate(MSD). The MS/MSD may be specified by the client or may be chosen from the samples in the batch.

NOTE: Each extraction batch of twenty or fewer samples will have the following QC items: method blank, LCS, LCSD, MS, and MSD. If there is not enough sample to perform the MS/MSD, the extraction log must be stamped "INSUFFIECIENT SAMPLE WAS AVAILABLE TO PERFROM THE MS/MSD" and the LCS extracted in duplicate(LCSD).

9.2.3 Add approximately 60g of powdered, purified sodium sulfate to each sample and MS/MSD and stir with a glass rod or stainless steel spatula to form a sandy, free-flowing mixture. The sodium sulfate combines with the water in the sample to "dry" the sample (remove the water). Additional sodium sulfate may be required if the sample is very wet.

NOTE: The next steps should be performed immediately after the sodium sulfate is added to minimize the loss of SVOC due to evaporation

9.2.4 Add 1.0mL of the appropriate surrogate spiking solution (Table 1) to the method blank, LCS, MS, MSD and each sample in the batch.

9.2.5 Add 1.0ml of the appropriate matrix spiking solution (Table 1) to the LCS, MS, and MSD. Place the extraction bottle under the hood near the sonicator

9.2.6 Working under a hood, immediately add 1:1 acetone/methylene chloride to the cover the sample approximately one inch above the solids. Stir the sample to break up any lumps that may have formed.

9.2.7 Check the "tune" of the sonicator using the procedure tested in SL SOP AN15: Tekmar Sonic Dismembrator Tuning Procedure.

9.2.8 Place the tip of the sonicator horn in the center of the beaker about ½ inch below the surface of the solvent but above the solid portion. More solvent may be added to bring the level to approximately one inch above the solid layer.

9.2.9 Sonicate for three (3) minutes with output control knob set at 10, mode switch to pulse, and percent duty cycle set at 50% If the sonication is properly performed, the solids and solvent will vigorously mix each time the sonicator pulses.

9.2.10 Decant the extract through the filter funnel and collect the extract in a beaker or directly in a labeled, "elongated" Zymark tube. The elongated tubes hold approximately 225mL of solvent; therefore, it is desireable to limit the volume of the three extracts to 225mL. If the sample is very wet and requires a large amount of sodium sulfate and a larger volume of solvent, the extracts are collected in separate Zyamrk tubes and combined prior to analysis to analysis.

9.2.11 Repeat steps 9.2.6 through 9.2.10 two more times with fresh portions of methylene chloride and collect the extract in the Zymark tube. Cover the Zymark tube with aluminum foil and leave it under the hood until the concentration step.

NOTE: Clean the sonicator horn between samples by rinsing with acetone. "Sonicate" an extraction bottle of acetone for 3 minutes with output control at 5 to further clean the horn (sodium sulfate may be added to the beaker to prevent cracking).

9.2.13 Dispose of extraction bottle and sample residue by placing in a chlorinated solvent waste container which is kept under a hood until removed from the laboratory.

10.0 ANALYTICAL PROCEDURE

No items in this revision.

11.0 CALCULATIONS

No items in this revision.

12.0 QUALITY CONTROL/QUALITY ASSURANCE

12.1 The analytical batch consists of up to twenty (20) client samples and the associated quality control items. The quality control items consist of a method (reagent) blank, a lab control standard (LCS), a matrix spike (MS), and a matrix spike duplicate (MSD). If insufficient sample is available for the MS/MSD, the LCS is prepared in duplicate.

SL SOP AN02: *Analytical Batching* contains guidance for evaluating the QC in an analytical batch.

12.2 The lab must perform a method detection limit (MDL) study annually in each matrix in accordance with SL SOP CA90: *Procedure for the Determination of Method Detection Limit (MDL).*

13.0 PREVENTIVE MAINTENANCE

No items in this revision.

14.0 TROUBLESHOOTING

No items in this revision.

15.0 REFERENCES

15.1 *Savannah Laboratories Comprehensive Quality Assurance Plan* and *Savannah Laboratories Corporate Quality Assurance Plan*, current revisions.

15.2 *Test Methods for Evaluating Solid Waste*, Third Edition, SW-846; vs. EPA Office of Solid Waste and Emergency Response: Washington, DC.

Table 1 -Surrogate and Matrix Spiking Solutions

METHODS	TYPES OF COMPOUNDS	SURROGATE SPIKING SOLUTION	MATRIX SPIKING SOLUTION
8040/8041	Phenols by GC-FID	SG ACID	8040
8060,8061	Phthalate esters by GC-FID	SG BASE	606/8060
8081, 8082	Chlorinated pesticides and PCBs	PEST	8080
8082	PCBs	PEST	PCB
8081	Chlorinated pesticides-TCLP	PEST	TCLP-PEST
8100	PAH by GC-FID	SG BASE	8100
8140,8141	Phosphorous and nitrogen containing pesticides	8141	8141
8270-TCL	BNA	625/8270	8270
8270-K001	BNA	625/8270	K001(8270)
8015-EXT	Petroleum products	SG BASE	Diesel-8015-mod Mineral spirits-8015-mod

Table 2 -Extraction Conditions

METHODS	TYPES OF COMPOUNDS	EXTRACTION CONDITIONS	SOLVENT	FINAL SOLVENT	FINAL VOLUME(mL)
8040,8041	Phenols by GC-FID	As received	1:1 Ace/MeCl2	MeCl2	1.0
8060,8061	Phthalate esters by GC-FID	As received	1:1 Ace/MeCl2	MeCl2	1.0
8081, 8082	Chlorinated pesticides and PCBs	As received	1:1 Ace/Hexane	Hexane	10mL
8100	PAH by GC-FID	As received	1:1 Ace/MeCl2	MeCl2	1.0mL
8140,8141	Phosphorous and nitrogen containing pesticides	As received	1:1 Ace/Hexane	Hexane	10mL
8270-TCL,K001	BNA	As received	1:1 Ace/MeCl2	MeCl2	1.0mL
8015-EXT	Petroleum products	As received	1:1 Ace/MeCl2	MeCl2	1.0mL

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EPA RESPONSE

ATTACHMENT D

ORGANOCHLORINE PESTICIDES AND PCBs BY GC
(Methods 608 and 8081A/8082)

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Approved by:

R Wayne Robb 3 April 2001
Date

Title: Technical Manager, QA

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1.0 SCOPE AND APPLICATION

1.1 This method is used to determine the concentration of various chlorinated pesticides and polychlorinated biphenyls (PCBs) in liquid and soil extracts. Appendix A gives an example of the retention times of the routine target compounds. A summary of the method QC requirements is provided in the Appendix C.

1.2 The reporting limit (RL), the method detection limit (MDL), and the accuracy and precision criteria are given in Section 5 of the current revision of the STL Savannah Laboratories Laboratory Quality Manual.

The procedures for chlorinated pesticides (8081A) and PCBs (8082) are given as separate methods separated in the latest update of SW-846. Until this update, the pesticides and PCBs were combined in both SW-846 Methods 8080 and 8081. The extraction and the analysis are combined in this SOP 1) to reduce the time of extraction and analysis; and 2) to reduce the amount of solvent used in the procedures (one extraction instead of two). If interferences or high levels of non-PCB compounds are present, a portion of the extract will be subjected to the acid cleanup and reanalyzed. Note that if the list of target analytes includes only a limited list of components (i.e. Toxaphene, Chlordane, or PCBs), these procedures may be abbreviated to address only the analytes of interest.

2.0 SUMMARY OF METHOD

2.1 Aqueous and leachate samples are extracted with methylene chloride using a continuous liquid/liquid extractor (SOP EX30) or separatory funnel (SOP EX35). Soils are extracted with 1:1 hexane/acetone or 1:1 acetone/methylene chloride using a sonic dismembrator (SOP EX40). The solvent is evaporated, the residue exchanged into hexane, and the sample adjusted to a final volume of 10mL or less. The preparation may also incorporate Florisil, copper (sulfur), acid (PCBs and Toxaphene only), or gel permeation chromatography (GPC) cleanups. Analysis of the extract is routinely performed on a GC equipped with dual capillary columns (different phases) connected to dual electron capture (EC) detectors, allowing simultaneous detection and confirmation of the target compounds. GC/MS confirmation can also be employed if analyte concentration is sufficiently high or if the sample extract is concentrated to an appropriate final volume. Quantitation may be performed using the external or internal standards calibration technique. The procedures for waste dilution are given in SOP EX42.

2.2 This method is based on the guidance in SW-846 Methods 8000B, 8081A, and 8082 and 40 CFR 136 Method 608.

3.0 SAFETY

3.1 Use good common sense when working in the lab. Do not perform any procedures that you do not understand or that will put you or others in potentially hazardous situations.

3.2 The analyst should wear an apron or lab coat, gloves, and eye protection when handling extracts. Dilutions should be performed under a hood or in a well-ventilated area.

3.3 The analyst must be familiar with the Material Safety Data Sheets (MSDS) for each reagent and standard used in the analysis of pesticides and PCBs. Many of these compounds are suspected carcinogens.

4.0 INTERFERENCES

4.1 Glassware should be scrupulously cleaned and solvent-rinsed in accordance with SOP AN60 to minimize artifacts and/or elevated baselines in gas chromatograms. Any vessel that comes in contact with the extract is a potential source for contamination. Method blanks that are extracted and analyzed with each batch of samples will provide clues to the source of contamination form the glassware and reagents.

4.2 Matrix interferences may be caused by contaminants that are co-extracted from the sample. See Section 9 for a table summary of the cleanups that may be employed to eliminate or reduce interferences. If matrix interferences continue after a clean up has been performed, the sample is diluted as needed for data analysis. If a cleanup is used, the method blank must also be subjected to the cleanup.

5.0 SAMPLE COLLECTION, HANDLING, AND PRESERVATION

Aqueous samples are collected in 1-L glass containers with Teflon-lined caps. Soil/sediment samples are collected in wide mouth glass jars equipped with Teflon lined caps. No preservative is added. The samples are iced at the time of collection and maintained at 4°C (less than 6C with no frozen samples) until extraction. Extraction must be performed within 7 days for aqueous samples and within 14 days of sampling for soils/solids. The extracts must be stored at 4°C (less than 6C) and must be analyzed within 40 days of extraction.

6.0 APPARATUS AND MATERIALS

6.1 Gas chromatograph (GC), temperatures programmable, equipped with single or dual electron capture (EC) detectors and a compatible autosampler. The GC should be capable of housing two columns and have make-up gas lines for each detector

6.2 Data system compatible with the GC, with appropriate software or integration capabilities

6.3 The following column pairs are recommended

DB-5 fused silica capillary column 30 M x 0.53 mm ID x 1.5 um film (J&W or equivalent)
DB-608 fused silica capillary column 30 M x 0.53 mm ID x 0.83 um film (J&W or equivalent)
<Or>
DB-5 fused silica capillary column 30 M x 0.32 mm ID x 0.5 um film (J&W or equivalent)
DB-17 fused silica capillary column 30 M x 0.32 mm ID x 0.5 um film (J&W or equivalent)
<Or>
DB-5 fused silica capillary column 30 M x 0.32 mm ID x 0.5 um film (J&W or equivalent)
DB-1701 fused silica capillary column 30 M x 0.32 mm ID x 0.5 um film (J&W or equivalent)

6.4 Microsyringes, appropriate volumes

6.5 Volumetric flasks, Class A, appropriate volumes

6.6 Autosampler vials, septa, and caps; compatible with the autosampler

7.0 REAGENTS

Hexane- pesticide grade, for preparation of standards

8.0 STANDARDS

The preparation of the calibration standards must be tracked in accordance with SOP AN41:*Standard Material Traceability*. General guidance on the preparation of standards is given in STL -SL SOP AN43:*Standard Preparation.*

The lab should purchase certified solutions from STL approved vendors, if available. The lab should prepare standards from neat materials only if a certified solution is not available. See SOP AN43 for guidance for standard preparation.

Calibration Standard Recipes

The standard concentrations given in Appendix B are provided for guidance. The recipes used for standard preparation must be clearly documented as a controlled posting or as a narrative in the traceability log. Note that the preparation of some of the calibration standards will include intermediate level standards.

The lowest level calibration standard should be at or below the equivalent of the reporting limit as defined in the LQM or client QAPP. The remaining standards will define the working range of the analytical system. When more calibration standards are analyzed than required, individual compounds may be eliminated from the lowest or highest concentration level(s) only. If points or levels are eliminated, analyte concentration in samples must fall within the range defined by the resulting curve. In no case should individual points in the middle of a calibration be eliminated without eliminating the entire level.

9.0 SAMPLE PREPARATION

The sample preparation and cleanup procedures are described in the following SOPs:

PROCEDURE	MATRIX	SOP
Continuous Liquid-liquid extraction	aqueous and leachates	EX30
Separatory funnel extraction	aqueous and leachates	EX35
Ultrasonic extraction	soils and sediments	EX40
Waste dilution	Waste samples (oils, products, etc)	EX42
Zymark extract concentration	Aqueous, leachate, and soil extracts	EX50

CLEAN-UP PROCEDURE	SOP	APPLICATION	EFFECTIVENESS
Florisil	EX62	pest/PCBs	Eliminates polar non-target compounds
Sulfuric acid / permanganate	EX60	PCBs and Toxaphene	Eliminates some unsaturated hydrocarbon interferences
Copper	EX60	pest/PCBs	Eliminates elemental sulfur
GPC	EX61	pest/PCBs	Eliminates high molecular weight non-target compounds and sulfur

10.0 ANALYTICAL PROCEDURE

10.1 Gas Chromatograph Operating Conditions

The instrument conditions listed in this section are for guidance. The actual conditions used by the lab must be documented in the instrument maintenance log, data system, or run log. The goal is to have maximum separation between the target compounds in the shortest run time while maintaining sufficient sensitivity to detect the target compounds at the reporting limit and MDL (if required).

10.1.1 Two configurations may be used for the analysis of pesticides and PCBs. A single column may be connected to the injection port or two columns may be connected to the injection port using a press-tight glass y-splitter and a guard column, a two-hole ferrule, or a glass tee to provide simultaneous detection and confirmation of the target analytes. The following stationary phase pairs are recommended:

DB-5 fused silica capillary column 30 M x 0.53 mm ID x 1.5 um film (J&W or equivalent)
DB-608 fused silica capillary column 30 M x 0.53 mm ID x 0.83 um film (J&W or equivalent)

DB-5 fused silica capillary column 30 M x 0.32 mm ID x 0.5 um film (J&W or equivalent)
DB-17 fused silica capillary column 30 M x 0.32 mm ID x 0.5 um film (J&W or equivalent)

DB-5 fused silica capillary column 30 M x 0.32 mm ID x 0.5 um film (J&W or equivalent)
DB-1701 fused silica capillary column 30 M x 0.32 mm ID x 0.5 um film (J&W or equivalent)

A guard column is recommended to help protect the analytical columns.

10.1.2 Example GC Parameters

Injector: 220 – 240°C
Detector: 300 – 320 °C
Carrier Gas Flow: Helium at 5 mL/min (per column)
Make-up Gas Flow: Nitrogen at 25 mL/min (per detector)-see manufacturer's recommended flows

Example chromatogram temperature program:

Initial Temp:	160 C
Initial Hold:	4.0 min
Program Rate:	10 C/min
Final Temp:	270 C (hold for 10 minutes)
Injected Volume:	2-4uL - 1-2uL per column (single injection into guard column and "Y" splitter)

NOTE: These conditions and parameters are given for guidance. The conditions and parameters may be modified to optimize the analytical system.

10.2 Column Evaluation

The column(s) must be evaluated prior to the analysis of the calibration standards. The column evaluation is performed by injecting Endrin and p,p'-DDT and calculating the percent breakdown of these compounds.. The column evaluation does not have to be performed if PCBs only are the target compounds. PCBs are stable and not subject to breakdown in the injection port.

If the instrument has not been in use for more than one day, a "priming" analysis may be beneficial. The analysis of a relatively high concentration pesticide or PCB standard may help to stabilize the response of the very sensitive EC detector. Inject a standard that is about 10x the concentration of the highest calibration standard and allow the instrument to cycle through the temperature program. It is not necessary to acquire the data but the baseline should be monitored before and after the priming analysis to gauge the condition of the detector. A hexane blank should be analyzed after the analysis of the priming standard and before the %breakdown check.

NOTE: The "priming" standard should be injected manually to avoid contaminating the autosampler syringe.

Inject the Endrin/DDT breakdown standard. Check the peak integrations and calculate the breakdown as follows:

$$\%\text{Breakdown Endrin} = \frac{\text{Area(Endrin Aldehyde} + \text{Endrin Ketone)}}{\text{Area(Endrin} + \text{Endrin aldehyde} + \text{Endrin Ketone)}} \otimes 100$$

$$\%\text{Breakdown DDT} = \frac{\text{Area(DDE} + \text{DDD)}}{\text{Area(DDT} + \text{DDE} + \text{DDD)}} \otimes 100$$

The breakdown for each compound must be less than 15%. If the breakdown exceeds 15%, the instrument will require column and/or injector port maintenance. The maintenance may include but is not limited to replacing the septum, clipping the front of the column, and replacing the glass injector sleeve.

10.2 Initial Calibration

The external standard calibration technique is routinely employed for the determination of the concentration of pesticides and PCBs. The lab also has the option of using internal standard calibration. Pentachloronitrobenzene (PCNB) or 2-Nitro-1-bromobenzeneis are suggested for use as internal standards.

10.2.1 Prepare and analyze the calibration standards. Injector port and column maintenance should be performed on the instrument prior to the analysis of the initial calibration standards. Guidance for establishing the analytical sequence is given in the SOP Summary.

Note that the following offers two (2) options for calibration and quantitation – average CF or regression curve. Only one need be chosen per analyte.

When more calibration standards are analyzed than required, individual compounds may be eliminated from the lowest or highest concentration level(s) only. If points or levels are eliminated, analyte concentration in samples must fall within the range defined by the resulting curve. In no case should individual points in the middle of a calibration be eliminated without eliminating the entire level.

10.2.2 Evaluate the standard chromatograms. Some questions to ask at this point are:

>Is there contamination in the hexane blank? If so, has maintenance been performed on the instrument lately? Has the septum been changed? Is the column properly seated in the injector and detector ports?
>Did all of the standards inject properly? Are there peaks for each of the standards analyzed? Do the patterns look normal?
>Are the peaks symmetrical? Is there tailing or fronting?
>Are the areas of the peaks normal for the sensitivity setting being used?

Inspect each chromatogram to ensure that the peaks are properly identified and that the correct areas have been associated with the corresponding standard peak RT in the data system tabulation.

10.2.3 Average CF or RF Option:
Calculate the calibration factor (CF) or the response factor (RF) of each calibration standard, the average calibration or response factor and the relative standard deviation using the following equations:

Calibration factor-external standard

$$CF = \frac{Rt}{Ct}$$

where
Rt = response (area or height) of the target compound
Ct = concentration of the target compound, usually expressed as ug/mL

Response factor-internal standard

$$RF = \frac{Ac}{Ais} \otimes \frac{Cis}{Cc}$$

where
Ac = area of the target compound
Ais = area of the internal standard
Cc = concentration or mass on-column of the target compound (ug/mL)
Cis = concentration or mass on-column of the internal standard (ug/mL)

Average Calibration Factor or Response Factor

$$CF_{avg} = \frac{CF_1 + CF_2 + CF_3 + \ldots CFn}{n}$$

Relative Standard Deviation

$$\% RSD = \frac{standard\ deviation}{\overline{CF_{avg}}} \otimes 100$$

$$Standard\ Deviation = \sqrt{\frac{\sum_{i=1}^{n}(CF_i - \overline{CF_{avg}})^2}{n-1}}$$

Where

CF_i = calibration factor (or response factor) of the individual calibration level
CF_{avg}= average calibration factor (or response factor)

10.2.4 Initial Calibration Criteria:

600-series: If the relative standard deviation is less than 10% for the target compounds in the initial calibration, the calibration is considered linear and the average calibration factor may be used for quantitation.

8000-series: If the relative standard deviation is less than 20% for the target compounds in the initial calibration, the calibration is considered linear and the average calibration factor may be used for quantitation.

8000-series ICAL grand mean exception:
If one or more compounds exceed the %RSD criteria, the average calibration factors can be used for quantitation if the average %RSD of ALL of the compounds (the grand mean) in the ICAL is less than or equal to 20%.

NOTE: If a target compound that passes by the "grand mean exception" is detected (>RL), the PM is notified via an anomaly report or case narrative. If the targets are <RL, no notification is required since the lab has demonstrated that the lowest standard in the calibration curve (the equivalent of the RL) can be detected.

10.2.5 Regression Curve Option: A calibration curve is established for each analyte by plotting the concentration along the x-axis and the corresponding response along the y-axis. If the correlation coefficient of the regression curve is greater than 0.99, the curve can be used to quantify samples. For 8000-series methods, a minimum of five points is required for a linear regression, six points for a second order curve, and seven or more for higher order fits. It is recommended that only linear and quadratic (second order) curves be used for quantitation. See STL-STL SL SOP AN67 for guidance on evaluation of calibration curves.

NOTE: Linear regression curves must be used for South Carolina DHEC compliance samples. See pre-project plans and client QAPPs for other exceptions to using non-linear curve fitting.

10.3 Calibration Verification

Calibration is verified at the frequency given in the SOP Summary. Note that the following criteria apply to calibration standards analyzed before and after samples. In situations where compounds fail criteria high and no positive for the compound(s) failing high are detected, these samples may be reported.

10.3.1 Analyze the mid-level standard(s). Tabulate the area of the target analytes and calculate the response factors if using the average RF/CF option. If using the calibration curve option, calculation of the RF is unnecessary.

Calculate the percent drift or percent difference between the initial and continuing calibration:

$$PercentDrift = \left| \frac{Cccv - Ctrue}{Ctrue} \right| \otimes 100$$

where
Cccv = concentration of CCV (ug/mL) quanted from regression curve or CFavg or RFavg
Ctrue = true concentration of the CCV (ug/mL)

$$PercentDifference = \left| \frac{CFccv - CFavg}{CFavg} \right| \otimes 100$$

where
CFccv = calibration factor (or RF) of CCV
CFavg = average calibration factor (or RFavg) from initial calibration

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10.3.2 Continuing Calibration Verification Criteria

Response Criteria:
If the CCV criterion is not met, another CCV should be analyzed. Repeated failure may be a sign of instrument or standard degradation. If the calibration verification criteria cannot be met, a new initial calibration must be prepared, analyzed, and evaluated.

600-series: If the percent drift or percent difference is less than or equal to 15%, the initial calibration is verified and the average response factor or regression curve can be used for quantitation.

8000-series: If the percent drift or percent difference is less than or equal to 15%, the calibration curve is verified and the average response factor is used for quantitation.

8000-series CCAL grand mean exception:
If one or more compounds exceed the %drift or %difference criteria, the average calibration factor or regression curve from the initial calibration can be used for quantitation if the average %drift or %difference of ALL of the compounds (the grand mean) in the CCV is less than or equal to 15%.

NOTE: If a target compound that passes by the "grand mean exception" is detected (>RL), the PM is notified via an anomaly report or case narrative. If the targets are <RL, no notification is required.

All samples analyzed must be bracketed by acceptable CCV. If the CCV standard analyzed after the samples fails to meet the acceptance criteria and the response of the mid point standard is *above* the criteria (that is the response of the analytical system has increased), samples which have no target compounds detected above the RL may be reported as <RL, since the compounds would have been detected if present. (SW-846 Method 8000B).

Retention Time Criteria
The retention time for the CCV must fall within the daily retention time window as defined in SOP AN66: *Determination of Retention Time Windows for Gas Chromatographic Analyses.*

10.4 Sample Analysis Sequence
The analytical sequences for the 600- and 8000-series methods are given in the SOP Summary in Appendix C.

10.4.1 The sample extract is injected using the same injection volume used for the calibration standards. Extracts that are known to be relatively clean should be analyzed first. Extracts suspected of containing high concentrations should be analyzed last. Instrument blanks may be analyzed after suspected high concentration samples to allow the detector response to stabilize.

10.4.2 If the concentration of target compounds exceeds the working range (defined by the highest standard in the initial calibration), the extract must be diluted in hexane and reanalyzed. A dilution should bring the area of the largest peak of interest into the upper half of the calibration curve.

NOTE: Unless otherwise specified by a client or QA plan, results from a single dilution are reportable as long as the largest target analyte (when multiple analytes are present) is in the upper half of the calibration range. When reporting results from dilutions, appropriate data flags should be used or qualification in a case narrative provided to the client.

For clients who demand lower detection limits, a general guide would be to report the dilution detailed above and one additional run at a dilution factor 1/10 the dilution factor with the highest target in the upper half of the calibration curve (i.e., a sample analyzed at a DF of 50 resulting in a hit in the upper half of the calibration curve would be reanalyzed at a DF of 5 to provide lower detection limits to the client). Project managers and lab staff must work together to balance client satisfaction with productivity.

10.5 Determination of Retention Time Windows

The procedure for the determination of retention time windows is given in SOP AN66: *Determination of Retention Time Windows for Gas Chromatographic Analyses.* If internal standard calibration is used, the determination of absolute retention time windows is not required. Relative retention times, as described in Section 11.1.4, are used to identify the target compounds.

11.0 DATA ANALYSIS/CALCULATIONS

The evaluation of chromatograms for target compounds must take into account the calibration of the analytical system (initial and continuing calibration response and retention times), the recovery and retention time shift of the surrogate compounds, whether the peak response falls within the working range of the calibration, and the integration of the peaks. Manual integration must be documented in accordance with SOP AN65. The analyst must also take into account the results from the method blank and lab control sample before reporting quantitative data.

The judgement and experience of the analyst and his/her colleagues are important factors in the evaluation of chromatographic data. The analyst should ask:

- Is there previous data or current information about the sample that would aid in evaluating the data?
- Do the peaks look normal?
- Are peaks properly integrated?
- Are co-eluting peaks or matrix interferences present?

11.1 Qualitative analysis

Identification of the surrogates and target compounds is based on retention time. The retention time (RT) windows calculated around the CCV retention times are used for the identification of the target compounds. The analyst should also note shifts in the retention times of the surrogate compounds or internal standard(s) to help gauge possible shifts in the RT of the target compounds. If, in the professional judgement of the analyst and supervisor, a peak within the retention time window can be reasonably excluded as a target, the result may be reported as a "non detect".

NOTE: It is important to note that the retention time window applies only to peaks that are within the calibration range of the curve. Peaks areas that exceed the established linear range of the calibration curve may result in significant retention time shifts; therefore, all peaks, which have significant areas and elute closely to a target compound should be tentatively identified as a target compound and evaluated as such. Peaks over-range are handled using dilutions as detailed above (10.4.2).

11.1.1 The surrogates should be evaluated first to check for shifts in retention times and to evaluate the surrogate recovery. The recovery criteria are given in Section 5 of the STL-Laboratory Quality Manual (LQM).

A minimum of two surrogates are spiked into each sample and QC item prior to preparation. 2,3,4,6-tetrachloro-m-xylene (TCMX) and decachlorobiphenyl (DCB) are the recommended surrogates. DCB should be evaluated as the primary surrogate; TCMX is evaluated if there is matrix interference with DCB.

Given the complicated nature of GC-ECD chromatograms, assessing surrogate recovery is frequently complicated by co-eluting positive and negative interferences. Generally, it is expedient to calculate the recovery of both surrogates on one chromatogram. If these recoveries are deemed acceptable, the other channel is not evaluated for recovery. If interferences are suspected, evaluate recoveries on the other channel. Note that given this nature, an extract is considered acceptable if one of the 4 potentially calculated recoveries is acceptable.

NOTE: If the recovery of the surrogate(s) is above the upper control limit and no target compounds are detected in the sample, results may be reported. Refer to section 13 of the current Laboratory Quality Manual regarding this issue.

11.1.2 Evaluate each peak that corresponds to a target compound. Observe the general appearance of the chromatogram for possible dilutions, matrix interferences, and the overall shapes of the peaks.

If the concentration is below the detection limit, the reporting limit (RL) for that compound is calculated (Section 11.2). The RL is calculated for all target compounds that are not detected on the primary analytical column. Peaks over-range are handled using dilutions as detailed above (10.3.2).

NOTE: If a peak is over range on the primary column, evaluate the confirmation column. If no peak is detected or if the concentration is within the calibration range, the analysis at a dilution is not necessary.

11.1.3 If the result for a target is above the reporting limit (RL) on the primary column, evaluate the confirmation column. Use the retention time window calculated using the CCV as guidance for the identification of the target compounds. Note shifts in the retention times of the surrogate compounds or internal standard(s) to help gauge possible shifts in the RT of the target compounds.

If the target compound is detected on the confirmation column, the concentration of the target compound is calculated and compared to the result from the primary column. The relative percent difference is calculated:

$$\%RPD = \left| \frac{(Cprim - Cconf)}{\frac{(Cprim + Cconf)}{2}} \right| \otimes 100$$

Where
Cprim = concentration of the target compound on the primary column
Cconf = concentration of the target compound on the confirmation column

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If the relative percent difference is less than 40%, the presence of the target compound is confirmed and the higher concentration is reported. If, in the professional judgement of the analyst and supervisor, a peak within the retention time window can be reasonably excluded as a target, the result may be reported as a "non detect".

NOTE: The relative percent difference between any two numbers will be a maximum of 200%. A large relative percent difference may be acceptable at concentrations near the reporting limit. If in doubt about whether to report a peak as a quantitative result, consult the section supervisor.

If the %RPD is greater than 40%, evaluate the chromatograms to determine if matrix interferences are present on one or both columns. If interference is detected, flag the result to note the disparity between the results. Alternatively, dilute the extract to a level that removes the interference and report the RL from this dilution.

The following table summarizes the general guidance for the evaluating of chromatographic data.

PEAK INFORMATION	ACTION	REPORT(1)
No peaks found on primary or secondary column		Report < RL
Peak found within RTW on primary column	Peak is tentatively identified as the target. If, in the professional judgement of the analyst and supervisor, the peak within the RTW can be reasonably excluded as a target, the result may be reported as a "non detect".	If concentration < RL, report < RL If concentration > RL, evaluate confirmation column.
Peak found within RTW on confirmation column	Peak is tentatively confirmed as the target. If, in the professional judgement of the analyst and supervisor, the peak within the RTW can be reasonably excluded as a target, the result may be reported as a "non-detect".	If concentration < RL, report <RL If concentration >RL, calculate %RPD -if %RPD <=40, report highest concentration of primary and confirmation analyses -if %RPD >40, report the lowest result or the result that is most reasonable for the sample matrix. and flag result to note the disparity Case narrative or note to PM may be required for complex matrices.

(1)RL may be the STL Reporting Limit in Table 5 of the LQM or may be defined by the client QAP or contract.

The analyst must clearly show how the reported sample results were determined. Manual calculations and integrations must be documented as described in STL SOP AN65.

11.1.4 Identification "Tools"

Analysis by GC/MS (scan or SIM) may be used to confirm the presence of the target compounds (see SOP SM06: *Guidelines for SIM Analysis by GC/MS.)*

11.1.4.1 Relative Retention Time

The retention time of a surrogate compound provides useful information about the stability of the GC system. If the surrogate RT has not changed, it is probable that the target analytes RTs have not changed. The relative retention time can help the analyst to evaluate a peak:

$$RRT = \frac{RT_{target}}{RT_{surrogate}}$$

The relative retention time will remain fairly constant under the same GC conditions. The expected retention time of the target can be estimated from the RRT and the RT of the reference (in this case, the surrogate):

$$RT_{target} = RRT \times RT_{surrogate}$$

The analyst must be alert for the presence of matrix interferences and evaluate the data on both columns before making an identification. Another useful tool that employs a similar idea to the RRT is to "overlay" the sample chromatogram with the calibration standard. If the chromatograms are scaled the same, the overlay provides good visual cues to the identification of the target compound.

11.1.4.2 Co-Injection

Another useful "tool" is to add a known amount of the target analyte to a portion of the extract. The analysis of this "fortified extract" may provide chromatographic information that supports or refutes the initial identification. The analyst is cautioned to use this approach with discretion and with consultation with the GC supervisor. As a general rule, spike a portion of the extract with an amount of target analyte that will result in about a 2-fold increase in response.

NOTE: Do not perform this procedure until you have exhausted all other avenues and have consulted with the GC supervisor or other manager with GC experience.

11.1.5 Qualitative Analysis of Multiple Peak Compounds

Identification of multicomponent pesticides/PCBs is based on the recognition of their chromatographic patterns. Quantitation is performed using the area of characteristic peaks in the sample and standard using external calibration procedures.

If compound identification or quantitation is precluded due to interference (e.g., broad, rounded peaks or ill-defined baselines are present) cleanup of the extract may be warranted. Suggested cleanup options are given in Section 4.

11.1.5.1 PCBs as Aroclors

PCBs are generally reported as Aroclors. The Aroclors have varying levels of PCB congeners with the last two numbers in the Aroclor designation indicating the weight percent of chlorine. For example, AR1221 is 21% chlorine by weight; AR1260 is 60% chlorine by weight. The 12- in the Aroclor designation represents the biphenyl molecule. The exception to this naming convention is AR1016, which is about 42% chlorine by weight. (Note that AR1026 and AR1242 have similar chromatograms - both Aroclors have almost the same weight of chlorine by weight and nearly the same PCB congeners.)

Aroclors are identified by matching the pattern of the sample with standards analyzed under the same analytical conditions. Interference may occur due to the presence of non-target analytes or due to "weathering" of the Aroclor in the environment. The presence of multiple Aroclors will also complicate the identification and quantitation of the Aroclors. Many matrix interferences may be reduced or eliminated by treating the sample extract with copper, sulfuric acid, and permanganate prior to analysis. STL SL SOP EX60 details this procedure.

NOTE: Do not use the acid or permanganate cleanup on the entire extract if pesticides are also to be reported as many of the pesticides are not stable in acid or strong oxidizer.

When a pattern matching an Aroclor is encountered, it may be quantitated using either the 3-5 characteristic peaks (recommended) or total area response. Total area quantitation should only be used as detailed below. Residues of either AR1016 or AR1260 are quantitated using the average RF/CF determined during initial calibration. The other Aroclors are quantitated against the RF/CF determined from their single-point analysis during initial calibration. Samples should be diluted when the amount of PCB in a sample extract exceeds the calibration range defined in initial calibration. Note that the AR1660 standard defines the working range for all the Aroclors (i.e. if AR1660 was calibrated from 0.10ug/mL to 5.0ug/ml, and a sample extract was analyzed containing 10ug/ml of AR1232, that extract would require dilution to get the amount of AR1232 to be less than 5.0ug/ml.)

In the 3-5 peak approach, use each peak in the standard to calculate a calibration factor for that peak, using the total mass of PCB in the standard. These calibration factors are then used to calculate the concentration of each corresponding peak in the sample chromatogram and the 3-5 resulting concentrations are averaged to provide the final result for the sample.

"Weathering" is the loss of part of the Aroclor pattern due to biological or chemical degradation of individual PCBs. When weathering is suspected, try to match the later eluting peaks first. Flag the results for a weathered Aroclor pattern as tentatively identified and make a note in the case narrative if provided.

The presence of multiple Aroclors can be a problem to identify since most Aroclors have at least a few PCBs in common. The easiest case would be to have early and late eluting Aroclors present. The most difficult cases will involve the presence of Aroclors with the same relative chlorine level. In cases where the identification of Aroclors cannot be clearly determined, quantify the Aroclors against the Aroclor that most closely matches the pattern of the sample using the total area of all peaks within the pattern range. The result should be flagged and noted in the case narrative if provided.

NOTE: When choosing individual peaks for quantitation, compare their responses in the sample and standard. If the peaks chosen do not correlate well (i.e. ratios to other peaks are close) between the sample and standard, review the chromatograms for other possible peaks for quantitation.

11.1.5.2 Toxaphene

Toxaphene is a mixture of chlorinated camphenes, which has a complex and characteristic pattern when analyzed by GC-ECD. A single Toxaphene standard is analyzed during the initial calibration for the purpose of pattern identification in samples. When a Toxaphene residue is detected in sample(s), sample analysis is stopped. A calibration curve with at minimum of 5 points bracketing the instrument calibration range for Toxaphene should be analyzed. Alternatively, single points may be prepared with Toxaphene concentrations within 2x the Toxaphene quantity detected in the samples. Generally, the calibration curve option is simpler. After analysis of the Toxaphene standard(s), the samples are re-analyzed using these standard(s) for quantitation. Note that when analysis of Toxaphene-containing samples occurs over an extended time, the calibration factor should be verified or regenerated every 12 hours.

If the sample and standard chromatograms agree well, Toxaphene is quantitated using 5 characteristic peaks (similar to the PCB approach, above). If the sample and standard pattern do not agree as well (i.e. individual peak ratios do not agree as well, but all the major Toxaphene components in the standard are present in the sample), a total area integration is more appropriate. To measure total area, construct the baseline of Toxaphene in the sample chromatogram between the retention times of the first and last eluting Toxaphene components in the standard. Note that in order to use the total area approach, the pattern in the sample chromatogram must be compared to that of the standard to ensure that all of the major components in the standard are present in the sample and that extraneous peaks or humps (contributed by non-Toxaphene components) are NOT included in the quantitation.

When Toxaphene is determined using the 5 peak approach, the analyst must take care to evaluate the relative areas of the peaks chosen in the sample and standard chromatograms. It is highly unlikely that the peaks will match exactly, but the analyst should not employ peaks from the sample chromatogram whose relative sizes or areas appear to be disproportionately larger or smaller in the sample compared to the standard.

In the 5-peak approach, use each peak in the standard to calculate a calibration factor for that peak, using the total mass of Toxaphene in the standard. These calibration factors are then used to calculate the concentration of each corresponding peak in the sample chromatogram and the 5 resulting concentrations are averaged to provide the final result for the sample.

11.1.5.3 Technical Chlordane –

Technical Chlordane is a mixture of at least 11 major components and 30 or more minor components that is used to prepare specific pesticide formulations. The following components are significant: α and γ Chlordane, trans-Nonachlor, Heptachlor, and Heptachlor-epoxide. The α and γ Chlordane isomers are the most prevalent and their detection as single components is a good indicator that Technical Chlordane may be present.

The following sections discuss three specific options: reporting Technical Chlordane, reporting Chlordane (not otherwise specified-"NOS"), and reporting the individual Chlordane components that can be identified under their individual CAS numbers.

When the GC pattern of the residue resembles that of the Technical Chlordane standard, quantitate Chlordane residues by comparing the area of 3 to 5 major peaks. Heptachlor and heptachlor epoxide should not be included in this quantitation but rather should be quantitated and reported separately.

The GC pattern of a Chlordane residue in a sample may differ considerably from that of the Technical Chlordane standard. In such instances, it may not be practical to relate a sample chromatogram back to the lab's Technical Chlordane Standard. Therefore, depending on the objectives of the analysis, the analyst may choose to report the sum of all the identifiable Chlordane components as "Chlordane (n.o.s.)" under the CAS number 57-74-9. This option should only be used at the direction of or in consultation with a project manager.

The third option is to quantitate the peaks of a-Chlordane and y-Chlordane separately against the appropriate reference materials, and report these individual components.. This option should be used only after consultation with the project manager. Note that quantitation values determined from the individual chlordane isomers will be substantially lower than those reported for the technical product.

When a Technical Chlordane residue is detected in sample(s), sample analysis is stopped. A calibration curve with at minimum of 5 points bracketing the instrument calibration range for technical chlordane should be analyzed. Alternatively, single points may be prepared with technical chlordane concentrations within 2x the Technical Chlordane quantity detected in the samples. Generally, the calibration curve option is simpler. After analysis of the technical chlordane standard(s), the samples are re-analyzed using these standard(s) for quantitation. Note that when analysis of technical chlordane-containing samples occurs over an extended time, the calibration factor should be verified or regenerated every 12 hours. Note that these procedures are not necessary if the lab is reporting chlordane as the α and γ chlordane isomers, not as the technical product.

11.2 Calculations-External Standard

Aqueous/Liquid Samples

If the regression curve option is used, the sample concentration is calculated:

$$Concentration(ug/L) = Ccurve \otimes \frac{F \otimes DF}{V}$$

where
Ccurve = concentration of analyte from curve (ug/mL)
F = final volume of the extract (mL)
DF = dilution factor
V = volume of sample extracted (L)

If the calibration factor option is chosen for quantitation:

$$Concentration(ug/L) = \frac{response}{CF_{avg}} \otimes \frac{F \otimes DF}{V}$$

where
Response = area (or height) of the target
CF_{avg} = average calibration factor (ICAL)
F = final volume of the extract (mL)
DF = dilution factor
V = volume of sample extracted (L)

Soils/Solids Samples

Regression Curve

$$Concentration(ug/L) = Ccurve \otimes \frac{F \otimes DF}{W \otimes solids}$$

where
Ccurve = concentration of analyte from curve (ug/mL)
F = final volume of the extract (mL)
DF = dilution factor
W = weight of sample extracted (kg)
solids = (percent solids)/100

If the calibration factor option is chosen for quantitation:

$$Concentration(ug/kg,dw) = \frac{response}{CF_{avg}} \otimes \frac{F \otimes DF}{W \otimes solids}$$

where
response = area (or height) of the target
CF_{avg} = average calibration factor
F = final volume of the extract (mL)
DF = dilution factor
V = volume of sample extracted (L)
W = weight of sample extracted (kg)
solids = (percent solids)/100

11.3 Internal Standard Calibration

Aqueous Samples

$$Concentration(ug/L) = \frac{Ac}{Ais} \otimes \frac{Cis}{RRFavg} \otimes \frac{FV}{V} \otimes DF$$

where
Ac = area of the target compound
Ais = area of the internal standard
Cis= concentration of the internal standard (ug/mL)
RRFavg = average response factor of the target compound from the ICAL
FV = final volume of the extract(mL)
V = volume of sample extracted (l)
DF =dilution factor

Soil Samples

$$Concentration(ug/kg,dw) = \frac{Ac}{Ais} \otimes \frac{Cis}{RRFavg} \otimes \frac{FV}{W \otimes solids} \otimes DF$$

where
Ac = area of the target compounds
Ais = area of the internal standard
Cis= concentration of the internal standard (ug/mL)
RRFavg = average response factor of the target compound from the ICAL
FV = final volume of the extract(mL)
W =weight of sample extracted (kg)
Solids = (percent solids)/100
DF =dilution factor

12. 0 QUALITY ASSURANCE /QUALITY CONTROL

12.1 The **analytical batch** is discussed in SOP AN02: *Analytical Batching*, and these criteria are summarized in the SOP Summary included in Appendix C. Calculation of QC data is also given in AN02.

12.2 The **method detection limit (MDL)** must be determined annually in each matrix of concern in accordance with SOP CA90: *Procedure for Determination of Method Detection Limit (MDL).*

12.3 Each analyst must participate (individually or as part of a work group) in the analysis and evaluation of QC samples to demonstrate minimum proficiency in this procedure. The IDOC samples are processed in the same manner as routine samples and evaluated according to SOP CA92.

13.0 PREVENTIVE MAINTENANCE

No items are included in this revision. See Section 10 of the current LQM.

14.0 TROUBLESHOOTING

No items are included in this revision.

15.0 REFERENCES

1. *Test Methods for Evaluating Solid Waste, Third Edition with Revisions and Updates, SW-846*; U.S. EPA Office of Solid Waste and Emergency Response: Washington, DC, November, 1986.

2. *Code of Federal Regulations, Title 40, Part 136*; U.S. Government Printing Office: Washington, DC, July 1, 1988.

3. STL Savannah Laboratories' *Laboratory Quality Manual*, current revision.

Appendix A

TABLE 1		
Compound	RT COL 1	RT COL 2
Tetrachloro-m-xylene	5.26	6.65
Alpha-BHC	7.39	7.71
Gamma-BHC (Lindane)	8.63	8.65
Beta-BHC	8.80	8.39
Heptachlor	9.54	10.61
Delta-BHC	9.83	9.19
Aldrin	10.38	11.53
Heptachlor epoxide	11.96	12.51
Gamma-Chlordane	12.31	13.04
Alpha-Chlordane	12.72	13.41
Endosulfan I	12.86	13.42
4,4'-DDE	13.39	13.84
Dieldrin	13.63	14.05
Endrin	14.45	14.53
4,4'-DDD	14.75	14.83
Endosulfan I	14.97	14.78
4,4'-DDT	15.54	15.78
Endrin aldehyde	15.76	15.21
Endosulfan sulfate	15.98	15.71
Dibutyl chlorendate	16.73	17.80
Methoxylchlor	17.60	17.04
Endrin ketone	17.79	16.82
Decachlorobiphenyl	21.36	22.36
Technical chlordane	MR	MR
Toxaphene	MR	MR
AR 1221	MR	MR
AR1232	MR	MR
AR1016	MR	MR
AR1242	MR	MR
AR1248	MR	MR
AR1254	MR	MR
AR1260	MR	MR
Isodrin	11.85	12.45
Chlorobenzilate	14.51	14.79
AR1268	MR	MR

MR = multi-peak/multi-response compounds COL1 = DB608 COL2 = DB-5

Appendix B:CHLORINATED PESTICIDES AND PCBs STANDARDS

Routine Targets

Target compound	ISMA-1 (ug/mL)	ISMA-2 (ug/mL)	ISMA-3 (ug/mL)	ISMA-4 (ug/mL)	ISMA-5 (ug/mL)
TCMX, DCB (surr)	0.0025	0.0050	0.010	0.020	0.040
g-BHC(Lindane), Heptachlor, Heptachlor epoxide, Endosulfan I	0.0050	0.010	0.020	0.030	0.050
Dieldrin, p,p'-DDT, Endosulfan II, Endrin aldehyde, Methoxychlor	0.010	0.020	0.040	0.060	0.10

Target compound	ISMB-1 (ug/mL)	ISMB-2 (ug/mL)	ISMB-3 (ug/mL)	ISMB-4 (ug/mL)	ISMB-5 (ug/mL)
TCMX,DCB (surr)	0.0025	0.0050	0.010	0.020	0.040
a-BHC, b-BHC, d-BHC, a-Chlordane, g-Chlordane,	0.0050	0.010	0.020	0.030	0.050
p,p'-DDE, Endrin p,p'-DDD, Endosulfan sulfate, Endrin ketone	0.010	0.020	0.040	0.060	0.10

DDT/Endrin Breakdown Evaluation Standard

Pesticide Evaluation Standard	CONC (ug/mL)
Endrin,	0.020
P,P'-DDT	0.020

Appendix IX Targets

Target compound	ISMB-1 (ug/mL)	ISMB-2 (ug/mL)	ISMB-3 (ug/mL)	ISMB-4 (ug/mL)	ISMB-5 (ug/mL)
TCMX,DCB (surr)	0.0025	0.0050	0.010	0.020	0.040
Isodrin	0.0050	0.010	0.020	0.030	0.050
Chlorobenzilate	0.050	0.10	0.20	0.50	1.0
Kepone	0.025	0.050	0.10	0.20	0.50

APPENDIX B

Technical Chlordane Five-point Curve

STOCK STANDARD	TCHLOR -1*	TCHLOR -2*	TCHLOR -3*	TCHLOR -4*	TCHLOR -5*
Technical Chlordane	0.100	0.20	0.40	0.60	0.80
DCB, TCMX (surr)	0.0025	0.0050	0.010	0.020	0.040

Toxaphene Five-point Curve- 0.10, 0.25, 0.50, 1.0, 2.0ug/mL

STOCK STANDARD	TOX -1*	TOX -2*	TOX -3*	TOX -4*	TOX -5*
Toxaphene	0.10	0.25	0.50	1.0	2.0
DCB, TCMX (surr)	0.0025	0.0050	0.010	0.020	0.040

PCBs as Aroclors

AR1660 Standards

Calibration Std	AR1016(ug/mL)	AR1260(ug/mL)	surrogates
AR1660-1	0.10	0.10	0.0025
AR1660-2	0.20	0.20	0.0050
AR1660-3	0.50	0.50	0.010
AR1660-4	1.0	1.0	0.020
AR1660-5	2.0	2.0	0.040

Single Point Aroclor Calibration Standards

Calibration Standard	Single Pont Concentration (ug/mL)	Surrogate Concentrations (ug/mL)
AR1221	1.0	0.020
AR1232	1.0	0.020
AR1242	1.0	0.020
AR1248	1.0	0.020
AR1254	1.0	0.020

If required, five point curves for AR1221, AR1232, AR1242, AR1248, and AR1254 are prepared at the same concentrations as the AR1660 curve.

Appendix C

608/8081/8082 METHOD SUMMARY

HOLD TIMES

MATRIX	Preservative/ Storage*	Routine Container	Sample Hold Time	Extract Hold Time
Aqueous	None; 4C	1-L amber	7 days	40 days
Soil/ Sediment	none; 4C	500-mL	14 days	40 days
Waste	none; 4C	Glass	14 days	40 days
TCLP	none; 4C	1-L amber	7 days (after leaching procedure)	40 days

*Storage temperature is 4C with a control criteria of less than 6C with no frozen samples

EXTRACTION

Aqueous: Approximately 1L of sample (contents of container) using continuous or separatory funnel extraction at pH 5-9 with methylene chloride; exchange to hexane and concentrate to final volume of 10mL

Soil/Solids: Approximately 30g of sample using sonication with 1:1 acetone/hexane or 1:1acetone/methylene chloride; Concentrate to final volume of 10mL in hexane

Wastes: Approximately 1g of sample diluted to final volume of 10mL with hexane

ANALYSIS

Dual capillary columns with dual EC; 2-5uL injection into glass tee or y-splitter; external or internal standard calibration

SEQUENCE-600-series

Endrin/p,p'-DDT breakdown evaluation (daily-every 24 hours)
Initial Calibration- 3 point single peaks compounds 1 point all Aroclors 1 point toxaphene 1 point technical chlordane
Initial Calibration Verification (ICV)
Sample analyses
Continuing calibration verification (CCV)-daily-every 24 hours Single peak compounds AR1660
RL standard(optional; required by state or client QAP)
Sample analyses

Sequence continues until all samples have been analyzed or the CCV fails the acceptance criteria. If a multi-peak target compound is detected, the extract is reanalyzed with a 3-point curve.

SURROGATE(S):
Tetrachloro-m-xylene- 0.20ug/L
Decachlorobiphenyl-0.20ug/L

BATCH QC
Method blank
LCS/LCSD- full target of single peak analytes @ 0.20ug/L
MS/MSD- full target of single peak analytes @ 0.20ug/L

Appendix C

SEQUENCE-8000-series

STANDARD/SAMPLES
Endrin/p,p'-DDT breakdown (every 12 hours)
Initial Calibration- 5 point single peaks 5 point Ar1660(note1) 1 point Toxaphene 1 point tech Chlordane 1 point remaining Aroclors
Up to twenty sample extracts
Endrin/p,p'-DDT breakdown (every 12 hours)
Continuing calibration check midpoint single peaks and midpoint Ar1660(note1)
RL Standard(optional)-lowest point on the calibration curve if required by state or client QAP
Up to twenty sample extracts
Continuing calibration check-midpoint single peaks and midpoint Ar1660(note1)

The sequence continues until all samples have been analyzed or until the calibration verification fails the acceptance criteria. All samples extract analyses must be bracketed by acceptable verification standards.

Note 1-A mixture of Ar1016 and Ar1260 will be used to calibrate and verify the response for PCBs and to verify the response for Toxaphene and technical Chlordane in the continuing calibration.

SURROGATE (S):
Tetrachloro-m-xylene- 0.20ug/L
Tecachlorobiphenyl-0.20ug/L

BATCH QC
Method blank
LCS- LQM subset
MS/MSD- LQM subset

Parameter	Aqueous(ug/L)	Soils(ug/kg)
Lindane	0.20	6.0
Aldrin	0.20	6.0
Heptachlor	0.20	6.0
Dieldrin	0.50	15
Endrin	0.50	15
p,p'-DDT	0.50	15

Appendix C

QC CHECK	FREQUENCY	ACEPTANCE CRITERIA	CORRECTIVE ACTION
p,p'-DDT and Endrin breakdown check -required for 8000-series, recommended for 600-series	Initially and every 12 hours	% breakdown of both compounds less than 20%	-re-analyze check solution -perform injector port and/or column maintenance and re-analyze
Initial Calibration- 600-series:3 point minimum with lowest point at RL 8000-series:5 point minimum with lowest point at RL	Initially prior to sample analysis, when major instrument maintenance performed, or when CCV fails	**600-series:** 1) RSD of each target <= 10%; OR 2) plot regression curve CC>=0.99 for each target **8000-series:** 1) RSD of each target <= 20%; OR 2) plot regression curve CC>=0.99 for each target (see previous page for exceptions)	-Evaluate chromatogram and integrations. Check calculations. -Reanalyze standard(s) -Remake and reanalyze standard(s) -Perform instrument or column maintenance and reanalyze standards
Continuing calibration verification(CCV)	After every ten to twenty sample analyses and at the end of the sequence if external standard calibration is used	**600-series**: <=10% Difference/Drift **8000-series**: Percent difference or drift <= 15% (see previous page for exceptions) Retention time of CCV must fall within the daily retention time window	-Evaluate chromatogram and integrations. Check calculations. -Reanalyze standard(s) -Remake and reanalyze standard(s) -Perform instrument or column maintenance and reanalyze standards

Appendix C

QC CHECK	FREQUENCY	ACEPTANCE CRITERIA	CORRECTIVE ACTION
Method blank	Per batch	All targets reported less than RL in Section 5 of the STL LQM	-Evaluate chromatogram and integrations. Check calculations. -Reanalyze - Follow guidance in SOP AN02 and Table 13.1 in LQM
Lab control sample (LCS)- Subset of targets in STL SL LQM	Per batch (If MS/MSD cannot be performed , the LCS must be performed in duplicate)	Recoveries within STL-SL LQM Section 5 limits	-Evaluate chromatogram and integrations. Check calculations. -Reanalyze - Follow guidance in SOP AN02 and Table 13.1 in LQM
Matrix spike(MS) and matrix spike duplicate (MSD)	Per batch	Recoveries within STL-SL LQM Section 5 limits	-Evaluate chromatogram and integrations. Check calculations. -Reanalyze - Follow guidance in SOP AN02 and Table 13.1 in LQM
Internal Standard Response	All samples, method blanks, and QC	Response with a factor of two from the midpoint standard in the initial calibration sequence	-Evaluate chromatogram and integrations. -Reanalyze or dilute and reanalyze -Flag data
Surrogates	All samples, method blanks, and QC	Recoveries within STL-SL LQM Table 5 limits See section 11.1.1. for specifics	-Evaluate chromatogram and integrations. Check calculations. -Reanalyze - Follow guidance in SOP AN02 and Table 13.1 in LQM
Reporting limit(RL) standard-standard at the reporting limit used to verify sensitivity of the instrument	Daily(optional-see specific state or client requirements for frequency)	Detected with reasonable sensitivity	-Reanalyze RL standard -Remake and reanalyze RL standard -Perform instrument or column maintenance, recalibrate, and reanalyze associated samples

Appendix C

QC CHECK	FREQUENCY	ACEPTANCE CRITERIA	CORRECTIVE ACTION
Retention time window determination	See guidance in SOP AN66	See guidance in SOP AN66	Use guidance in SOP AN66: *Determination of Retention Time Windows in Gas Chromatographic Analyses*
Initial demonstration of Capability (the analyst has to perform the IDOC for either of the analogous 600 or 8000 series methods- not both)	Per work group or analyst	Within the 600- or 8000-series method limits (see SOP CA92)	-Reanalyze QC sample for the targets that failed to meet the criteria (see SOP CA92)
Method detection limit(MDL)	See SOP CA90	Evaluate data using criteria SOP CA90	-Evaluate data. Check calculations. -Reanalyze MDL samples.

SEVERN TRENT SERVICES

CHANGE -IN-PROGRESS ATTACHMENT

SOP Document No: SG45:01.05.00:6

SOP Description: Organochlorine Pesticides and PCBs by GC (Methods 608 and 8081A/8082)

Approval Signature: R. Wayne Robbins 6 Sept 2001
Date

Title: Technical Manager, QA

STL X Savannah __ Tallahassee __ Mobile __ Tampa West

The following revisions or additions have been made to the referenced SOP.

The following attachments are for a specific project and will be effective from the date of approval until the date that the project is completed. The purpose of this CIPA is to document changes or additions to the standard operating procedures requested for the Sauget Area 2 Sites Group and EPA Region V.

The attachments are tables of the project RLs and MDLs, including the QC limits, and an excerpt from the Sauget Area 2 Sites Group QAPP.

SEVERN TRENT SERVICES

Chlorinated Pesticides by GC (8081) Water

PARAMETER	METHOD	%REC	%RPD	MDL(ug/L)	RL(ug/L)
Aldrin (MS)	8081	38-129	<=25	0.0054	0.050
alpha BHC	8081	46-131	<=30	0.0051	0.012
beta BHC	8081	36-153	<=35	0.0060	0.012
delta BHC	8081	53-137	<=41	0.0090	0.012
gamma BHC (Lindane) (MS)	8081	40-139	<=26	0.0048	0.012
alpha Chlordane	8081	55-125	<=17	0.0048	0.050
gamma Chlordane	8081	54-128	<=18	0.0043	0.050
Technical Chlordane	8081	54-140	<=30	0.068	0.50
Chlorobenzilate	8081	50-150	<=40	0.16	0.50
4,4'-DDD	8081	32-155	<=39	0.0082	0.10
4,4'-DDE	8081	48-145	<=18	0.0095	0.10
4,4'-DDT (MS)	8081	50-147	<=27	0.0091	0.10
Dieldrin (MS)	8081	34-150	<=42	0.0060	0.10
Endosulfan I	8081	34-161	<=24	0.0048	0.050
Endosulfan II	8081	40-162	<=22	0.0065	0.10
Endosulfan sulfate	8081	28-156	<=28	0.0088	0.10
Endrin (MS)	8081	41-158	<=25	0.011	0.10
Endrin aldehyde	8081	20-146	<=34	0.0088	0.10
Endrin ketone	8081	42-122	<=25	0.0085	0.10
Heptachlor (MS)	8081	37-148	<=26	0.0040	0.050
Heptachlor epoxide	8081	43-141	<=31	0.0048	0.050
Isodrin	8081	55-110	<=40	0.0097	0.050
Methoxychlor	8081	60-155	<=43	0.0068	0.50
Toxaphene	8081	12-130	<=30	0.38	5.0
Surrogates					
2,4,5,6-Tetrachloro-m-xylene (TCMX)	8081	30-150	NA	NA	NA
Decachlorobiphenyl (DCB)	8081	30-150	NA	NA	NA

Chlorinated Pesticides by GC (8081) Soils

PARAMETER	METHOD	%REC	%RPD	MDL(ug/L)	RL(ug/L)
Aldrin (MS)	8081	10-144	<=38	0.29	1.7
alpha-BHC	8081	22-101	<=40	0.12	0.42
beta-BHC	8081	12-120	<=40	0.12	0.42
Gamma-BHC (Lindane) (MS)	8081	12-138	<=37	0.11	0.42
delta-BHC	8081	10-142	<=47	0.25	0.42
alpha Chlordane	8081	45-140	<=40	0.097	1.7
Gamma Chlordane	8081	11-141	<=40	0.1	1.7
Technical Chlordane	8081	45-119	<=40	1.5	17
Chlorobenzilate	8081	50-150	<=40	7.4	17
4,4'-DDD	8081	28-134	<=50	0.34	3.3
4,4'-DDE	8081	34-121	<=25	0.3	3.3
4,4'-DDT (MS)	8081	29-134	<=26	0.54	3.3
Dieldrin (MS)	8081	28-137	<=30	0.26	3.3
Endosulfan I	8081	10-141	<=40	0.12	1.7
Endosulfan II	8081	10-159	<=65	0.39	3.3
Endosulfan sulfate	8081	26-144	<=50	0.34	3.3
Endrin (MS)	8081	33-149	<=32	0.38	3.3
Endrin aldehyde	8081	10-130	<=86	0.38	3.3
Endrin ketone	8081	29-112	<=31	0.3	3.3
Heptachlor (MS)	8081	17-138	<=38	0.19	1.7
Heptachlor epoxide	8081	15-142	<=40	0.13	1.7
Isodrin	8081	10-150	<=50	1.2	3.3
Methoxychlor	8081	24-152	<=40	0.28	17
Toxaphene	8081	41-126	<=50	11	170
Surrogates					
Tetrachloro-m-xylene (TCMX)	8081	30-150	NA	NA	NA
Decachlorobiphenyl (DCB)	8081	30-150	NA	NA	NA

SEVERN TRENT SERVICES

Table 7C. *Pesticides SW-846 Method 8081A, Herbicides SW-846 Method 8151A, and TPH, as Diesel range organics (DRO) SW-846 Method 8015B Quality Control Requirements and Corrective Actions.*

Audit	Frequency	Control Limits	Corrective Action
Holding times	Samples must be extracted and analyzed within holding time.	Extract within 7 days for aqueous and 14 days for soil samples from collection. Analyze extracts within 40 days.	If holding times are exceeded for initial or any re-analyses required due to QC excursions, notify QAO immediately since re-sampling may be required.
Initial Calibration	Prior to start up and when criteria are exceeded for continuing calibration.	1. Minimally five concentrations, one calibration standard must be at concentration less than or equal to the PQL. 2. Toxaphene, technical chlordane require a single point calibration. If detected in samples, the samples are re-analyzed behind a five point calibration for each detected analyte. 3. If RSD <20% the average RRF may be used for quantitation. If RSD >20% a first or second order calibration curve with a correlation coefficient >0.99 must be used for quantitation.	1. Identify and correct problem. 2. Recalibration instrument; samples must not be analyzed until initial calibration criteria are met.
Calibration Verification	Calibration standards must contain target compounds at mid-range concentration. Minimally, analyze calibration standards daily and every 12 hours. Calibration verification standards should be analyzed every 20 samples.	%D <15%	1. Reanalyze. 2. If criteria are still not met, identify and correct problem, recalibrate; reanalyze samples back to last compliant calibration standard. Samples must be bracketed by compliant calibration standards. If the laboratory chooses to apply the grand mean exception (average % drift or % difference is less than 15%), the QAO* will be contacted prior to proceeding with analysis.
Retention Time Windows	Retention time windows must be established in accordance with USEPA method 8000 or relative retention times must be used if internal standards are employed.	Compounds must be within established retention time windows or within laboratory established relative retention time criteria for the succeeding calibration standards.	1. Reanalyze. 2. If criteria are still not met, identify and correct problem, recalibrate; reanalyze samples back to last compliant calibration standard.

SEVERN TRENT SERVICES

Table 7C. *Pesticides SW-846 Method 8081A, Herbicides SW-846 Method 8151A, and TPH, as Diesel range organics (DRO) SW-846 Method 8015B Quality Control Requirements and Corrective Actions.*

Audit	Frequency	Control Limits	Corrective Action
Surrogate Spike	Samples, blanks, MS/MSDs, and LCSs must be spiked with method specific surrogate compounds.	1. Recovery within laboratory control limits. 2. Corrective action is not required if one of the two required surrogates has recovery outside of control limits if the recovery is >10%.	1. Reanalyze 2. If recovery is still outside control limits but >10%, document in case narrative report. 3. If recovery is <10% with re-analysis, re-extract and re-analyze the sample if the holding time has not elapsed. If holding time has elapsed, notify the QAO immediately prior to proceeding since resampling may be required. Special Circumstances: If matrix interferences is present (as demonstrated by the lab and documented in the case narrative): 1. Reanalyze (may be at a higher dilution) 2. If surrogate standard is >10%, report runs. 3. In surrogate standard is <10%, contact QAO*.
Identification	Samples, blanks, and QC data.	1. Retention times must be within established retention time windows or must meet relative retention time criteria. 2. Confirmation analysis is required.	1. Investigate problem; re-analyze calibration standards to check for retention time shift.
Quantitation	Samples, blanks, and QC data.	1. Internal and external standard method. Verify concentration is within linear calibration range. 2. For DROs, use the sum of the areas of peaks eluting between C10 and C28. 3. Every effort must be made to meet specified PQL requirements. Soil samples concentrations must be corrected to dry weight.	1. If concentration is above linear calibration range, dilute sample and re-analyze. Dilution should result in concentration in the upper calibration range of the instrument.
Field/ Equipment Blank Analysis	Collected one per sampling equipment and after every 10 samples.	Compounds concentrations must be <PQL.	1. Investigate problem; re-analyze to verify laboratory cross contamination is not a factor. 2. Notify the QAO immediately since resampling may be necessary.

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EPA RESPONSE

ATTACHMENT E

CHLORINATED HERBICIDES
(615 and 8151A)

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1.0 SCOPE AND APPLICATION

1.1 This procedure can be used to determine the concentration of various chlorinated herbicides in water, groundwater, leachate, soil, sediment, and waste samples extracts. Table 1 lists the target compounds and the retention times for each target compound.

1.2 The reporting limit (RL), the method detection limit (MDL), and the accuracy and precision criteria are given in Section 5 of the current revisions of the Savannah Laboratories' quality assurance plans.

2.0 SUMMARY OF METHOD

2.1 A known volume or weight of sample is extracted in accordance with SL SOP EX45. The extracted chlorinated herbicide methyl derivatives are analyzed by gas chromatography (GC) configured with dual capillary columns and dual electron capture (EC) detectors. This configuration allows for simultaneous detection and confirmation of the herbicides. Identification of the target compounds in samples is done by comparing the retention times of the peaks with standards analyzed under the same GC conditions.

GC/MS confirmation may be employed if the target compound concentration is sufficiently high or if the extract is concentrated to an appropriate final volume. The esterified extract must be used for the GC/MS confirmation-do not use the 8270 extract.

2.2 This SOP is based on the guidance in SW-846 Method 8000B and Method 8151A and EPA Method 615.

3.0 SAFETY

3.1 Use good common sense when working in the lab. Do not perform any procedures that you do not understand or that will put you or others in potentially dangerous situations.

3.2 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined. Each chemical compound should be treated as a potential health hazard. Exposure to these chemicals must be reduced to the lowest level possible. Lab coats, gloves, and eye protection(lab glasses or face shields), must be worn. Standards and highly contaminated samples should be handled in a hood.

3.3 Material Safety Data Sheets (MSDS) are available to the analyst at each lab division. These sheets specify the type of hazard that each chemical poses and the procedures that are used to safely handle these materials.

3.4 Diethyl ether is a flammable solvent and it must be used in a well-ventilated hood or extraction area. The solvent vapors will tend to accumulate along the floor. High concentrations of diethyl ether can cause drowsiness, dizziness, and headache.

4.0 INTERFERENCES

4.1 Method interferences may be caused by contaminants in solvents, reagents, or glassware. The glassware must be scrupulously cleaned (SL SOP AN60: Glassware Cleaning Procedures). All of the materials and reagents must be demonstrated to be free from contaminants by the analysis of reagent blanks (method blanks). Glassware and/or extraction vessels that have not been properly cleaned may contribute artifacts that make identification and quantification of the target compounds difficult.

4.2 Matrix interferences may be caused by contaminants that are extracted from the sample matrix. The sample may require dilution prior to analysis to reduce or eliminate the interferences. The extraction procedure described in SL SOP EX45 has several steps that are designed to eliminate or minimize interferences due to sample matrix.

5.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

5.1 Aqueous samples are routinely collected in 1-L amber glass containers equipped with Teflon-lined caps. No preservative is required. The sample is iced at the time of collection and stored at 4C (less than 6C with no frozen samples) in the lab. Sample must be extracted within seven (7) days of collection and the extract must be analyzed within forty (40) days of extraction.

TCLP leachate samples are stored in the same manner as aqueous field samples. The extraction must be performed within seven(7) days of the leaching procedure and the extract analyzed within forty(40) days of extraction

5.2 Soils, sediments, sludges, and wastes are collected in glass containers equipped with Teflon-lined caps. The routine container is 500-mL glass. Larger or smaller containers may be supplied. No preservative is required. The samples are iced at the time of collection and stored at 4C (less than 6C with no frozen samples) in the lab. The hold time for herbicides in solid and non-aqueous matrices is 14 days from the date of collection. The extract must be analyzed within 40 days of extraction.

6.0 APPARATUS AND MATERIALS

6.1 Gas chromatograph equipped with dual electron capture detectors and automatic liquid samplers.

6.2 Recommended Columns:

J&W DB-5 fused silica column, 30M x 0.53mm ID, 1.5um film
J&W DB-608 fused silica column, 30M x 0.53mm ID, 0.83um film

6.3 Data system compatible with the GC and capable of detecting and storing chromatographic data. Nelson 2600 or equivalent

6.4 Autosampler vials, septa, and caps

6.5 Microsyringes- 10-uL, 25-uL, 50-uL, 100-uL

7.0 REAGENTS

Hexane: Pesticide grade or equivalent

8.0 STANDARDS

Calibration and spike solutions are prepared from either certified stock solutions or from stock solutions purchased from vendors or from stock standards prepared from neat materials. Certificates of analysis or purity must be received with all neat compounds or stock solutions. All preparation steps must be in accordance with SL SOP AN41:*Standard Material Traceability*.

Preparation of the Calibration Standards

If the stock standard is prepared using the free acid form, no correction is required for the concentration. The concentration of the standard is based on the weight of free acids added per unit volume prior to derivitization. A stock standard prepared from neat herbicide acids has to be derivitivized prior to analysis. If a herbicide standard is purchased as a neat methyl ester, the concentration of the standard must be corrected to the free acid concentration. See SL SOP AN43: Standard Preparation for guidance on the preparation of standards.

The calibration standards must be corrected to the weight of the acid. This will eliminate the need to correct the final concentration of the sample. The correction factors are given in Table 2.

The stock standards are prepared in hexane from either the stock standard mixes purchased from vendors or from the individual stock standards prepared in-house. An example of the preparation of the calibration

standard is given in Table 3

9.0 SAMPLE PREPARATION

Sample preparation steps are given in SL SOP EX45.

10.0 PROCEDURE

10.1 GC Conditions

The columns and analytical conditions listed in this section are given for guidance. The lab must document the actual columns and conditions used for each analysis in the instrument maintenance, data system, or on the sample log.

10.1.1 Recommended Columns:

J&W DB-5 fused silica column, 30M x 0.53mm ID, 1.5um film
J&W DB-608 fused silica column, 30M x 0.53mm ID, 0.83um film

The columns are connected to a single injection port with either a glass Tee-splitter or a glass y-splitter. This configuration allows for the simultaneous analysis and confirmation of the target compounds.

Carrier gas flow: He at approximately 7mL/min (per column)
Make-up gas flow: N2 at approximately 25mL/min (per detector)

10.1.2 Suggested GC temperature programs

APP 9 temperature program:
Initial temperature: 170 C
Initial hold time: 4 minutes
Program rate: 8 C / minute
Final temperature: 280 C
Final hold: 2 minutes
TOTAL TIME: 20 minutes

8151 Full List temperature program
Initial temperature: 100 C
Initial hold time: 2 minutes
Program rate: 8 C / minute
Final temperature : 280-C
Final hold: 2 minutes
TOTAL TIME: 27 minutes

10.1.3 Heated zone temperatures

Injector: 240-260 C
Detector: 300C

10.1.4 Injection volume: 2-4uL (1-2-uL per column)

10.2 Initial Calibration
The external standard calibration technique is routinely employed for the determination of the concentration of herbicides. The lab also has the option of using internal standard calibration. Pentachloronitrobenzene (PCNB) may be a suitable compound to use as an internal standard

10.2.1 Prepare and inject the calibration standards using the guidelines listed in Section 8 of this SOP. Injector port and column maintenance should be performed on the instrument prior to the analysis of the initial calibration standards. Guidance for establishing the analytical sequence is given in Section 10.3.

Note that the following offers two (2) options for calibration and quantitation – average RF or regression curve. Only one need be chosen per analyte.

When more calibration standards are analyzed than required, individual compounds may be eliminated from the lowest or highest concentration level(s) only. If points or levels are eliminated, analyte concentration in samples must fall within the range defined by the resulting curve. In no case should individual points in the middle of a calibration be eliminated without eliminating the entire level.

10.2.2 Evaluate the standard chromatograms. Some questions to ask at this point are:

>Is there contamination in the hexane blank? If so, has maintenance been performed on the instrument lately? Has the septum been changed?

>Did all of the standards inject properly? Are there peaks for each of the standards analyzed? Do the patterns look normal?

>Are the peaks symmetrical? Is there tailing or fronting?

>Are the areas of the peaks normal for the sensitivity setting being used?

Inspect each chromatogram to ensure that the peaks are properly identified and that the correct areas have been associated with the corresponding standard peak RT in the data system tabulation.

10.2.3 Average RF/CF Option:

Calculate the response factor of each calibration standard, the average response factor and the relative standard deviation using the following equations:

Response Factor-external standard

$$X_{RF} = \frac{mg/mL}{area} = \frac{mg}{mL\ area}$$

Note that the inverse relationship can also be used to evaluate the response of the detector. Dividing the area of the standard by the concentration is referred to as the calibration factor.

Response factor-internal standard

$$RF = \frac{Ac}{Ais} \otimes \frac{Cis}{Cc}$$

where

Ac = area of the target compound
Ais = area of the internal standard
Cc = concentration or mass on-column of the target compound (ug/mL)
Cis = concentration or mass on-column of the internal standard (ug/mL)

Average Response Factor

$$RF_{avg} = \frac{RF_1 + RF_2 + RF_3 + \ldots RFn}{n}$$

Relative Standard Deviation

$$\% RSD = \frac{standard\ deviation}{\overline{RF}} \otimes 100$$

and

$$Standard\ Deviation = \sqrt{\frac{\sum_{i=1}^{n}(RF_i - \overline{RF})^2}{n-1}}$$

Where

RF_i = response factor of the individual calibration level
$\overline{RF}$ = average response factor

Initial Calibration Criteria:

600-series: If the relative standard deviation is less than 10% for the target compounds in the initial calibration, the calibration is considered linear and the average response factor (or calibration factor) may be used for quantitation.

8000-series:If the relative standard deviation is less than 20% for the target compounds in the initial calibration, the calibration is considered linear and the average response factor (or calibration factor) may be used for quantitation.

8000-series ICAL grand mean exception:
If one or more compounds exceed the %RSD criteria, the average response factors can be used for quantitation if the average %RSD of ALL of the compounds (the grand mean) in the ICAL is less than or equal to 20%.

NOTE: If a target compound that passes by the "grand mean exception" is detected (>RL), the PM is notified via an anomaly report or case narrative. If the targets are <RL, no notification is required since the lab has demonstrated that the lowest standard in the calibration curve (the equivalent of the RL) can be detected.

10.2.4 Regression Curve Option: A calibration curve is established for each analyte by plotting the concentration along the x-axis and the corresponding response along the y-axis. If the correlation coefficient of the regression curve is greater than 0.99, the curve can be used to quantify samples.

NOTE: Linear regression curves must be used for South Carolina DHEC compliance samples. See pre-project plans and client QAPs for other exceptions to using non-linear curve fitting.

10.3 Calibration Verification

Calibration is verified every 24 hours for 600-series methods and every 12 hours or 20 samples, whichever is more frequent, for 8000-series methods by the analysis of continuing calibration check standards. Note that the following criteria apply to calibration standards analyzed before and after samples. In situations where compounds fail criteria high and no positive for the compound(s) failing high are detected, these samples may be reported.

10.3.1 Analyze the mid-level standard(s). Tabulate the area of the target analytes and calculate the response factors if using the average RF/CF option. If using the calibration curve option, calculation of the RF is unnecessary.

Calculate the percent drift or percent difference between the initial and continuing calibration:

$$\%Drift = \frac{result - expected}{expected} x\ 100$$

Where
result = concentration or nanograms on-column of the calibration check standard quanted against the curve
expected = true concentration or nanograms on-column of the calibration check standard

$$\%Difference = \frac{RF_{init} - RF_{cont}}{RF_{init}} x\ 100$$

Where
RF_{init} = average response factor from the initial calibration curve
Rf_{cont}= response factor from the continuing calibration standard

10.3.2 Continuing Calibration Verification Criteria

If the CCV criterion is not met, another CCV should be analyzed. Repeated failure may be a sign of instrument or standard degradation. If the calibration verification criteria cannot be met, a new initial calibration must be prepared, analyzed, and evaluated.

600-series: If the percent drift or percent difference is less than or equal to 10%, the initial calibration is verified and the average response factor or regression curve can be used for quantitation.

8000-series: If the percent drift or percent difference is less than or equal to 15%, the calibration curve is verified and the average response factor is used for quantitation.

8000-series CCAL grand mean exception:
If one or more compounds exceed the %drift or %difference criteria, the average response factor from the initial calibration can be used for quantitation if the average %drift or %difference of ALL of the compounds (the grand mean) in the CCV is less than or equal to 15%.

NOTE: If a target compound that passes by the "grand mean exception" is detected (>RL), the PM is notified via an anomaly report or case narrative. If the targets are <RL, no notification is required.

External Standard CCV: Samples analyzed by external standard calibration require bracketing by CCV. If the CCV standard analyzed after the samples fails to meet the acceptance criteria and the response of the mid point standard is *above* the criteria (that is the response of the analytical system has increased), samples which have no target compounds detected above the RL may be reported as <RL, since the compounds would have been detected if present. (SW-846 Method 8000B).

10.4 Sample Analysis Sequence
The analytical sequences for the 600- and 8000-series methods are given in the SOP Summary after Section 15.

10.4.1 The sample extract is injected using the same injection volume used for the calibration standards. Extracts that are known to be relatively clean should be analyzed first. Extracts suspected of containing high concentrations should be analyzed last. Instrument blanks (hexane) may be analyzed after suspected high concentration samples to allow the detector response to stabilize.

10.4.2 If the concentration of target compounds exceeds the working range (defined by the highest standard in the initial calibration), the extract must be diluted and reanalyzed. A dilution should bring the area of the largest peak of interest into the upper half of the calibration curve. For the single point multicomponent products, the extract should be diluted until the area is no more than a factor of two above the area of the single point standard (see section 11.1 for quantitation of multi-peak target compounds).

NOTE: Unless otherwise specified by a client or QA plan, results from a single dilution are reportable as long as the largest target analyte (when multiple analytes are present) is in the upper half of the calibration range. When reporting results from dilutions, appropriate data flags should be used (*F34 or *F42) or qualification in a case narrative provided to the client. For TCLP analyses, every effort should be made to achieve the regulatory level without substantial instrument overload.

For clients who demand we provide lower detection limits, a general guide would be to report the dilution detailed above and one additional run at a dilution factor 1/10 the dilution factor with the highest target in the upper half of the calibration curve (i.e., a sample analyzed at a DF of 50 resulting in a hit in the upper half of the calibration curve would be reanalyzed at a DF of 5 to provide lower detection limits to the client). Project managers and lab staff must work together to balance client satisfaction with productivity.

10.5 Determination of Retention Time Windows

The procedure for the determination of retention time windows is given in SL SOP AN66: Determination of Retention Time Windows for Gas Chromatographic Analyses. If internal standard calibration is used, the determination of absolute retention time windows is not required. Relative retention times, as described in Section 11.4, are used to identify the target compounds.

11.0 DATA ANALYSIS/CALCULATIONS

The evaluation of chromatograms for target compounds must take into account the calibration of the analytical system (initial and continuing calibration response and retention times), the recovery and retention time shift of the surrogate compounds, whether the peak response falls within the working range of the calibration, and the integration of the peaks. Manual integration must be documented in accordance with SL SOP AN65. The analyst must also take into account the results from the method blank and lab control sample before reporting quantitative data.

The judgement and experience of the analyst and his/her colleagues is an important part of the evaluation of chromatographic data. The analyst should ask:

- Is there previous data or current information about the sample that would aid in evaluating the data?
- Do the peaks look normal?
- Are peaks correctly integrated?
- Are there co-eluting peaks or matrix interferences?

11.1 Qualitative analysis

Identification of the target compounds is based on retention time. The analyst should scan the sample chromatogram for the target compounds on the primary analytical column. The analyst should use the retention time (RT) window calculated around the CCV as guidance for the identification of the target compounds. The analyst should also note shifts in the retention times of the surrogate compounds to help gauge possible shifts in the RT of the target compounds. See SL SOP AN66.

NOTE: It is important to note that the retention time window applies only to peaks that are within the calibration range of the curve. Peaks areas that exceed the established linear range of the calibration curve may result in significant retention time shifts; therefore, all peaks which have significant areas and elute closely to a target compound should be tentatively identified as a target compound and evaluated as such. Peaks over-range are handled using dilutions as detailed above (10.3.2).

11.1.1 The surrogate should be evaluated first to check for shifts in retention times and to evaluate the surrogate recovery.

The extract contains the surrogate Dichloroacetic acid (DCAA). The recovery criteria are given in Section 5 of the SL QAPs.

Given the complicated nature of GC-ECD chromatograms, assessing surrogate recovery is frequently complicated by co-eluting positive and negative interferences. Generally, it is expedient to calculate the recovery on one chromatogram. If this recovery is acceptable, the other channel is not evaluated for recovery. If interferences are suspected, evaluate recovery on the other channel. Note that given this nature, an extract is considered acceptable if one of the 2 potentially calculated recoveries is acceptable.

NOTE: If the recovery of the surrogate is above the upper control limit and no target compounds are detected in the sample, results may be reported. Refer to section 13 of the current QA Plan regarding this issue.

11.1.2 Label and calculate the concentration of each peak that corresponds to a target compound. Observe the general appearance of the chromatogram for possible dilutions, matrix interferences and the overall shapes of the peaks.

If the concentration is below the detection limit, the reporting limit (RL) for that compound is calculated (Section 11.2). The RL is calculated for all target compounds that are not detected on the primary analytical column. Peaks over-range are handled using dilutions as detailed above (10.3.2).

NOTE: If a peak is over range on the primary column, evaluate the confirmation column. If no peak is detected or if the concentration is within the calibration range, the analysis at a dilution is not necessary.

11.1.3 If the result for a target is above the reporting limit (RL) on the primary column, evaluate the confirmation column. Use the retention time window calculated using the CCV as guidance for the identification of the target compounds. Note shifts in the retention times of the surrogate compounds to help gauge possible shifts in the RT of the target compounds.

If the target compound is detected on the confirmation column, the concentration of the target compound is calculated and compared to the result from the primary column. The relative percent difference is calculated:

$$\%RPD = \left| \frac{(Cprim - Cconf)}{\frac{(Cprim + Cconf)}{2}} \right| \otimes 100$$

Where
Cprim = concentration of the target compound on the primary column
Cconf = concentration of the target compound on the confirmation column

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If the relative percent difference is less than 40%, the presence of the target compound is confirmed and the lower concentration is reported.

NOTE: The relative percent difference between any two numbers will be a maximum of 200%. A large relative percent difference may be acceptable at concentrations near the reporting limit. If in doubt about whether to report a peak as a quantitative result, consult the section supervisor.

If the %RPD is greater than 40%, evaluate the chromatograms to determine if matrix interferences are present on one or both columns. If interference is detected, flag the result to note the disparity between the results. Alternatively, dilute the extract to a level that removes the interference and report the RL from this dilution.

The following table summarizes the general guidance for the evaluating of chromatographic data. The table assumes that the calibration criteria have been met and that the sample has acceptable associated surrogate and lab spike recoveries.

PEAK INFORMATION	ACTION	REPORT*
No peaks found on primary or secondary column		Report < RL
Peak found within RTW on primary column	Peak is tentatively identified as the target	If concentration < RL, report < RL If concentration > RL, evaluate confirmation column.
Peak found within RTW on confirmation column	Peak is confirmed as the target	If concentration <RL, report <RL If concentration >RL, calculate %RPD -if %RPD <40%, report lower concentration of primary and confirmation analyses. -if %RPD >40%, flag result to note the disparity Case narrative or note to PM may be required for complex matrices.

*RL may be the SL Reporting Limit in Table 5 of the CQAP or may be defined by the client QAP or contract.

The analyst must clearly show how the reported sample results were determined.

11.1.4 Identification "Tools"

Analysis by GC/MS (scan or SIM) may be used to confirm the presence of chlorinated herbicides (see SL SOP SM06: *Guidelines for SIM Analysis by GC/MS.)* The herbicide extract must be used to perform the GC/MS confirmation-unesterified extracts (e.g., the GC/MS extract) are not suitable for herbicide analysis or confirmation.

11.1.4.1 Relative Retention Time

The retention time of a surrogate compound provides useful information about the stability of the GC system. If the surrogate RT has not changed, it is probable that the target analytes RTs have not changed. The relative retention time can help the analyst to evaluate a peak:

$$RRT = \frac{RT_{target}}{RT_{surrogate}}$$

The relative retention time will remain fairly constant under the same GC conditions.. The expected retention time of the target can be estimated from the RRT and the RT of the reference (in this case, the surrogate):

$$RT_{target} = RRT \times RT_{surrogate}$$

The analyst must be alert for the presence of matrix interferences and evaluate the data on both columns before making an identification.

11.1.4.2 Co-Injection

Another useful "tool" is to add a known amount of the target analyte to a portion of the extract. The analysis of this "fortified extract" may provide chromatographic information that supports or refutes the sinitial identification. The analyst is cautioned to use this approach with discretion and with consultation

with the GC supervisor. As a general rule, spike a portion of the extract with an amount of target analyte that will result in about a 2-fold increase in response.

NOTE: Do not perform this procedure until you have exhausted all other avenues and have consulted with the GC supervisor or other manager with GC experience. The extract must be fortified with herbicides as methyl esters-unesterified herbicides are not amenable to GC analysis.

11.2 Calculations-External Standard

Aqueous/Liquid Samples

If the regression curve option is used, the sample concentration is calculated:

$$Concentration(ug/L) = Ccurve \otimes \frac{F \otimes DF}{V}$$

where
Ccurve = concentration of analyte from curve (ug/mL)
F = final volume of the extract (mL)
DF = dilution factor
V = volume of sample extracted (L)

If the response factor option is chosen for quantitation:

$$Concentration(ug/L) = \frac{ug/mL}{response} \otimes response \otimes \frac{F \otimes DF}{V}$$

where
F = final volume of the extract (mL)
DF = dilution factor
V = volume of sample extracted (L)

Soils/Solids Samples

Regression Curve

$$Concentration(ug/L) = Ccurve \otimes \frac{F \otimes DF}{W \otimes solids}$$

where
Ccurve = concentration of analyte from curve (ug/mL)
F = final volume of the extract (mL)
DF = dilution factor
W = weight of sample extracted (kg)
solids = (percent solids)/100

If the response factor option is chosen for quantitation:

$$Concentration(ug/kg,dw) = \frac{ug/mL}{response} \otimes response \otimes \frac{F \otimes DF}{W \otimes solids}$$

where
F = final volume of the extract (mL)
DF = dilution factor
V = volume of sample extracted (L)
W = weight of sample extracted (kg)
solids = (percent solids)/100

11.3 Internal Standard Calibration

Aqueous Samples

$$Concentration(ug/L) = \frac{Ac}{Ais} \otimes \frac{Cis}{RRFavg} \otimes \frac{FV}{V} \otimes DF$$

where
Ac = area of the target compounds
Ais = area of the internal standard
Cis= concentration of the internal standard (ug/mL)
RRFavg = average response factor of the target compound from the ICAL
FV = final volume of the extract(mL)
V = volume of sample extracted (l)
DF =dilution factor

Soil Samples

$$Concentration(ug/kg,dw) = \frac{Ac}{Ais} \otimes \frac{Cis}{RRFavg} \otimes \frac{FV}{W \otimes solids} \otimes DF$$

where
Ac = area of the target compounds
Ais = area of the internal standard
Cis= concentration of the internal standard (ug/mL)
RRFavg = average response factor of the target compound from the ICAL
FV = final volume of the extract(mL)
W =weight of sample extracted (kg)
Solids = (percent solids)/100
DF =dilution factor

12. 0 QUALITY ASSURANCE /QUALITY CONTROL

12.1 The **analytical batch** is discussed in SL SOP AN02: *Analytical Batching*, and these criteria are summarized in the SOP Summary included in this SOP. Calculation of QC is also given in AN02.

12.2 The **method detection limit (MDL)** is defined as the concentration of the an analyte that can be measured with a 99% confidence that the result is greater than zero. See SL SOP CA90: *Procedure for Determination of Method Detection Limit (MDL).*

13.0 PREVENTIVE MAINTENANCE

No items are included in this revision. See Section 10 of the current SL QAP.

14.0 TROUBLESHOOTING

No items are included in this revision.

15.0 REFERENCES

1. *Test Methods for Evaluating Solid Waste, Third Edition with Revisions and Updates, SW-846*; U.S. EPA Office of Solid Waste and Emergency Response: Washington, DC, November, 1986.

2. *Code of Federal Regulations, Title 40, Part 136*; U.S. Government Printing Office: Washington, DC, July 1, 1988.

3. Savannah Laboratories' *Comprehensive Quality Assurance Plan* and *Corporate Quality Assurance Plan*, current revision.

METHOD SUMMARY

HOLD/STORAGE

Parameter	Aqueous	Soils/Solids/Wastes
Routine Container	1-L amber glass fitted with Teflon-lined cap	500-mL or smaller glass fitted with Teflon-lined cap
Preservative	None	None
Hold time	7 days from date of collection; 40 days from date of extraction	14 days from date of collection; 40 days from date of extraction
Storage	4C (less than 6C with no frozen samples) from collection to analysis	4C (less than 6C with no frozen samples) from collection to analysis

EXTRACTION

Aquoues-500mL of sample; separatory funnel extraction at pH >12 with diethyl ether followed extraction at pH<2 with diethyl ether; esterify and dilute to 10mL final volume with hexane

Soils- acidify 30g of sample mixed with acidified sodium sulfate; sonication or Soxhlet extraction with 1:1methylene chloride/acetone; concentrate and hydrolyze with KOH, treat same as aqueous sample from this point forward.

SEQUENCE

615

Initial Calibration Standards
Client samples analyzed until 24 hour clock expires
Calibration Verification standard – mid-level concentration
Client samples analyzed until 24 hour clock expires

8151

Initial Calibration Standards
20 client samples or 12 hours
Calibration Verification standard – mid-level concentration
20 client samples or 12 hours
Calibration Verification standard – mid-level concentration

The sequence continues until all samples are analyzed or until the CCV standard fails to meet the acceptance criteria.

QC CHECK	FREQUENCY	ACEPTANCE CRITERIA	CORRECTIVE ACTION
Initial Calibration- 5 point minimum with lowest point at RL	Prior to sample analysis or when CCV fails	1) RSD of each target <= 20%(8151) or 10% RSD (615); OR 2) plot regression curve (CC>=0.99) (see Section 10.2 for 8000-series "grand mean" exception)	-Evaluate chromatogram and integrations. Check calculations. -Reanalyze standard(s) -Remake and reanalyze standard(s) -Perform instrument or column maintenance and reanalyze standards
Continuing calibration verification(CCV)	After every twenty sample analyses (or 12 hours) and at the end of the sequence	8151: Percent difference or drift <= 15% 615: Percent difference or drift <= 10% (see Section 10.3 for 8000-series "grand mean" exception)	-Evaluate chromatogram and integrations. Check calculations. -Reanalyze standard(s) -Remake and reanalyze standard(s) -Perform instrument or column maintenance and reanalyze standards
Method blank	Per batch	All targets reported less than RL in Table 5 of the SL CQAP	-Evaluate chromatogram and integrations. Check calculations. -Reanalyze - Follow guidance in SL SOP AN02 and Table 13.1 in CQAP -Perform instrument or column maintenance, recalibrate, and reanalyze
Lab control sample (LCS)- Subset of targets in SL CQAP	Per batch	Recoveries within SL CQAP Table 5 limits	-Evaluate chromatogram and integrations. Check calculations. -Reanalyze - Follow guidance in SL SOP AN02 and Table 13.1 in CQAP -Perform instrument or column maintenance, recalibrate, and reanalyze

QC CHECK	FREQUENCY	ACEPTANCE CRITERIA	CORRECTIVE ACTION
Matrix spike(MS) and matrix spike duplicate (MSD)	Per batch	Recoveries within SL CQAP Table 5 limits	-Evaluate chromatogram and integrations. Check calculations. - Follow guidance in SL SOP AN02 and Table 13.1 in CQAP -Perform instrument or column maintenance, recalibrate, and reanalyze
Surrogate	All samples, method blanks, and QC	Recoveries within SL CQAP Table 5 limits	-Evaluate chromatogram and integrations. Check calculations. -Reanalyze - Follow guidance in SL SOP AN02 and Table 13.1 in CQAP -Perform instrument or column maintenance, recalibrate, and reanalyze
Reporting limit(RL) standard-lowest level calibration standard	Daily-required for Fla DEP	Detected with reasonable sensitivity	-Reanalyze RL standard -Remake and reanalyze RL standard -Perform instrument or column maintenance, recalibrate, and reanalyze associated samples
Initial Demonstration of Capability (IDOC)	Initially and when new analysts trained	Evaluate in accordance with method criteria	Repeat test for analytes that fail criteria
Method Detection Limit (MDL)	See SL SOP CA90	Evaluate in accordance with SL SOP CA90	Evaluate in accordance with SL SOP CA90
Retention time window determination	See SOP AN66	See SOP AN66	See SOP AN66

TABLE 1-"full list"		
Compound	RT COL 1	RT COL 2
Dalapon	2.90	3.35
DCAA (surrogate)	13.18	13.41
MCPP	13.56	14.08
Dicamba	13.66	13.63
MCPA	14.30	14.44
Dichlorprop	14.94	15.36
2,4-D	16.10	15.89
2,4,5-TP (Silvex)	18.27	19.22
2,4,5-T	20.49	20.33
Dinoseb	21.00	23.06
2,4-DB	22.81	23.36

COL1 = DB608 COL2 = DB-5

TABLE 1A-"short list"		
Compound	RT COL 1	RT COL 2
DCAA (surrogate)	5.38	5.75
2,4-D	7.65	7.61
2,4,5-TP (Silvex)	8.80	9.31
2,4,5-T	9.68	9.74

COL1 = DB608 COL2 = DB-5

TABLE 2

HERBICIDE MOLECULAR WEIGHTS AND CORRECTION FACTORS

Herbicide acid	MWacid	MWester/ether	Correction factor
2,4-D	221.04	235.07	0.940
Dalapon	142.97	157.00	0.911
2,4-DB	249.09	263.12	0.947
Dicamba	221.04	235.07	0.940
Dichloroprop	235.07	249.09	0.944
Dinsoeb	240.22	254.24	0.945
MCPA	200.62	214.65	0.935
MCPP	214.65	228.67	0.939
2,4,5-TP(Silvex)	269.51	283.54	0.951
2,4,5-T	255.48	269.51	0.948
DCAA	205.04	219.07	0.936
Picloram	241.48	255.51	0.945
Pentachlorophenol	266.35	280.37	0.950

Example Calculation

$$CF(2,4-D) = \frac{Wacid}{Wester} = \frac{221.04}{235.07} = 0.94$$

If the standard is expressed as mass of ester per volume, convert the concentration to he acid form by multiplying by the correction factor (CF).

Table 3-Example Standard Preparation "Recipes"

"Short List" Herbicide Intermediate Standard

STOCK STANDARD	VENDOR/ PART NO.	CONC. (ug/mL)	mL of stock	fvol (mL)	conc (ug/mL)
Herbicides	Ultra HBM-815M	100	1.0	10	10
DCAA	Ultra PPS-161	100	1.0		10

Solvent is hexane

"Short" list Calibration Standards

STOCK STANDARD	CONC. (ug/mL)	1*	2*	3*	4*	5*	6*	7*
"short" list herbicide intermediate std	10	50	100	200	250	500	750	1000

* microliters of intermediate standard to 10mL of hexane. Seven standards are prepared and analyzed but only 5 are used. MCPP and MCPA are difficult to calibrate at low concentrations.

"Short" list Calibration Standards

Target Compounds	1*	2*	3*	4*	5*	6*	7*
DCAA, 2,4,-D, 2,4,5-TP (Silvex), 2,4,5-T	0.05	0.10	0.20	0.25	0.50	0.75	1.0

* ug/mL

"Full" list Calibration Standards

STOCK STANDARD	CONC. (ug/mL)	1*	2*	3*	4*	5*	6*	7*
Ultra HBM-8150M		5	10	12.5	20	50	67	100
Dicamba, 2,4,5-TP (Silvex), 2,4,5-T	10							
2,4-D, 2,4-DB, Dichlorprop	100							
Dinoseb	50							
MCPA, MCPP	10000							

* microliters to 10mL hexane

Table 3-Example Standard Preparation "Recipes"

"Full" list Calibration Standards

STOCK STANDARD	CONC. (ug/mL)	1*	2*	3*	4*	5*	6*	7*
Ultra HBM-8150M								
Dicamba, 2,4,5-TP (Silvex), 2,4,5-T	10	0.005	0.010	0.0125	0.020	0.050	0.067	0.10
2,4-D, 2,4-DB, Dichlorprop	100	0.050	0.10	0.125	0.20	0.50	0.67	1.0
Dinoseb	50	0.025	0.050	0.0625	0.10	0.25	0.33	0.50
MCPA, MCPP	10000	5.0	10	12.5	20	50	67	100

*ug/mL

SEVERN TRENT SERVICES

CHANGE -IN-PROGRESS ATTACHMENT

SOP Document No: SG65:01.12.99:4

SOP Description: Chlorinated Herbicides

Approval Signature: R. Wayne Robbins 6 Sept 2001
Date

Title: Technical Manager, QA

STL X Savannah __ Tallahassee __ Mobile __ Tampa West

The following revisions or additions have been made to the referenced SOP.

The following attachments are for a specific project and will be effective from the date of approval until the date that the project is completed. The purpose of this CIPA is to document changes or additions to the standard operating procedures requested for the Sauget Area 2 Sites Group and EPA Region V.

The attachments are tables of the project RLs and MDLs, including the QC limits, and an excerpt from the Sauget Area 2 Sites Group QAPP.

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Chlorinated Herbicides by GC (8151) Water

PARAMETER	METHOD	%REC	%RPD	MDL(ug/L)	RL(ug/L)
2,4-D (MS)	8151	11-154	<=78	0.15	0.50
2,4-DB	8151	55-167	<=43	0.13	0.50
2,4,5-T (MS)	8151	25-128	<=48	0.036	0.50
2,4,5-TP (Silvex) (MS)	8151	10-100	<=66	0.031	0.50
Dalapon	8151	26-97	<=68	0.87	120
Dicamba	8151	38-152	<=46	0.057	1.2
Dichlorprop	8151	27-209	<=95	0.043	6.0
Dinoseb	8151	D-127	<=115	0.034	6.0
MCPA	8151	20-150	<=28	8.0	120
MCPP	8151	10-164	<=78	5.4	120
Pentachlorophenol	8151	11-110	<=34	0.090	1.0
Surrogate					
2,4-Dichlorophenylacetic acid(DCAA)	8151	27-133			

D= detected

Chlorinated Herbicides by GC (8151) Soils

PARAMETER	METHOD	%REC	%RPD	MDL (ug/kg)	RL(ug/kg)
2,4-D (MS)	8151	19-153	<=47	2.4	8.3
Dalapon	8151	10-170	<=40	2	2000
2,4-DB	8151	20-160	<=40	1.1	8.3
Dicamba	8151	20-160	<=40	1.7	20
Dichlorprop	8151	30-170	<=40	0.8	100
Dinoseb	8151	D-130	<=50	31	100
MCPA	8151	10-130	<=50	74	2000
MCPP	8151	10-130	<=50	120	2000
Pentachlorophenol	8151	10-150	<=40	0.72	17
2,4,5-T (MS)	8151	14-143	<=59	0.87	8.3
2,4,5-TP (Silvex) (MS)	8151	27-120	<=51	1.5	8.3
Surrogates					
2,4-Dichlorophenyl acetic acid (DCAA)	8151	30-189	NA	NA	NA

D= detected

SEVERN TRENT SERVICES

Table 7C. *Pesticides SW-846 Method 8081A, Herbicides SW-846 Method 8151A, and TPH, as Diesel range organics (DRO) SW-846 Method 8015B Quality Control Requirements and Corrective Actions.*

Audit	Frequency	Control Limits	Corrective Action
Holding times	Samples must be extracted and analyzed within holding time.	Extract within 7 days for aqueous and 14 days for soil samples from collection. Analyze extracts within 40 days.	If holding times are exceeded for initial or any re-analyses required due to QC excursions, notify QAO immediately since re-sampling may be required.
Initial Calibration	Prior to start up and when criteria are exceeded for continuing calibration.	1. Minimally five concentrations, one calibration standard must be at concentration less than or equal to the PQL. 2. Toxaphene, technical chlordane require a single point calibration. If detected in samples, the samples are re-analyzed behind a five point calibration for each detected analyte. 3. If RSD <20% the average RRF may be used for quantitation. If RSD >20% a first or second order calibration curve with a correlation coefficient >0.99 must be used for quantitation.	1. Identify and correct problem. 2. Recalibration instrument; samples must not be analyzed until initial calibration criteria are met.
Calibration Verification	Calibration standards must contain target compounds at mid-range concentration. Minimally, analyze calibration standards daily and every 12 hours. Calibration verification standards should be analyzed every 20 samples.	%D <15%	1. Reanalyze. 2. If criteria are still not met, identify and correct problem, recalibrate; reanalyze samples back to last compliant calibration standard. Samples must be bracketed by compliant calibration standards. If the laboratory chooses to apply the grand mean exception (average % drift or % difference is less than 15%), the QAO* will be contacted prior to proceeding with analysis.
Retention Time Windows	Retention time windows must be established in accordance with USEPA method 8000 or relative retention times must be used if internal standards are employed.	Compounds must be within established retention time windows or within laboratory established relative retention time criteria for the succeeding calibration standards.	1. Reanalyze. 2. If criteria are still not met, identify and correct problem, recalibrate; reanalyze samples back to last compliant calibration standard.

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Table 7C. *Pesticides SW-846 Method 8081A, Herbicides SW-846 Method 8151A, and TPH, as Diesel range organics (DRO) SW-846 Method 8015B Quality Control Requirements and Corrective Actions.*

Audit	Frequency	Control Limits	Corrective Action
Surrogate Spike	Samples, blanks, MS/MSDs, and LCSs must be spiked with method specific surrogate compounds.	1. Recovery within laboratory control limits. 2. Corrective action is not required if one of the two required surrogates has recovery outside of control limits if the recovery is >10%.	1. Reanalyze 2. If recovery is still outside control limits but >10%, document in case narrative report. 3. If recovery is <10% with re-analysis, re-extract and re-analyze the sample if the holding time has not elapsed. If holding time has elapsed, notify the QAO immediately prior to proceeding since resampling may be required. Special Circumstances: If matrix interferences is present (as demonstrated by the lab and documented in the case narrative): 1. Reanalyze (may be at a higher dilution) 2. If surrogate standard is >10%, report runs. 3. In surrogate standard is <10%, contact QAO*.
Identification	Samples, blanks, and QC data.	1. Retention times must be within established retention time windows or must meet relative retention time criteria. 2. Confirmation analysis is required.	1. Investigate problem; re-analyze calibration standards to check for retention time shift.
Quantitation	Samples, blanks, and QC data.	1. Internal and external standard method. Verify concentration is within linear calibration range. 2. For DROs, use the sum of the areas of peaks eluting between C10 and C28. 3. Every effort must be made to meet specified PQL requirements. Soil samples concentrations must be corrected to dry weight.	1. If concentration is above linear calibration range, dilute sample and re-analyze. Dilution should result in concentration in the upper calibration range of the instrument.
Field/ Equipment Blank Analysis	Collected one per sampling equipment and after every 10 samples.	Compounds concentrations must be <PQL.	1. Investigate problem; re-analyze to verify laboratory cross contamination is not a factor. 2. Notify the QAO immediately since resampling may be necessary.

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EPA RESPONSE

ATTACHMENT F

EXTRACTION OF CHLORINATED HERBICIDES IN WATER, SOILS, AND WASTES

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Approved by:
Kristin McCracken 8/22/01
Date
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1.0 SCOPE AND APPLICATION

This SOP describes the process for extracting chlorinated phenoxy herbicides from aqueous samples, soils and sediments, and solid matrices.

2.0 SUMMARY OF METHOD

2.1 A known volume of aqueous sample, nominally 500mL, is transferred to a Teflon or glass separatory funnel. The sample is made basic (pH>12) by adding sodium hydroxide and allowed to hydrolyze for at least one hour. The hydrolysis step is necessary to convert herbicides in the acid or ester form to the corresponding water-soluble salt. The sample is extracted with diethyl ether to remove non-target compounds (the herbicide salts remain in the water). The sample is acidified to convert the herbicide salts to the acid form and extracted with diethyl ether. The diethyl ether extract is concentrated and the herbicides are converted to methyl esters by diazomethane esterification. The methyl esters are dissolved in hexane and analyzed by GC/electron capture (STL SOP SG65).

2.2 A known weight of a sample (approximately 30g wet weight) is acidified with HCl and combined with acidified sodium sulfate to form a free flowing, sandy mixture. Diethyl ether is added to the dried sample and the sample is extracted using an ultrasonic disrupter for three (3) minutes. The solvent is decanted and collected and the extraction is repeated two more times. The extract is concentrated and transferred to a separatory funnel containing 500mL of reagent water. The water is adjusted to pH>12 with sodium hydroxide and the sample is allowed to hydrolyze for one hour. The extract is treated in the same manner as aqueous samples from this point, except that methylene chloride is used to remove non-target compounds from the hydrolyzed extract.

2.3 A known weight of waste, nominally 1g, is diluted to 10mL with diethyl ether. The extract is transferred to a separatory funnel containing 500mL of reagent water that has been adjusted to a pH >12 with sodium hydroxide. The sample is allowed to hydrolyze for one hour under basic conditions and is treated in the same manner as an aqueous sample from this point forward.

2.4 This procedure is based on SW-846 Method 8151A. The following modifications have been made to the procedure as given in SW-846 Method 8151A:

-Ethyl ether is used to extract non-targets from the hydrolyzed sample matrix instead of the recommended methylene chloride. This modification was made to reduce the amount of methylene chloride used in the lab.

-Ethyl ether is used as the extraction solvent for soils in place of 1:1 acetone/methylene chloride. This step was modified to improve recovery of chlorinated herbicides; recoveries of the herbicides using acetone/methylene chloride were found to be less than 10%.

3.0 SAFETY

3.1 Use good common sense when working in the lab. Do not perform any procedures that you do not understand or that will put you or others in potentially dangerous situations.

3.2 This SOP contains procedures that are designed to reduce the exposure of lab personnel to solvent vapors and to minimize the amount of solvent introduced into the lab air. All solvent transfer steps should be performed quickly and under a hood, if possible. Use the minimum amount of solvent to get the job done. Do not allow open containers of solvent or extracts to evaporate into the lab.

3.3 A lab coat or apron should be worn to protect clothing and skin from acids, bases, and solvents. Gloves must be worn to protect hands and eye protection (safety glasses, goggles) must be worn at all times in the lab. An analyst should not work alone in an isolated area.

3.4 Diethyl ether is a flammable solvent that can cause drowsiness. The extraction analyst using diethyl ether must not work alone in an isolated area of the lab. A solvent such as diethyl ether can cause a burning sensation when it contacts the skin. The rapid evaporation of the solvent causes a rapid heat loss in the skin, which is similar to frost bite. If this occurs, rinse the exposed skin in cold water to reduce the solvent evaporation.

3.5 The lab should keep the minimum supply of diethyl ether. Diethyl ether will form explosive peroxides if stored in the lab for long periods of time. Opened containers of diethyl ether should be checked periodically for peroxides using peroxide test strips.

3.6 The analyst should become familiar with the Material Safety Data Sheets (MSDS) for each reagent used in the extraction lab.

4.0 INTERFERENCES

4.1 Improperly cleaned glassware can contribute interferences to the sample extract. Material that is left inside the extraction vessels and glassware after cleaning may show up in the next extraction. The glassware must be properly cleaned according to STL SOP AN60.

4.2 Samples with high levels of organic material (oils, particulates, etc.) may cause the formation of emulsions during the extraction. Emulsions will occur most readily during the "base shake" to remove the non-target compounds. The extract may be filtered or stirred to remove the emulsion or may be "salted out" by the addition of sodium chloride.

4.3 The glassware used for herbicides should not be used to extract or concentrate dioxins and furans. Several of the herbicides are precursors to the formation of dioxins or are associated with the presence of dioxins in the environment

5.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

5.1 Aqueous samples are routinely collected in 1-L amber glass containers equipped with Teflon-lined caps. No preservative is required. The sample is iced at the time of collection and stored at 4C (less than 6C with no frozen samples) in the lab. Sample must be extracted within seven (7) days of collection and the extract must be analyzed within forty (40) days of extraction.

TCLP leachate samples are stored in the same manner as aqueous field samples. The extraction must be performed within seven(7) days of the leaching procedure and the extract analyzed within forty(40) days of extraction

5.2 Soils, sediments, sludges, and wastes are collected in glass containers equipped with Teflon-lined caps. The routine container is 500-mL glass. Larger or smaller containers may be supplied. No preservative is required. The samples are iced at the time of collection and stored at 4C (less than 6C with no frozen samples) in the lab. The hold time for herbicides in solid and non-aqueous matrices is 14 days from the date of collection. The extract must be analyzed within 40 days of extraction.

6.0 APPARATUS AND MATERIALS

6.1 Separatory funnels - 1-L and 2-L, Teflon with Teflon stopcocks. Glass funnels may also be used.

6.2 Chromatography columns

6.3 Large funnels

6.4 Pyrex glass wool - purified by Soxhlet extraction with methylene chloride. The glass wool should be rinsed with acidified methanol prior to use.

6.5 Disposable, glass volumetric pipettes - 1.0-mL and 10-mL

6.6 Stainless steel spatulas

6.7 Wide range and narrow range pH paper

6.8 Pre-cleaned 500ml extraction bottles, P/N SAV-145. Discard after use.

6.9 1-L pre-cleaned containers. This is the same container used to collect the sample and can be used to collect the aqueous phase during cleanup. Discard after use.

6.10 Ultrasonic disrupter: Tekmar Model or equivalent with horn-type titanium-tipped sonication probe. The sonicator should be capable of operating in the pulse mode at full power.

6.11 Sonabox - the sonicator should be placed in the sonabox to reduce noise. The sonabox must be placed under a fume hood.

6.12 Filter paper-grade 414, 18.5cm diameter (VWR 28320-143)

6.13 Disposable volumetric pipettes

6.14 Top-loading balance - capable of weighing to 0.1g. The balance calibration must be verified according to STL SOP AN10 each time the balance is used.

6.15 12mL vials with Teflon-lined caps.

6.16 Diazomethane generator.

NOTE: If the herbicide blank is contaminated, clean the generator tubing and vessels with methylene chloride, methanol, and ether, in that order, and purge the apparatus with nitrogen to dry. Replace the Teflon tubing and vessels if the solvent cleaning does not improve the blank.

7.0 REAGENTS

Reagents must be tracked in accordance with STL SOP AN44: *Reagent Traceability*.

7.1 Reagent water-lab generated deionized water

7.2 Sodium sulfate, powdered and granular, anhydrous - purified by heating at 400C for four (hours) in a shallow tray.

7.3 Acidified sodium sulfate-Transfer purified sodium sulfate to a suitable glass container until the container is about ¾ full. Working under a hood, add enough diethyl ether to wet the sodium sulfate. Add 1-2mL of concentrated sulfuric acid for each kilogram of sodium sulfate and stir to mix the acid into the solvent and sodium sulfate. Add more diethyl ether to keep the sodium sulfate wetted while stirring the sodium sulfate. The acid must be thoroughly mixed into the sodium sulfate and diethyl ether. Pour off the excess solvent and allow the ether to evaporate under a hood for 24 hours. Store in a glass container. Check the pH of the acidified sodium sulfate by mixing 1g and 5mL of water in a small container. The pH of the solution should be less than 4.

7.4 Methanol - residue grade or better

7.5 Diethyl ether-residue grade or better. Check periodically for formation of peroxides.

7.6 Sodium hydroxide (NaOH) - reagent grade

7.7 Sodium hydroxide solution (10N): Dissolve 400g of NaOH pellets into about 500mL of reagent water contained in a 2-L beaker on a magnetic stirrer. Add the NaOH in small portions, with constant stirring, to minimize the time it takes to dissolve the pellets. A good deal of heat will be generated as the NaOH dissolves. After all 400g has been added, carefully dilute to 1000mL with reagent water. Mix the solution thoroughly and transfer to a storage container. Do not store sodium hydroxide solution in volumetric glassware or in containers with ground glass joints.

7.8 Sulfuric acid (H_2SO_4) - concentrated reagent grade

7.9 Sulfuric acid solution (1:1 v/v): Slowly and carefully add 550mL of concentrated H_2SO_4 to 500mL of reagent water contained in a 2-L beaker on a magnetic stirrer. Add the acid in small portions with constant stirring to reduce the heat evolved when the acid and water are combined. Cool and transfer the solution to a labeled storage container.

7.10 Hydrochloric acid (HCl)-concentrated, reagent grade

7.11 Potassium hydroxide-reagent grade

7.12 Potassium hydroxide solution(37%)-weight 37g of KOH into a 100mL volumetric flask and dilute to volume with reagent water.

7.13 Acidified methanol (approximately 0.12N). Carefully add 5mL of concentrated HCl to 400mL of methanol in a 500mL volumetric flask. Dilute to volume with methanol. Larger volumes may be prepared.

7.14 Diazald (N-methyl-N-nitroso-toluenesulfonamide)-reagent grade

7.15 Carbitol-reagent grade or better

7.16 Silicic acid

7.17 Hexane-residue grade or better

7.18 Sodium chloride-reagent grade, purified, if necessary, by Soxhlet extraction with methylene chloride or by heating at 400C for four hours in a shallow tray.

8.0 STANDARDS

The preparation of the spiking solutions must be tracked in accordance with STL SOP AN41:*Standard Material Traceability*. General guidance on the preparation of standards is given in STL SOP AN43:*Standard Preparation.*

The lab should purchase certified solutions from STL-approved vendors, if available. The lab should prepare standards from neat materials only if a certified solution is not available. See STL SOP AN43 for guidance for standard preparation.

The following "recipes" provide guidance for the preparation of the surrogate and matrix spiking solutions.

8.1 Preparation of the Herbicide Surrogate Spiking Solution

8151 Surrogate Spiking Solution

Stock Standards	*Cstock* (ug/mL)	*Vstock* (mL)	*Vspike* (mL)	*Cspike* (ug/mL)
DCAA (Fisher M-8150B-SS-PAK)	100	1.0	50	2.0

Solvent: Methanol

8.2 Preparation of the Herbicide Matrix Spiking Solutions

8151 Matrix Spiking Solution

Stock Standards	*Cstock* (ug/mL)	*Vstock* (mL)	*Vspike* (mL)	*Cspike* (ug/mL)
Chlorinated Herbicides Mixture (Ultra HBM-815A)	100	0.50	50	1.0

Solvent: Methanol

8151-TCLP Matrix Spiking Solution

Stock Standards	*Cstock* (ug/mL)	*Vstock* (mL)	*Vspike* (mL)	*Cspike* (ug/mL)
Herbicide TCLP Mix (Restek 32014)	2000	0.025	50	1.0

Solvent: Methanol

8151-Full Target Matrix Spiking Solution

Stock Standards	*Cstock* (ug/mL)	*Vstock* (uL)	*Vspike* (mL)	*Cspike* (ug/mL)
Chlorinated Herbicides Mixture 8150B(NSI-C-418-SAV)		50	10	
Dicamba, Silvex, 2,4,5-T Dinoseb, 2,4-D, Dichorprop, 2,4-DB, Dalapon	200			1.0
MCPA, MCPP	20,000			100

Solvent: Methanol

9.0 SAMPLE PREPARATION

The samples and QC items must be clearly and unambiguously labeled during each step of the extraction and analysis process. Labeling tape should be used to identify the glassware associated with each sample. Solvents will erase grease pens and "Sharpies." Use of different colored labeling tape will aid the analyst in keeping up the extracts during each step of the extraction and concentration

9.1 Extraction of Aqueous Samples and TCLP Leachates

9.1.1 Remove the samples from the storage refrigerator and allow the sample to come to room temperature. Begin filling out the extraction log and gathering the required glassware while the samples are warming up. The glassware should be rinsed with acidified methanol and then with diethyl ether prior to extraction.

NOTE: All glassware used in this procedure must be rinsed with acidified methanol and diethyl ether prior to use.

9.1.2 Inspect the samples. Determine if the samples have multiple layers such as sediment or an oil layer. Sample with large amounts of sediments or particulates may clog the stopcock on the separatory funnel. Consult with the supervisor or technical manager if the sample matrix is unusual or is difficult to categorize or handle. Any unusual sample preparation steps required prior to the extraction must be noted on the extraction log or in an anomaly report.

9.1.3 Thoroughly mix the sample by inverting the container several times and pour 500mL of the sample container into a graduated cylinder that has been rinsed with acidified methanol. Transfer the sample to a properly labeled 1-L or 2-L Teflon separatory funnel. For TCLP samples, transfer 10mL of the leachate to a separatory funnel and dilute to 500mL with reagent water

Transfer two additional 500-mL aliquots of the sample selected for the MS and MSD to labeled separatory funnels.

9.1.4 Add 500mL of reagent water to each of two separatory funnels to serve as the method blank and lab spike (LCS).

9.1.5 Add 1.0 mL of surrogate to each sample, method blank, lab spike and matrix spike.

9.1.6 Add 1.0 mL of matrix spiking solution to all appropriate lab spikes and matrix spikes.

NOTE: Every extraction batch of 20 or fewer samples will have a method blank and a laboratory control spike (LCS). A matrix spike(MS) and a matrix spike duplicate (MSD) are prepared at a frequency of 5% of samples (one MS and one MSD per 20 samples) or as required by contract or client QAP. If insufficient sample is available for the MS/MSD, the extraction log must be stamped: " Insufficient sample is available to perform the MS/MSD".

9.1.7 Add 100g of sodium chloride to each sample and QC item as needed.

9.1.8 Adjust the pH of the sample to >12 with 10N NaOH. Check the pH with narrow range pH paper. Allow the samples to stand for at least one hour with intermittent shaking or shake on the automatic shaker for one hour.

NOTE: This step is necessary to convert the acid and ester forms of the herbicides to the water-soluble salts. After the hydrolysis step, the non-target compounds are extracted out of the sample with ether. The rest of the extraction steps may be performed with manual or automatic shaking.

9.1.9 Add 200 mL of diethyl ether to each separatory funnel.

9.1.10 Shake each separatory funnel for three minutes with periodic venting to release any excess pressure. If an automatic shaker is used, shake the samples for 10 minutes. Allow ten minutes for complete separation between the lower water and upper solvent phase.

NOTE: The separatory funnel should be vented under a hood to remove the solvent fumes from the lab.

9.1.11 Drain the lower water phase into a pre-cleaned 1-L container that has been rinsed with acidified methanol . The container must be large enough to hold more than 500mL because some of the diethyl ether will dissolve into the water. Discard the organic phase. If the sample contains high levels of organics, the solvent clean-up may be repeated two more times.

NOTE: Samples with high levels of organic material (oils, particulates, etc.) may cause the formation of emulsions during the extraction. Emulsions will occur most readily during the "base shake" to remove the non-target compounds. The extract may be filtered or stirred to remove the emulsion. Small aliquots of sodium sulfate may also be gently added to the extract to remove the emulsion.

9.1.12 Pour the sample back into the separatory funnel and adjust the pH of each sample and the QC items to <2 with cold 1:1 sulfuric acid. Add the acid slowly and gently swirl the separatory funnels after the addition of the acid to ensure that the acid and base have reacted. Acid/base neutralization reactions can be violent if mixed too quickly. Check the pH of the samples and QC items to ensure that the pH < 2.

9.1.13 Add 200mL of diethyl ether to each sample and QC item.

-If performing a "manual shake", shake the funnels intermittently over a period of one hour, venting frequently to release any pressure.

-If using the automatic shaker, shake the samples continuously for 30 minutes, releasing the pressure periodically.

9.1.14 After the extraction, allow the layers to separate for at least 10 minutes. Collect the water layer in a large beaker or flask for disposal. Try and remove as much of the water as possible. Discard the water layer.

9.1.15 Collect the extract (upper layer) into a 500mL pre-cleaned extraction bottle containing 30g of acidified sodium sulfate. Allow the extract and sodium sulfate to remain in contact at least two hours but preferably overnight. This is a good stopping point.

9.1.16 Place a piece of filter paper into a glass funnel and add a small amount of purified, acidified sodium sulfate. Filter the extract through the glass funnel and collect the extract directly into a labeled K-D apparatus.

9.1.17 The extract is concentrated to a final volume of approximately 10mL. The extract may be left in the 10mL graduated concentrator tube or transferred to a labeled storage vial. The extract is now ready for the diazomethane esterification.

9.2 Extraction of Soils and Solids

9.2.1 Remove samples to be extracted from the storage refrigerator and allow the samples to come to room temperature while the extraction glassware is being prepared. Begin filling out the extraction log and gathering the required glassware while the samples are warming up. The glassware should be rinsed with acidified methanol and then with diethyl ether prior to extraction.

Check the "tune" of the sonicator using the procedure tested in STL SOP AN15: *Tekmar Sonic Dismembrator Tuning Procedure*.

9.2.2 Collect the appropriate glassware and rinse with acidified methanol and diethyl ether prior to use.

9.2.3 Prepare a number of funnels to filter the extracts by placing a piece of folded filter paper into the

funnel. Rinse with acidified methanol and discard the solvent.

NOTE: Record as much information on the extraction log as possible before beginning the extraction to minimize the number of entries required during the extraction.

9.2.4 Open the sample container and inspect the sample. Note any unusual characteristics such as the presence of rocks, sticks, leaves, or other materials. Thoroughly homogenize the sample, mixing in any water that may be present on top of the sediment or soil. STL SOP AN70 gives guidance for homogenization of samples.

NOTE: If it is difficult to homogenize the sample or if the sample matrix is difficult to characterize, contact the supervisor before preceding with the extraction. A careful inspection of the sample at this point can save time and effort later on in the analysis. Any unusual sample preparation steps required prior to the extraction must be noted on the extraction log or in an anomaly report.

9.2.5 Weigh 30.0 - 30.5g of the homogenized sample into a pre-cleaned, labeled 500-mL extraction bottle. Record the weight for all samples in this batch.

9.2.6 Weight 30g of powdered, purified sodium sulfate into two separate beakers to serve as the method blank and lab control sample(LCS).

9.2.7 Weigh two additional 30g portions of the sample in the batch selected as the matrix spike (MS) and matrix spike duplicate(MSD).

NOTE: Each extraction batch of twenty or fewer samples will have the following QC items: method blank and LCS. MS and MSD are prepared at a frequency of 5% of samples (one MS and one MSD per 20 samples). If there is not enough sample to perform the MS/MSD, the extraction log must be stamped "INSUFFIECIENT SAMPLE WAS AVAILABLE TO PERFROM THE MS/MSD."

9.2.8 Working under a hood, acidify each sample and QC item with 0.1 to 0.2mL of concentrated hydrochloric acid. Add the acid to the sample slowly and carefully, stirring the sample with a stainless steel spatula or glass rod or pipette. Continue to add acid until the pH <2 when read with narrow range pH paper.

9.2.9 Add powdered, acidified sodium sulfate to each sample and QC item. Stir with a glass rod or stainless steel spatula to form a sandy, free-flowing mixture. The sodium sulfate combines with the water in the sample to "dry" the sample (remove the water). More sodium sulfate may be required if the sample is very wet. Precede to the next step as quickly as possible.

9.2.10 Add 1.0mL of the herbicide surrogate spiking solution to the method blank, LCS, MS, MSD and each sample in the batch.

9.2.11 Add 1.0ml of the appropriate herbicide matrix spiking solution to the LCS, MS, and MSD. Transfer the extraction bottle to a hood near the sonicator.

9.2.12 Under a hood, add 100mL of diethyl ether to each sample and QC item. Stir the sample to break up any lumps that may have formed. Add more solvent until the solids are covered by about one inch.

9.2.13 Place the tip of the sonicator horn in the center of the beaker about ½ inch below the surface of

the solvent but above the solid portion. More solvent may be added to bring the level to approximately one inch above the solid layer.

9.2.14 Sonicate for three (3) minutes with output control knob set at 10, mode switch to pulse, and percent duty cycle set at 50% If the sonication is properly performed, the solids and solvent will vigorously mix each time the sonicator pulses.

9.2.15 Under a hood, decant the extract through the filter funnel and collect the extract directly into an K-D apparatus. The extract may also be collected in a labeled, pre-cleaned 500mL extraction bottle or Erlenmeyer flask,

9.2.16 Repeat the extraction two more time two more times with fresh portions of solvent , collecting the solvent in the K-D apparatus or in the 500mL bottle each time.

NOTE: Clean the sonicator horn between samples by rinsing with ether.

9.2.17 Concentrate the extract to approximately 10mL using the K-D concentration apparatus. The water bath should be 60-70C. Remove the K-D from the water bath and allow the extract to cool.

9.2.18 Transfer the extract to a 2-L Teflon separatory funnel containing 500mL of reagent water. Use several small aliquots of ether to rinse the K-D body and the concentrator tube, adding the rinsings to the separatory funnel.

9.2.19 Adjust the pH of the sample to >12 with 10N NaOH. Check the pH with narrow range pH paper. Allow the samples to stand for at least one hour with intermittent shaking or shake on the automatic shaker for one hour.

NOTE: This step is necessary to convert the acid and ester forms of the herbicides to the water-soluble salts. After the hydrolysis step, the non-target compounds are extracted out of the sample with methylene chloride. The rest of the extraction steps may be performed with manual or automatic shaking.

9.2.20 Add 200 mL of methylene chloride to each separatory funnel.

9.2.21 Shake each separatory funnel for three minutes with periodic venting to release any excess pressure. If an automatic shaker is used, shake the samples for 10 minutes, Allow ten minutes for complete separation between the lower water and upper solvent phase.

NOTE: The separatory funnel should be vented under a hood to remove the solvent fumes from the lab.

9.2.22 Discard the lower methylene chloride phase into the solvent waste. If the sample contains high levels of organics, the solvent clean-up may be repeated two more times.

NOTE: Samples with high levels of organic material (oils, particulates, etc.) may cause the formation of emulsions during the extraction. Emulsions will occur most readily during the "base shake" to remove the non-target compounds. The extract may be filtered or stirred to remove the emulsion. Small aliquots of sodium sulfate may also be gently added to the extract to remove the emulsion.

9.2.23 Adjust the pH of each sample and the QC items to <2 with cold 1:1 sulfuric acid. Add the acid slowly and gently swirl the separatory funnels after the addition of the acid to ensure that the acid and base have reacted. Acid/base neutralization reactions can be violent if mixed too quickly. Check the pH of the samples and QC items to ensure that the pH < 2.

9.2.24 Add 200mL of diethyl ether to each sample and QC item.

-If performing a "manual shake", shake the funnels intermittently over a period of one hour, venting frequently to release any pressure.

-If using the automatic shaker, shake the samples continuously for 30 minutes, releasing the pressure periodically.

9.2.25 After the extraction, allow the layers to separate for at least 10 minutes. Collect the water layer in a large beaker or flask for disposal. Try and remove as much of the water as possible. Discard the water layer.

9.2.26 Collect the extract (upper layer) into a 500mL pre-cleaned extraction bottle containing 30g of acidified sodium sulfate. Allow the extract and sodium sulfate to remain in contact at least two hours but preferably overnight. This is a good stopping point.

9.2.27 Place a piece of filter paper into a glass funnel and add a small amount of purified, acidified sodium sulfate. Filter the extract through the glass funnel and collect the extract directly into a labeled K-D apparatus.

9.2.28 The extract is concentrated to a final volume of approximately 10mL. The extract can be left in the 10mL graduated concentrator tube or transferred to a labeled storage vial. The extract is now ready for the diazomethane esterification.

9.3 Extraction of Wastes

9.3.1 Remove samples to be extracted from the storage refrigerator and allow the samples to come to room temperature while the extraction glassware is being prepared. Begin filling out the extraction log and gathering the required glassware while the samples are warming up. The glassware should be rinsed with acidified methanol and then with diethyl ether prior to extraction.

9.3.2 Prepare a number of funnels to filter the extracts by adding a small plug of glass wool that has been rinsed with acidified methanol and about 2 - 3 inches of purified, acidified granular sodium sulfate to the glass funnel.

NOTE: Record as much information on the extraction log as possible before beginning the extraction to minimize the number of entries required during the extraction.

9.3.3 Open the sample container and inspect the sample. Note any unusual characteristics such as the presence of rocks, sticks, leaves, or other materials. Thoroughly homogenize the sample.

NOTE: If it is difficult to homogenize the sample or if the sample matrix is difficult to characterize, contact the supervisor before preceding with the extraction. A careful inspection of the sample at this point can save time and effort later on in the analysis. Any unusual sample preparation steps required prior to the extraction must be noted on the extraction log or in an anomaly report.

9.3.4 Weigh 1-1.2g of the homogenized sample into a labeled, calibrated 12mL vial. Record the weight for all samples in this batch. Weigh two additional 1g aliquots of one sample to serve as the MS and MSD.

NOTE: Each extraction batch of twenty or fewer samples will have the following QC items: method blank, LCS, LCSD, MS, and MSD. If there is not enough sample to perform the MS/MSD, the extraction log must be stamped "INSUFFIECIENT SAMPLE WAS AVAILABLE TO PERFROM THE MS/MSD" and the LCS extracted in duplicate(LCSD).

9.3.5 Add 1.0mL of the herbicide surrogate spiking solution to the method blank, LCS, MS, MSD and each sample in the batch.

9.3.6 Add 1.0ml of the appropriate herbicide matrix spiking solution to the LCS, MS, and MSD.

9.3.7 Add diethyl ether to the sample until the volume comes up to the calibration line. Mix the sample, solvent, and surrogates and/or matrix spiking solutions by inverting the vials several times.

9.3.8 Add 500mL of reagent water to 1-L or 2-L separatory funnels and adjust the pH of the water to >12 with 10N NaOH. Label the separatory funnels and pour the extracts into the corresponding extraction vessel. Check the pH with wide range pH and adjust to pH > 12 if necessary with 10N NaOH. Allow the samples to stand for at least one hour with intermittent shaking or shake on the automatic shaker for one hour.

9.3.9 Starting at Section 9.1.8, continue the clean-up, extraction, and esterification in the same manner as aqueous samples.

9.4 Esterification with Diazomethane

The extracts are contained in a 10mL graduated concentrator tube or should be transferred to 10mL graduated tubes prior to the esterification. The esterification of the extracts must be performed under a hood.

9.4.1 Concentrate the extracts to approximately 1mL under a gentle stream of nitrogen.

9.4.2 After all of the extracts have been concentrated, prepare the diazomethane generation device (Figure 1) for the esterification. Inspect the lines to ensure that there are no leaks or broken connections.

9.4.3 Place the extracts on the support. Replace all of the needles and place the needles into the first extracts to be esterified.

9.4.4 Add diethyl ether to the first container on the diazomethane generation device until the container is about ¾ full.

9.4.5 Add the following to the second container to esterify approximately 20 samples.

50mL diethyl ether
50mL 37% potassium hydroxide
50mL Carbitol
5g Diazald

NOTE: Smaller volumes and weights of reagents may be used if the ratios above are maintained.

Quickly attach the container to the diazomethane device and start the nitrogen flow. Recall that the needles should already be placed in the samples that are to be esterified first. The gas flow should be steady but not so high that the sample is bubbled out of the concentrator tube or that the sample is evaporated before the esterification can take place.

9.4.6 Allow the diazomethane to flow through the sample extracts until a persistent yellow color remains. This will usually take two to three minutes. The esterification process will take longer as the diazomethane is exhausted.

NOTE: For dark extracts where the persistent yellow color cannot be distinguished, esterify the sample for 10 minutes.

9.4.7 After the persistent yellow color remains, remove the needle from the tube in that position and replace it with a new needle. Place the needle into the next sample to esterify. Repeat for all samples in the batch, replacing the needle for each new extract.. If a yellow color cannot be formed in a clear extract, the diazomethane has most likely been exhausted. Pour the used reagents into a waste container (under a hood) and replenish the reagents in the second container. Add more diethyl ether to the first container if needed.

9.4.8 After all of extracts have been esterified, add a small amount (about 0.1g) of silicic acid to each sample extract, cover the concentrator tubes with aluminum foil and allow the extracts to sit for 30 minutes. The silicic acid will destroy any unreacted diazomethane. Dilute to 10mL with hexane and transfer the extract to a labeled storage vial. Store the extracts at 4C until the time of

analysis.

10.0 ANALYTICAL PROCEDURE

No items in this revision. The analytical procedure is described in STL SOP SG65.

11.0 CALCULATIONS

No items in this revision.

12.0 QUALITY CONTROL/QUALITY ASSURANCE

12.1 The analytical batch consists of up to twenty (20) client samples and the associated quality control items. The quality control items consist of a method (reagent) blank, a lab control standard (LCS), a matrix spike (MS), and a matrix spike duplicate (MSD). If insufficient sample is available for the MS/MSD, the LCS is prepared in duplicate.

STL SOP AN02: *Analytical Batching* contains guidance for evaluating the QC in an analytical batch.

12.2 The lab must perform a method detection limit (MDL) study annually in each matrix in accordance with STL SOP CA90: *Procedure for the Determination of Method Detection Limit (MDL).*

13.0 PREVENTIVE MAINTENANCE

No items in this revision.

14.0 TROUBLESHOOTING

No items in this revision.

15.0 REFERENCES

15.1 *STL Comprehensive Quality Assurance Plan* and *STL Corporate Quality Assurance Plan*, current revisions.

15.2 *Test Methods for Evaluating Solid Waste*, Third Edition, SW-846; vs. EPA Office of Solid Waste and Emergency Response: Washington, DC.

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ATTACHMENT G

Polychlorinated Biphenyls (PCBs) by GC/MS (Method 680)

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1.0 SCOPE AND APPLICATION

1.1 This method can be used to determine the concentration of polychlorinated biphenyls (PCBs) in groundwater, soils, sediments, wastes, and biological tissues by GC/MS. PCBs are reported by the level of chlorination: monochlorobiphenyls, dichlorobiphenyls, trichlorobiphenyls, etc., up to decachlorobiphenyl.

1.2 The reporting limit (RL), the method detection limit (MDL), and the accuracy and precision limits for each target compound is given in Section 5 of the current revisions of the STL's *Comprehensive Quality Assurance Plan* and *Corporate Quality Assurance Plan*.

2.0 SUMMARY OF METHOD

2.1 A measured volume or weight of sample is spiked with a surrogate and extracted using an appropriate extraction procedure. The extract is dried, concentrated to a volume of 1.0mL, and analyzed by GC/MS operated in the Selected Ion Monitoring Mode (SIM). Windows are established to monitor for the characteristic masses of the various PCB congeners. Qualitative identification of the target compounds in the extract is based on the presence of the peak within the SIM window and the mass ratio between the primary and confirmation ions. Quantitative analysis is performed using the internal standard technique with a single characteristic ion. Results are reported as total monochlorobiphenyls, total dichlorobiphenyls, etc.

The default identification and quantitation procedure will be to use only the quantitation and confirmation ions for the PCB congeners. Interference check ions, as described in Section 11.2.3, will not be used routinely to evaluate peaks as PCB congeners unless specified in a client QAP or agency requirement or the sample concentration is near a critical quantitation limit. Samples evaluated according to the default quantitation procedures may be slightly high biased.

2.2 This procedure is based on the guidance provided in EPA Method 680. The method has been modified to include the use of a carbon-13 labeled analogue of decachlorobiphenyl (13C12-DCB) as the surrogate in place of the labeled BHC and DDT compounds. 13C12-DCB can be subjected to the optional acid cleanup (the unlabeled analogue, decachlorobiphenyl, is routinely used in SW-846 Method 8082). A window-defining mix containing the first and last eluting isomers of each level of chlorination is used as an aid to establish and verify that the SIM windows are properly set. Preparation procedures are also referenced for soils and biological tissues, which are not included in EPA Method 680.

3.0 SAFETY

3.1 Use good common sense when working in the lab. Do not perform any procedures that you do not understand or that will put you or others in potentially dangerous situations.

3.2 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined. Each chemical compound should be treated as a potential health hazard. Exposure to these chemicals must be reduced to the lowest level possible. Lab coats, gloves, and lab glasses or face shield should be worn while handling extracts and standards. Standard preparation, addition of the internal standard solution, and sample extract dilution should be performed in a hood or well ventilated area.

3.2 Material Safety Data Sheets (MSDS) are available to the analyst at each lab division. These sheets specify the type of hazard that each chemical poses and the procedures that are used to handle these materials safely.

4.0 INTERFERENCES

4.1 Method interferences may be caused by contaminants in solvents, reagents, or glassware. Glassware and/or extraction vessels that have not been properly cleaned may contribute artifacts that make identification and quantification of the target compounds difficult. Elevated baselines may be due to oils, greases, or other hydrocarbons that may be extracted from improperly cleaned glassware or extraction vessels.

4.2 Matrix interferences may be caused by contaminants that are extracted from the sample matrix. The sample may require cleanup or dilution prior to analysis to reduce or eliminate the interferences. Sample extracts that contain high concentrations of non-volatile material such as lipids and high molecular weight resins and polymers may require the optional GPC cleanup prior to analysis. The GPC cleanup is generally not effective in removing non-target material that is associated with common petroleum products such as diesel or waste oil. GPC cleanup may be necessary for biological tissues.
Acid cleanup may be employed as an additional cleanup tool.

5.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

MATRIX	Preservative/ Storage	Container	Sample Hold Time[1]	Extract Hold Time[1]
Aqueous	none; 4C +/- 2C	1-L amber	7 days	40 days
Soil/ Sediment	none; 4C +/- 2C	500-mL	14 days	40 days
Biological	Frozen	Glass or wrapped in aluminum foil	6 months	40 days

[1] Holding times are advisory - no holding times are defined in method 680.

6.0 APPARATUS AND MATERIALS

6.1 GC/MS System with compatible data system autosampler, splitless injector, and direct capillary interface.

6.2 Recommended Capillary column-HP-5MS, 30m x 0.25mm ID, 0.50um film thickness. Equivalent columns can be used.

6.3 Microsyringes-

6.4 Volumetric flasks, Class A-appropriate volumes

6.5 Analytical balance

7.0 REAGENTS

7.1 Hexane

8.0 STANDARDS

The preparation of the calibration standards must be tracked in accordance with STL SOP AN41:*Standard Material Traceability*. General guidance on the preparation of standards is given in STL SOP AN43:*Standard Preparation.*

The lab should purchase certified solutions from STL-approved vendors, if available. The lab should prepare standards from neat materials only if a certified solution is not available. See STL SOP AN43 for guidance for standard preparation from neat materials.

8.1 The recommended calibration standards are listed in Appendix A, Table 1. Prepare these standards at the stated concentrations in hexane.

8.2 The surrogate compound, 13C12-Decachlorobiphenyl, is prepared at a concentration of 1.0ug/mL and
1.0mL of this solution is spiked into all samples and QC items prior to extraction.

8.3 The matrix spiking solution contains one PCB congener of each chlorination level except for the nonachlorobiphenyls. The solution is prepared at the indicated concentrations in acetone and 1.0mL of this solution is spiked into all lab spikes and matrix spikes.

COMPOUND	CONCENTRATION (ug/mL)
2-Chlorobiphenyl	2.0
2,3-Dichlorobiphenyl	2.0
2,4,5-Trichlorobiphenyl	2.0
2,2',4,6-Tetrachlorobiphenyl	4.0
2,2',3,4,5'-Pentachlorobiphenyl	4.0
2,2',4,4',5,6'-Hexachlorobiphenyl	4.0
2,2',3,4',5,6,6'-Heptachlorobiphenyl	6.0
2,2',3,3',4,5',6,6'-Octachlorobiphenyl	6.0
Decachlorobiphenyl	10

9.0 SAMPLE PREPARATION

9.1 The sample extraction procedures are given in the following SOPs:

Matrix	SOP Number	Extraction Technique
Aqueous	EX30	Continuous Liquid-liquid Extraction
Aqueous	EX35	Separatory Funnel
Soils/Sediments and Biological	EX40, PS15	Sonication

9.2 The sample concentration procedures are given in STL SOP EX 50: Zymark Nitrogen Concentration.

9.3 Gel permeation chromatography (STL SOP EX61) may help to eliminate or minimize matrix interferences in a limited number of samples. The GPC cleanup is generally not effective on samples containing petroleum products. Acid cleanup (STL SOP EX60) is recommended as a routine cleanup prior to analysis. Sulfur cleanup may be necessary if the sample extract contains high levels of sulfur.

10.0 PROCEDURE

10.1 Instrument Conditions

Instrument conditions may vary according to the sensitivity of each instrument. The following conditions are provided for guidance. The lab must document the conditions used for the analysis of SVOC by GC/MS.

Recommended Column:
HP-5MS 30m x 0.25mm ID, 0.50um film thickness or equivalent

Column flow: Approximately 1mL/min helium

GC Oven temperatures:
Initial column temperature: 45 C for 1 minutes
Column temperature program 1 : 20C per minute to 150C, hold 1 minute
Column temperature program 2 : 10C per minute to 310C, hold until DCB and 13C12-DCB elute

GC injector parameters
Injector temperature : 250-260EC
Injector : splitless
Inlet purge time : 0.8 minutes
Injector liner : 4mm ID quartz or 4mm glass, deactivated
Sample injection volume : 2uL

Mass Spectrometer and interface parameters
Mass spectrometer interface: 300C
Mass spectrometer source temperature: Factory Set
Mass range: SIM (see Table 3 in Appendix B for ions to monitor)
Mass range for DFTPP analysis: 35-500amu at 1 scan per second or less.

10.2 Tune Criteria

Twenty nanograms of DFTPP are analyzed at the beginning of each 12 hour clock as a check on the "tune" of the mass spectrometer. The DFTPP analysis is performed using scan analysis and the same tune parameters are used for the SIM analysis of the calibration standards and samples.

10.2.1 Prepare a 10ng/uL solution of DFTPP column evaluation standard. The standard must also contain p,p'-DDT (4,4'-DDT).

10.2.2 Analyze a 1uL aliquot of the 10ng/uL DFTPP solution using the same temperature program that is used for SIM analysis of the calibration standards, samples, and QC samples.

10.2.3 Evaluate the DFTPP peak.

-The chromatogram should exhibit acceptable baseline behavior and the DFTPP peak should be symmetrical.

-The spectrum of the DFTPP must meet the criteria listed in the SOP Summary. Background subtraction must be straightforward and designed only to eliminate column bleed or instrumental background. Scans +/- 2 scans from the apex can be evaluated for the DFTPP criteria. Consecutive scans within this range may be averaged to meet the criteria.

NOTE: The DFTPP analysis should be evaluated as to the relative size of the DFTPP peak under the m/z 198 profile. A benchmark area window should be established for each instrument and data system. Area outside of this window suggests instrumental problems such as a bad injection, clogged autosampler syringe, leaking injector, reduced or elevated detector sensitivity, improper electron multiplier voltage selection, wrong tune method or tune file selected for this analysis, PFTBA valve left open , etc.

If the DFTPP fails to meet the criteria, the instrument may require tuning (manually or automatically with PFTBA). Depending on the nature of the results from the DFTPP analysis, other corrective measures may include remaking the DFTPP standard, cleaning the mass spectrometer source, etc.

10.3 Window-Defining Solution and SIM Parameters

10.3.1 Analyze 1uL of the window-defining solutions in the scan mode from 45amu to 500amu at > 1 scan per second. Use the same temperature program that will be used for the SIM analysis of PCBs. The window defining solutions may be analyzed separately or may be combined into a single solution.

10.3.2 Determine the retention times of the first and last eluting congeners at each level of chlorination. The quantiation and confirmation masses are listed in Table 3 of Appendix B.

10.3.3 Set the SIM parameters as follows. Refer to Table 3 of Appendix B for the ion sets.

-Begin data acquisition with ion set #1 before the elution of PCB congener #1, Stop the acquisition of ion set #1 and begin acquisition of ion set #2 approximately 10 seconds before the elution of PCB congener #104.
-Stop the acquisition of ion set #2 and begin the acquisition of ion set #3 approximately 10 seconds after the elution of PCB congener #77..
-Stop the acquisition of ion set #3 and begin the acquisition of ion set #4 approximately 10 seconds after the elution of 4,4'-DDT. (the retention time of 4,4'-DDT is determined from the scan analysis of the DFTPP solution that is analyzed at the beginning of each 12-hour clock.).
-Stop the acquisition of ion set #4 and begin the acquisition of ion set #5 approximately 10 seconds before the elution of PCB congener #208.

10.4 Initial Calibration

After the SIM windows are established and verified and the DFTPP criteria has been met, the initial calibration standards are analyzed. Note that a single PCB congener of each chlorination level is used for calibration and quantiation. Decachlorobiphenyl is used to quantify nonachlorobiphenyls.

10.4.1 Prepare the initial calibration standards. The lowest calibration standard should be at the RL and the rest of the standards will define the working range.

10.4.2 Set up a sequence and analyze the calibration standards. The injection volume must be the same for the calibration standards and all sample extracts. The routine volume is 1uL.

10.4.3 Identify the internal standards, surrogates, and the target compounds. The data system must be updated with the proper retention times and ion data.

10.4.4The relative response factor for each compound is calculated as follows:

$$RRF = \frac{(Ax)(Cis)}{(Ais)(Cx)}$$

where

Ax = area of the characteristic ion of the calibration congener
Ais = area of the characteristic ion for Chrysene-d10
Cx = concentration of the compound being measured (ug/mL)
Cis = concentration of the internal standard (40ug/mL)

NOTE: Use Chrysene-d10 as the internal standard unless matrix interferences are encountered. If phenthrene-d10 must be used, the calibration must be re-evaluated and verified using the second internal standard

10.4.5 Calculate the average relative response factor (RRF_{avg}) for each target compound and each surrogate compound:

$$RRF_{avg} = \frac{RRF1 + RRF2 + RRF3.... + RRFn}{n}$$

RRF1 = relative response factor of the first standard
RRFn = relative response factor of the last standard
n = number of calibration standards

10.4.6Calculate the standard deviation (SD) for the initial calibration standards:

$$SD = \sqrt{\frac{\sum_{i-1}^{n_1}}{} \frac{(RRF_i - RRF_{avg})^2}{n-1}}$$

10.4.7Calculate the relative standard deviation (%RSD) of the target compounds in the calibration standards.

$$\%RSD = \frac{SD}{RRF_{avg}} x\ 100$$

- If the %RSD of each target compound is less than or equal to 20%, the average response factor can be used for quantitation of samples.

- If the %RSD of the target compound is greater than 20%, the curve should be evaluated for errors and one or more standards re-analyzed. Take corrective action until the %RSD of each target is less than 20%.

10.4.8 Performance Criteria
In addition to meeting the calibration criteria, the following performance criteria must also be met for the mid-level standard.

-Mass abundance ratios of all calibration congeners within acceptance range (see Table 4,Appendix B)
-Baseline separation of PCB congener #87 from congeners #154 and #77
-Signal-to-noise ratio of >=5 for decachlorobiphenyl ion 499 and chrysene-d12 ion 241
-decachlorobiphenyl mass abundance: mass 500 >=70% but <=95% of mass 498

10.5 Continuing Calibration Verification
Samples are analyzed only after the DFTPP criteria and the calibration acceptance criteria have been met. The analytical system must be evaluated every 12 hours by the analysis and evaluation of the DFTPP and a mid-level calibration standard prior tot he analysis of samples and after the samples by the analysis and evaluation of a mid-level standard.

10.5.1 The percent difference or percent drift between the continuing calibration RRF and the average relative response factor (RRFavg) is calculated for each target compound and each surrogate compound:

$$\%difference = \left| \frac{RRF - RRFavg}{RRFavg} \right| \otimes 100$$

where
RRF = relative response factor from CCV
RRFavg = average relative response factor from initial calibration curve

If the percent difference is less than or equal to 20% for each target compound, the initial calibration is verified.

If the continuing calibration criteria are not met, action must be taken to bring the analytical system into compliance with the criteria. This action may include injection port maintenance, source cleaning, changing the column, or replacement of injection port lines and assembly. In any case, if the criteria are not met, the analysis of the continuing calibration standard must be repeated. The analyst must be aware of the 12-hour clock-DFTPP criteria must be met prior to the analysis of the calibration standards. If the continuing calibration standard repeatedly fails the calibration verification criteria, the initial calibration curve must be reanalyzed and reevaluated.

The performance criteria given in Section 10.4.8 must also be met prior to the analysis of samples.

10.6 Sample Analysis
Remove the sample extracts to be analyzed from the refrigerator and allow the sample to come to ambient temperature.

10.6.1 Add 30uL of the internal standard mix (25ug/mL) to each 1-mL aliquot of the sample extract. The concentration of the internal standard in the extract is 0.75 ng/uL.

10.6.2 Mix the contents of the autosampler vial by inverting several times.

10.6.3 Determine the concentration of the samples and QC items using the procedures of Section 11. If the concentration of a sample is above the highest calibration standard, the sample must be diluted and reanalyzed.

10.6.4 The dilution factor is calculated by dividing the volume of sample extract in microliters into 1000. For example, if 100uL of a sample extract is diluted to final volume of 1.0mL, the dilution factor is 10.
(1000/100 = 10). The following table gives some dilution factors:

Dilution Preparation

uL extract-Vext	uL MeCl2	volume of dilution (Vdil-uL)	uL ISTD (25ug/mL)-Vistd	DF
1000	0	1000	30	1
500	500	1000	15*	2
200	800	1000	24	5
100	900	1000	27	10
50	950	1000	28.5	20
20	980	1000	30	50

*assumes dilution of a 1.0mL extract or 1mL aliquot of an extract that has been spiked with the internal standard at 0.75ug/mL using 30ul of a 25.0ug/mL internal standard solution

The concentration of internal standards must remain constant for all extracts and extract dilutions at 0.75ug/mL. The following equation can be used to determine the volume of the 25.0 ug/mL internal standard solution to add to an extract when a dilution is prepared from an extract that has already been spiked with the internal standard solution:

$$Vistd(uL) = 30uL - \left(\frac{Vext}{Vdil} \otimes 30ul\right)$$

Vistd = volume of 25.0ug/mL internal standard to add to the diluted extract (uL)
Vext = volume of extract used to prepare the dilution (uL)
Vdil = final volume of the dilution (uL)-1000uL (1.0mL)

11.0 DATA ANALYSIS/CALCULATIONS

11.1 Qualitative Analysis

The default procedure will be to use only the quantitation and confirmation ions for identification and quantification of PCB congeners. Interference check ions, as described in Section 11.2.3, will not be used routinely to evaluate peaks as PCB congeners unless specified in a client QAP or agency requirement or the sample concentration is near a critical quantitation limit.

11.1.1 Examine the Selected Ion Current Profiles (SICP) for the internal standards. Confirm that the RT and response of the internal standards are within the acceptance criteria specified in the SOP Summary. If the internal standard retention times have changed significantly or the peaks cannot be located, stop and analysis and correct the problem. Reanalyze any associated samples.

11.1.2 Evaluate the peaks for candidates to be identified as PCBs. A peak is tentatively identified as a PCB if

-The peak falls within the retention time range bordered by the first and last eluting isomer of that chlorination level

-The ratio of the quantitation and confirmation ions are present and the area ratios fall within the acceptance criteria in Appendix B, Table 4. The scans must maximize within one scan of each other. Examine the data for the presence of a coeluting PCB of higher chlorination if both ions and the M-70 ions are present and the ratio does fall within the acceptance limits.

-The areas for the quantiation and confirmation ions must be greater than three times the background noise and must fall within the working range of the calibration curve (must not saturate the detector

-At least one ion in the M-70 cluster must be present

11.1.3 Evaluate each PCB candidate in the Cl-3 to Cl-7 range for the presence of coeluting PCBs containing one or two additional chlorines. An intense M+35 ion at the retention time may indicate a PCB with one additional chlorine and the presence of an intense M+70 would indicate a co-eluting PCB containing two additional chlorines. Use the information in Tables 5 and 6 of Appendix B to correct for the interfering ion(s).

For example, if a Cl-7-PCB and a Cl-5-PCB coelute, the Cl-7-PCB will contribute to the quantiation and confirmation ions for the Cl-5-PCB. Cl-7-PCB produces a cluster of three ions by the loss of two chlorines-ions 322,324, and 326. Two of these ions-324 and 326-are also ions contained in the molecular ion cluster of Cl-5-PCB. To determine the ion 326 and 324 areas produced only by the Cl-5-PCB, calculate the contribution to each and subtract it from the measured areas. See Tables 5 and 6 in Appendix B for the percentage of the interference peak to subtract from the quantiation and confirmation ions. In this example, 164% of the area measured for ion 322 should be subtracted from the area measured for ion 324 and 108% of the area measured for ion 322 should be subtracted from ion 326.

NOTE: A coeluting PCB with one more chlorine will affect only the quantiation ion (Table 6). The interference from a coeluting PCB containing one more chlorine, due to the natural abundance of 13C12, is small and can usually be neglected except when measuring the area of a small amount of a PCB coeluting with a large amount of a another PCB containing one more chlorine.

11.2 Calculations for Samples-Internal Standard Technique
These calculations assume that the same volume is injected for standards and samples.

11.2.1 Aqueous Samples

$$concentration(ug/L) = \frac{Ax}{Ais} \otimes \frac{Cis}{RRFavg} \otimes \frac{F}{V} \otimes DF$$

where

Ax =	sum of areas of the characteristic ion of the PCB chlorination level being measured
Ais =	area of the characteristic ion of the internal standard
Cis =	concentration of the internal standard (ug/mL)
RRFavg =	average response factor of the compound being measured
F =	final volume of extract (mL)
V =	volume of sample extracted (L)
DF =	dilution factor

The reporting limit (RL) for each sample is given:

$$RL(ug/L) = RLqap \otimes \frac{F}{Fqap} \otimes \frac{Vqap}{V} \otimes DF$$

where

F =	final volume of extract (mL)
Fqap =	1.0mL
Vqap =	1.0L
V =	volume of sample extracted
DF =	dilution factor. The STL CQAP Table 5 RL(RLqap) assumes a DF of 1.

NOTE: If V = 800mL to 1200mL, assume that Vqap/ V = 1 in the calculation of the reporting limit.

11.2.2 Soils

$$concentration(ug/kg,dw) = \frac{Ax}{Ais} \otimes \frac{Cis}{RRFavg} \otimes \frac{F}{(W)(solids)} \otimes DF$$

where

Ax =	sum of areas of the characteristic ion of the PCB chlorination level being measured
Ais =	area of the characteristic ion of the internal standard
Cis =	concentration of the internal standard (ug/mL)
RRFavg =	average response factor of the compound being measured
F =	final volume of extract (mL)
W =	weight of sample extracted (kg)
solids =	(percent solids)/100
DF =	dilution factor

The reporting limit (RL) for each sample is given:

$$RL = RLqap \otimes \frac{F}{Fqap} \otimes \frac{Wqap}{(W)(solids)} \otimes DF$$

where

F = final volume of extract (mL)
W = weight of sample extracted (kg)
solids = (percent solids)/100

The STL CQAP assumes Wqap = 30g, solids = 1, Fqap = 1.0mL, and DF = 1.

12.0 QUALITY ASSURANCE /QUALITY CONTROL

12.1 The analytical batch consists of up to twenty client samples and the associated QC items that are analyzed together. The matrix spike and LCS frequency is defined in AN02: *Analytical Batching*. STL SOP AN02 also describes the procedure for evaluating batch-specific QC. The attached SOP summary and Table 13.1 in the STL Corporate QA Plan provide guidance for evaluating sample data.

12.2 Initial Demonstration of Capability (IDOC) to Generate Acceptable Accuracy and Precision

Each laboratory must demonstrate competence in the analysis of samples by this procedure. The minimum criteria for this demonstration are the preparation and analysis of spiked reagent water. The criteria for IDOC accuracy and precision are the accuracy and precision criteria listed in Table 5 of the STL QAP.

12.3 Method Detection Limit

The method detection limit is determined by each lab annually in accordance with STL SOP CA90:*Procedure for Determination of Method Detection Limit (MDL)*.

13.0 PREVENTIVE MAINTENANCE

Preventive maintenance items will be added at a later date. See Section 10 of the current STL Quality Assurance Plan.

14.0 TROUBLE-SHOOTING-Trouble-shooting items will be added at a later time.

15.0 REFERENCES

15.1 *STL's Comprehensive Quality Assurance Plan* and STL's *Corporate Quality Assurance Plan*, current revisions.

15.2 *Method 680: Determination of Pesticides and PCBs in Water and Soils/Sediment by Gas Chromatography/Mass Spectrometry*. November 1985. Physical and Chemical Methods Branch, Environmental Monitoring and Support Laboratory, Office of Research and Development, USEPA, Cincinnati, OH

APPENDIX A

TABLE 1 CALIBRATION STANDARDS

CALIBRATION COMPONENTS	CAL 1	CAL 2	CAL3	CAL4	CAL5
Calibration Congener					
2-chlorobiphenyl (1)	0.10	0.50	1.0	2.0	5.0
2,3-dichlorobiphenyl(5)	0.10	0.50	1.0	2.0	5.0
2,4,5-trichlorobiphenyl(29)	0.10	0.50	1.0	2.0	5.0
2,2',4,6-tetrachlorobiphenyl(50)	0.20	1.0	2.0	4.0	10
2,2',3,4,5'-Pentachlorobiphenyl (87)	0.20	1.0	2.0	4.0	10
2,2',4,4',5,6'-hexachlorobiphenyl(154)	0.20	1.0	2.0	4.0	10
2,2',3,4',5,6,6'-heptachlorobiphenyl(188)	0.30	1.5	3.0	6.0	15
2,2',3,3',4,5,5',6,6'-octachlorobiphenyl(200)	0.30	1.5	3.0	6.0	15
Decachlorobiphenyl	0.50	2.5	5.0	10	25
Retention Time Congeners					
3,3',4,4-tetrachlorobiphenyl(77)	0.20	1.0	2.0	4.0	10
2,2',4,6,6'-Pentachlorobiphenyl (104)	0.20	1.0	2.0	4.0	10
2,2',3,3',4,5,5',6,7'-nonachlorobiphenyl(208)	0.40	2.0	4.0	8.0	20
Surrogate					
13C12-Decachlorobiphenyl	0.50	2.5	5.0	10	25
Internal Standards					
Phenathrene-d10	0.75	0.75	0.75	0.75	0.75
Chrysene-d12	0.75	0.75	0.75	0.75	0.75

TABLE 2 –First and Last Eluting Isomers

Congener	First Eluting Isomer	Last Eluting Isomer
Cl-1	2-chlorobiphenyl	4-Chlorobiphenyl
Cl-2	2,6-dichlorobiphenyl	4,4'-dichlorobiphenyl
Cl-3	2,2',6-trichlorobiphenyl	3,4,4'-trichlorobiphenyl
Cl-4	2,2',6,6'-tetrachlorobiphenyl	3,3',4,4'-tetrachlorobiphenyl
Cl-5	2,2',4,6,6'-pentachlorobiphenyl	3,3',4,4',5-pentachlorobiphenyl
Cl-6	2,2',4,4',6,6'-hexachlorobiphenyl	3,3',4,4',5,5'-hexachlorobiphenyl
Cl-7	2,2',3,4',5,6,6'-heptachlorobiphenyl	2,3,3',4,4',5,5'-heptachlorobiphenyl
Cl-8	2,2',3,3',5,5',6,6'-octachlorobiphenyl	2,3,3',4,4',5,5',6-octachlorobiphenyl
Cl-9	2,2',3,3',4,5,5',6,6'-nonachlorobiphenyl	2,2',3,3',4,4',5,5',6-nonachlorobiphenyl

APPENDIX B
SIM IONS

Table 3-Ions for SIM Acquisition

ION Set 1 (a)	ION Set 2 (b)	ION Set 3 (c)	ION Set 4 (d)	ION Set5 (e)
152	186	248	240	356
153	188	249	241	358
186	220	254	288	360
187	222	256	290	390
188	254	288	322	392
189	255	290	324	394
190	256	322	326	424
220	258	323	356	425
221	288	324	357	426
222	289	326	358	428
224	290	328	360	430
255	292	357	362	432
256	294	358	391	462
258	323	360	392	464
290	324	362	394	466
292	326	392	396	496
294	328	394	398	498
	358	396	428	499
	360	398	430	500
	362		432	502

(a) Cl-1 to Cl-4 and Phenthrene-d10
(b) Cl-3 to-Cl-6
(c) Cl5 to Cl-7
(d) Cl-6 to Cl-8 and Chrysene-d12
(e) Cl-8 to Cl-10 and 13C12-DCB

TABLE 4-Approximate Retention Times for PCB Isomer Groups and Calibration Congeners

PCB Isomer Group	Approximate RRT Range	Calibration Congener	Approximate Calibration Congener RRT
Cl-1	0.30-0.35	2-chlorobiphenyl (1)	0.30
Cl-2	0.38-0.50	2,3-dichlorobiphenyl(5)	0.43
Cl-3	0.46-0.64	2,4,5-trichlorobiphenyl(29)	0.54
Cl-4	0.55-0.82	2,2',4,6-tetrachlorobiphenyl(50)	0.56
Cl-5	0.64-0.92	2,2',3,4,5'-entachlorobiphenyl (87)	0.80
Cl-6	0.75-1.1	2,2',4,4',5,6'-hexachlorobiphenyl(154)	0.82
Cl-7	0.88-1.2	2,2',3,4',5,6,6'-heptachlorobiphenyl(188)	0.88
Cl-8	0.99-1.21	2,2',3,3',4,5,5',6,6'-octachlorobiphenyl(200)	1.03
Cl-9	0.16-1.28	Decachlorobiphenyl	1.3
Cl-10	1.3	Decachlorobiphenyl	1.3

RRT = retention time relative to Chrysene-d12

Table 4 Quantitation and Interference Check Ions

PCB Isomer Group	Quant ION	Confirmation ION	Expected Ratio(a)	Acceptable Ratio(a)	M-70 Confirmation ION	Interference Check ION M+70	Interference Check ION M+35
Cl-1	188	190	3.0	2.5-3.5	152	256	222
Cl-2	222	224	1.5	1.3-1.7	152	292	256
Cl-3	256	258	1.0	0.8-1.2	186	326	290
Cl-4	292	290	1.3	1.1-1.5	220	360	326
Cl-5	326	324	1.6	1.4-1.8	354	394	360
Cl-6	360	362	1.2	1.0-1.4	288	430	394
Cl-7	394	396	1.0	0.8-1.2	322	464	430
Cl-8	430	428	1.1	0.9-1.3	356	498	464
Cl-9	464	466	1.3	1.1-1.5	390		498
Cl-10	498	500	1.1	0.9-1.3	424		
Chrysene-d12	240	241	5.1	4.3-5.9			
Phenathrene-d10	188	189	6.6	6.0-7.2			
13C12-DCB (surrogate)	510	512					

(a) ratio of quantitation ion to confirmation ion

TABLE 5-Corrections for Interference of PCB Containing Two Additional Chlorines

PCB Isomer Group	Quant ION	Confirmation ION	Ion Measured to Determine Interference	Percent Ion area to be subtracted from QUNAT ION Area	Percent Ion area to be subtracted from CONFIRMATION ION Area
Cl-3	256	258	254	99	33
Cl-4	292	290	288	65	131
Cl-5	326	324	322	108	164
Cl-6	360	362	356	161	71
Cl-7	394	396	390	225	123

TABLE 6-Corrections for Interference of PCB Containing One Additional Chlorine

PCB Isomer Group	Quant ION	Ion Measured to Determine Interference	Percent Ion area to be subtracted from QUNAT ION Area
Cl-2	222	221	13.5
Cl-3	256	255	13.5
Cl-4	292	289	17.4
Cl-5	326	323	22.0
Cl-6	360	357	26.5
Cl-7	394	391	30.9
Cl-8	430	425	40.0

APPENDIX C
680 SOP SUMMARY

HOLD TIMES

MATRIX	Preservative/ Storage	Routine Container	Sample Hold Time	Extract Hold Time
Aqueous	none; 4C	1-L amber	7 days	40 days
Soil/ Sediment	none; 4C	500-mL	14 days	40 days
Biological	Frozen	Glass or aluminum foil	6 months	40 days

ANALYSIS SEQUENCE

INITIAL CALIBRATION	CONTINUING CALIBRATION
DFTPP 10ng on column Clock starts at injection	DFTPP 10ng on column Clock starts at injection
Calibration standards- minimum of five cal levels	Mid point calibration verification
Samples and the capping standard must be analyzed within 12 hours of the start of the clock	Samples and the capping standard must be analyzed within 12 hours of the start of the clock
Capping standard	Capping standard

DFTPP CRITERIA

m/z	Ion Abundance Criteria
127	40-60% of mass 198
197	<1.0% of mass 198
198	Base peak, 100% relative abundance
199	5-9% of mass 198
275	10-30% of mass 198
365	>1% of mass 198
441	Present but less than mass443
442	>40% of mass 198
443	17-23% of mass 442

ANALYTICAL BATCH
SEE STL SOP AN02.

CALIBRATION ACCEPTANCE CRITERIA

Initial Calibration	Continuing Calibration
RRFavg <= 20% RSD	Percent difference <= 20% difference from initial calibration

QC Item	Frequency	Acceptance Criteria	Corrective Action
Tune/Column Evaluation Standard DFTPP 20ng	Prior to analysis of calibration standards every 12 hours	DFTPP - within criteria	-Evaluate alternative scans -Reanalyze and evaluate -Retune and reanalyze -Clean source, retune, reanalyze
Initial Calibration-minimum of five calibration standards	After Tune Check and when calibration verification standard fails acceptance criteria.	%RSD <= 20%	-Reanalyze standard(s) -Prepare new standard(s) and reanalyze -Perform injector port maintenance and reanalyze standards -Retune and reanalyze standards -Replace column and reanalyze standards -Clean source and reanalyze standards
Performance Criteria	Evaluate mid level calibration standard each clock	-Mass abundance ratios of all calibration congeners within acceptance range (see Appendix B) -Baseline separation of PCB congener #87 from congeners #154 and #77 -Signal-to-noise ratio of >=5 for decachlorobiphenyl ion 499 and chrysene-d12 ion 241 -decachlorobiphenyl mass abundance: mass 500 >=70% but <=95% of mass 498	-Reanalyze standard -Prepare new standard and reanalyze -Recalibrate
Continuing Calibration Verification	After tune check; every 12 hours prior to analysis of samples and at the end of the analytical sequence	%Difference <= 20%	-Reanalyze standard -Prepare new standard and reanalyze -Recalibrate

QC Item	Frequency	Acceptance Criteria	Corrective Action
Internal Standard Areas	Evaluate all standards and samples	Areas in continuing calibration verification must be within 30% of the previous CCV and within 50% of the initial calibration Areas in samples should be evaluated for gross error . Consult superior	-Evaluate chromatogram, spectra, and integrations -Reanalyze extract -Perform instrument maintenance and reanalyze extract -Re-extract and reanalyze if sufficient sample available
Surrogate recovery	Evaluate for all samples and QC items if extract is not diluted OR If diluted, where >RL	Within Section 5 QAP limits	-Evaluate chromatogram, spectra, and integrations -Reanalyze extract(s) -Re-extract and reanalyze if sufficient sample available
Method Blank	Per batch	All targets < RL in Section 5 Table of QAP	-Evaluate chromatogram, spectra, and integrations -Reanalyze extract -Follow guidance in STL SOP AN02 and STL QAP Table 13.1
Lab Control Standard (LCS) - QAP subset	See AN02	All spiked targets within the accuracy criteria in Section 5 Table of QAP	-Evaluate chromatogram, spectra, and integrations -Reanalyze extract -Follow guidance in STL SOP AN02 and STL QAP Table 13.1
Matrix spike (MS) Matrix spike duplicate (MSD)	Per batch if sufficient sample volume/weight supplied See AN02	All targets within the accuracy and precision criteria in Section 5 Table of QAP	-Evaluate chromatogram, spectra, and integrations -Reanalyze extract -Follow guidance in STL SOP AN02 and STL QAP Table 13.1

QC Item	Frequency	Acceptance Criteria	Corrective Action
Initial Demonstration of Capability (IDOC)	Per analyst	Accuracy and precision within method specified criteria	-Evaluate data -Reanalyze extracts if warranted -Re-extract and reanalyze for targets that fail criteria
Method Detection Limit (MDL)	See CA90	Evaluate according to STL SOP CA90	Evaluate according to STL SOP CA90

Method 680. Determination of Pesticides and PCBs in Water and Soil/Sediment by Gas Chromatography/Mass Spectrometry

November 1985

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1	Total ion current profile of PCB calibration congeners and pesticide Analytes
2	Diagram indicating approximate relative retention times of PCB isomer groups and retention time congeners.

1. SCOPE AND APPLICATION

1.1. This method provides procedures for mass spectrometric determination of polychlorinated biphenyls (PCBs) and the listed pesticides in water, soil, or sediment. This method is applicable to samples containing PCBs as single congeners or as complex mixtures, such as commercial Aroclors. PCBs are identified and measured as isomer groups (i.e., by level of chlorination). The existence of 209 possible PCB congeners makes impractical the listing of the Chemical Abstracts Service Registry Number (CASRN) for each potential method analyte. Because PCBs are identified and measured as isomer groups, the non-specific CASRN for each level of chlorination is used to describe method analytes.

Analyte(s)	Formula	CASRN
Aldrin	$C_{12}H_8Cl_6$	309-00-2
BHCs		
alpha isomer	$C_6H_6Cl_6$	319-84-6
beta isomer	$C_6H_6Cl_6$	319-85-7
delta isomer	$C_6H_6Cl_6$	319-86-8
gamma isomer(lindane)	$C_6H_6Cl_6$	58-89-9
Chlordane (technical)		57-74-9
alpha-chlordane	$C_{10}H_6Cl_8$	5103-71-9
gamma-chlordane	$C_{10}H_6Cl_8$	5103-74-2
trans-nonachlor	$C_{10}H_5Cl_9$	39765-80-5
4,4'-DDD	$C_{14}H_{10}Cl_4$	72-54-8
4,4'-DDE	$C_{14}H_8Cl_4$	72-55-9
4,4'-DDT	$C_{14}H_9Cl_5$	50-29-3
Dieldrin	$C_{12}H_8Cl_6O$	60-57-1
Endosulfan I	$C_9H_6Cl_6O_3S$	959-98-8
Endosulfan II	$C_8H_6Cl_6O_3S$	33213-65-9
Endosulfan sulfate	$C_9H_4Cl_6O_4S$	1031-07-8
Endrin	$C_{12}H_8Cl_6O$	72-20-8
Endrin aldehyde	$C_{12}H_8Cl_6O$	7421-93-4
Endrin ketone	$C_{12}H_8Cl_6O$	53494-70-5
Heptachlor	$C_{10}H_5Cl_7$	76-44-8
Heptachlor epoxide	$C_{10}H_5Cl_7O$	1024-57-3
Methoxychlor	$C_{16}H_{15}Cl_3O_2$	72-43-5
PCBs		
Monochlorobiphenyls	$C_{12}H_9Cl$	27323-18-8
Dichlorobiphenyls	$C_{12}H_8Cl_2$	25512-42-9
Trichlorobiphenyls	$C_{12}H_7Cl_3$	25323-68-6
Tetrachlorobiphenyls	$C_{12}H_6Cl_4$	26914-33-0
Pentachlorobiphenyls	$C_{12}H_5Cl_5$	25429-29-2
Hexachlorobiphenyls	$C_{12}H_4Cl_6$	26601-64-9
Heptachlorobiphenyls	$C_{12}H_3Cl_7$	28655-71-2
Octachlorobiphenyls	$C_{12}H_2Cl_8$	31472-83-0
Nonachlorobiphenyls	$C_{12}HCl_9$	53742-07-7
Decachlorobiphenyl	$C_{12}Cl_{10}$	2051-24-3

1.2 Detection limits vary among method analytes and with sample matrix, sample preparation procedures, condition of the GC/MS system, type of data acquisition, and individual samples. The calculated method detection limit (MDL) for each pesticide in fortified reagent water extracts analyzed with full-range data acquisition is presented in Sect. 14. Analysis of calibration solutions indicated that the calculated MDLs do not accurately reflect instrumental detection limits. The following guidance is based on numerous analyses of calibration solutions with one instrument over a period of approximately six months. Pesticide analytes other than endosulfans I and II can be identified and accurately measured when the injected aliquot contains 2 ng of each analyte; the endosulfans require about 4 ng each. With selected-ion-monitoring (SIM) data acquisition, pesticide analyte detection limits are lowered by at least a factor of five. Detection limits for individual PCB congeners increase with increasing number of chlorine atoms, with the detection limit for decachlorobiphenyl being about 5-10 times higher than that of a monochlorobiphenyl. A monochlorobiphenyl can be identified and accurately measured when the injected extract aliquot contains 1 ng and full-range data are acquired. The detection limit for total PCBs will depend on the number of individual PCB congeners present. SIM data acquisition procedures reduce the detection limit for PCBs by at least a factor of three.

2. SUMMARY OF METHOD

A 1-L water sample is placed in a separatory funnel and extracted with methylene chloride. Appropriate extraction procedures for soil/sediment samples will be added when results are obtained from ongoing experiments. The extract is dried and exchanged to hexane during concentration to a final volume of 1 mL or less. Sample extract components are separated with capillary column gas chromatography (GC) and identified and measured with low resolution, electron ionization mass spectrometry (MS). An interfaced data system (DS) to control data acquisition and to store, retrieve, and manipulate mass spectral data is essential. Either full-range or selected-ion-monitoring (SIM) data are acquired, depending on the concentration range of concern. If full-range data are acquired, all method analytes can be identified and measured with one GC/MS analysis. If all pesticides and PCBs must be determined and if SIM data are necessary to meet required detection limits, two GC/MS analyses are necessary, one to detect and measure pesticides and one to detect and measure PCBs.

Two surrogate compounds are added to each sample before sample preparation; these compounds are $^{13}C_{12}$-4,4'-DDT and $^{13}C_6$-gamma-BHC. Two internal standards, chrysene-d_{12} and phenanthrene-d_{10}, are added to each sample extract before GC/MS analysis and are used to calibrate MS response. Each concentration measurement is based on an integrated ion abundance of one characteristic ion. All pesticides are identified as individual compounds, and a concentration is calculated by relating the MS response of each compound to the MS response of the internal standard with GC retention time nearer that of the pesticide analyte. The extent of sample contamination with technical chlordane is indicated by identification and measurement of the two most persistent components, gamma-chlordane and nonachlor. (Alpha-chlordane and heptachlor, other major components of technical chlordane, may also be present and will be detected and measured with this method.)

PCBs are identified and measured as isomer groups (i.e., by level of chlorination). A concentration is measured for each PCB isomer group; total PCB concentration in each sample extract is obtained by summing isomer group concentrations.

Nine selected PCB congeners are used as calibration standards, and one internal standard, chrysene-d_{12}, is used to calibrate MS response to PCBs, unless sample conditions require the use of the second internal standard, phenanthrene-d_{10}.

3. DEFINITIONS

3.1 CONCENTRATION CALIBRATION SOLUTION (CAL) -- A solution of method analytes used to calibrate the mass spectrometer response.

3.2 CONGENER NUMBER -- Throughout this method, individual PCBs are described with the number assigned by Ballschmiter and Zell (2). (This number is also used to describe PCB congeners in catalogs produced by Ultra Scientific, Hope, RI.)

3.3 INTERNAL STANDARD -- A pure compound added to a sample extract in known amounts and used to calibrate concentration measurements of other compounds that are sample components. The internal standard must be a compound that is not a sample component.

3.4 LABORATORY DUPLICATES (LD1 and LD2) --Two sample aliquots taken in the analytical laboratory are analyzed with identical procedures. Analysis of laboratory duplicates indicates precision associated with laboratory procedures but not with sample collection, preservation or storage procedures.

3.5 LABORATORY PERFORMANCE CHECK SOLUTION (LPC) -- A solution of method analytes, surrogate compounds, and internal standards used to evaluate the performance of the GC/MS/DS with respect to a defined set of method criteria.

3.6 LABORATORY REAGENT BLANK (LRB) -- An aliquot of reagent water or neutral solid reference material that is treated as a sample. It is exposed to all glassware and apparatus, and all method solvents, reagents, internal standards, and surrogate compounds are used. The extract is concentrated to the final volume used for samples and is analyzed the same as a sample extract.

3.7 LABORATORY SPIKE DUPLICATE SAMPLE -- One aliquot (LSD) of a sample is analyzed before fortification with any method analytes. In the laboratory, a known quantity of method analytes (LSA) is added to two independent aliquots of the same sample, and final analyte concentrations (LF1 and LF2) are measured with the same analytical procedures used to measure LSD.

3.8 LABORATORY SURROGATE SPIKE

3.8.1 Measured Value (LS1) -- Surrogate compound concentration measured with the same procedures used to measure sample components.

3.8.2 Theoretical Value (LS2) -- The concentration of surrogate compound added to a sample aliquot before extraction. This value is determined from standard gravimetric and volumetric techniques used during sample fortification.

3.9 METHOD DETECTION LIMIT (MDL) -- A statistically determined value (1) indicating the minimum concentration of an analyte that can be identified and measured in a sample matrix with 99% confidence that the analyte concentration is greater than zero. This value varies with the precision of the replicate measurements used for the calculation.

3.10 PERFORMANCE EVALUATION SAMPLE -- A sample containing known concentrations of method analytes that has been analyzed by multiple laboratories to determine statistically the accuracy and precision that can be expected when a method is performed by a competent analyst. Analyte concentrations are unknown to the analyst.

3.11 QUALITY CONTROL (QC) CHECK SAMPLE -- A sample containing known concentrations of analytes that is analyzed by a laboratory to demonstrate that it can obtain acceptable identifications and measurements with procedures to be used to analyze environmental samples containing the same or similar analytes. Analyte concentrations are known by the analyst. Preparation of the QC check sample by a laboratory other than the laboratory performing the analysis is highly desirable.

3.12 SURROGATE COMPOUND -- A compound not expected to be found in the sample is added to a sample aliquot before extraction and is measured with the same procedures used to measure sample components. Associated with the surrogate compound are two values, laboratory surrogate spike- measured value (LS1) and laboratory surrogate spike - theoretical value (LS2). The purpose of a surrogate compound is to monitor method performance with each sample.

4. INTERFERENCES

4.1 Interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing equipment. Laboratory reagent blanks (LRBs) are analyzed routinely to demonstrate that these materials are free of interferences under the analytical conditions used for samples.

4.2 To minimize interferences, glassware (including sample bottles) should be meticulously cleaned. As soon as possible after use, rinse glassware with the last solvent used. Then wash with detergent in hot water and rinse with tap water followed by distilled water. Drain dry and heat in a muffle furnace at 450°C for a few hours. After cooling, store glassware inverted or covered with aluminum foil. Before using, rinse each piece with an appropriate solvent. Volumetric glassware should not be heated in a muffle furnace.

4.3 For both pesticides and PCBs, interference can be caused by the presence of much greater quantities of other sample components that overload the capillary column; additional sample extract preparation procedures must then be used to eliminate interferences. Capillary column GC retention times and the compound-specific characteristics of mass spectra eliminate many interferences that formerly were of concern with pesticide/PCB determinations with electron capture detection. The approach and identification criteria used in this method for PCBs eliminate interference by most chlorinated compounds other than other PCBs. With the isomer group approach, coeluting PCBs that contain the same number of chlorines are identified and measured together. Therefore, coeluting PCBs are a problem only if they contain a different number of chlorine atoms. This interference problem is obviated by rigorous application of the identification criteria described in this method.

4.4 For SIM identification and measurement of pesticides, other chlorinated sample components that produce the same quantitation and confirmation ions may interfere, but only if retention times are nearly equivalent.

5. SAFETY

5.1 The toxicity or carcinogenicity of each chemical used in this method has not been precisely defined. Therefore, each should be treated as a potential health hazard, and exposure should be reduced to the lowest feasible level. Each laboratory is responsible for safely disposing materials and for maintaining awareness of OSHA regulations regarding safe handling of the chemicals used in this method. A reference file of material data handling sheets should be made available to all personnel involved in analyses. Additional information on laboratory safety is available (3-5).

5.2 The following method analytes have been classified as known or suspected human or mammalian carcinogens: BHCs, 4,4'-DDD, 4,4'-DDT, and PCBs. Primary standards of these compounds should be prepared in a hood. A toxic gas respirator should be worn when the analyst handles solutions containing high concentrations of these compounds.

6. APPARATUS AND EQUIPMENT

6.1 SAMPLING EQUIPMENT

6.1.1 Water Sample Bottles -- Meticulously cleaned (Sect. 4.2) 1-L or 1-qt amber glass fitted with a Teflon-lined screw cap. (Bottles in which high purity solvents were received can be used as sample bottles without additional cleaning if they have been handled carefully to avoid contamination during and after use of original contents.)

6.1.2 Soil/Sediment Sample Bottles -- Appropriate containers will be specified when appropriate extraction procedures are determined.

6.2 GLASSWARE

6.2.1 Separatory Funnel -- 2-L with Teflon stopcock.

6.2.2 Drying Column -- glass column approximately 400 mm long X 19 mm ID with coarse frit filter disc.

6.2.3 Chromatography Column -- glass column approximately 400 mm long X 19 mm ID with coarse frit filter disc and Teflon stopcock.

6.2.4 Concentrator Tube -- 10-mL graduated Kuderna-Danish design with ground-glass stopper.

6.2.5 Evaporative Flask -- 500-mL Kuderna-Danish design that is attached to concentrator tube with springs.

6.2.6 Snyder Column -- three-ball macro Kuderna-Danish design.

6.2.7 Vials -- 10- to 15-mL amber glass with Teflon-lined screw caps.

6.3 COMPUTERIZED GC/MS SYSTEM

6.3.1 The GC must be capable of temperature programming and be equipped with all required accessories, such as syringes, gases, and a capillary column. The GC injection port must be designed for capillary columns. Manual splitless injections were used to acquire data used as the basis for quality control requirements. An automatic injector, however, is desirable, because it should provide more precise retention times and areas. On-column injection with an uncoated precolumn is encouraged, because high mass descrimination and analyte degradation problems are minimized with this technique. With some GCs, however, the irreproducibility of the low initial column temperature required for on-column injections will cause irreproducible retention times (RTs) and relative retention times (RRTs). That can result in an inability to distinguish between two closely-eluting pesticide isomers and may cause ion sets to be changed at inappropriate times during SIM data acquistion. Splitting injections are not recommended.

6.3.2 Either full range or SIM mass spectral data are obtained with electron ionization at a nominal electron energy of 70 eV. To ensure sufficient precision of mass spectral data, the required MS scan rate must allow acquisition of at least five full-range mass spectra or five data points for each monitored ion while a sample component elutes from the GC. The MS must produce a mass spectrum meeting all criteria for $\leq$20 ng of decafluorotriphenylphosphine (DFTPP) introduced through the GC inlet.

6.3.3 An interfaced data system (DS) is required to acquire, store, reduce, and output mass spectral data. The DS must be capable of searching a data file for specific ions and plotting ion abundances versus time or spectrum number to produce selected ion current profiles (SICPs) and extracted ion current profiles (EICPs). Also required is the capability to obtain chromatographic peak areas between specified times or spectrum numbers in SICPs or EICPs. Total data acquisition time per cycle should be $\geq$0.5 s and must not exceed 1.5 s.

6.3.4 SIM Option -- For SIM data acquisition, the DS must be equipped with software capable of acquiring data for multiple groups of ions, and the DS must allow automated and rapid changes of the set of ions being monitored. To acquire all PCB data needed for implementation of two currently-available automated interpretation procedures, the SIM program must be capable of acquiring data for four groups (or mass ranges) each consisting of $\leq$35 ions or for five groups of $\leq$20 ions each. The times spent monitoring ions during sample analyses must be the same as the times used when calibration solutions were analyzed.

6.4 GC COLUMN -- A 30 m X 0.32 mm ID fused silica capillary column coated with a 0.25 um or thicker film crosslinked phenyl methyl silicone (such as Durabond-5 (DB-5), J and W Scientific, Rancho Cordova, CA) or polydiphenyl vinyl dimethyl siloxane (such as SE-54, Alltech Associates, Deerfield, IL) is required. Operating conditions known to produce acceptable results with these columns are shown in Table 1; separation of pesticide analytes and PCB calibration congeners with a DB-5 column and those operating conditions is shown in Figure 1. Retention times have been reported (6) for all 209 PCB

congeners with an SE-54 column, which provides the same retention order for PCBs and essentially the same separation capabilities as a DB-5 column.

6.5 MISCELLANEOUS EQUIPMENT

6.5.1 Volumetric flasks - 2-mL, 5-mL, 10-mL, 25-mL, and 50-mL with ground glass stoppers.

6.5.2 Microsyringes - various standard sizes.

6.5.3 Boiling Chips -- approximately 10/40 mesh. Heat at 400°C for 30 min or extract with methylene chloride in a Soxhlet apparatus.

6.5.4 Water Bath -- heated, with concentric ring cover, capable of temperature control within ± 2°C.

6.5.5 Analytical Balance -- capable of accurately weighing to 0.0001 g.

7. REAGENTS AND CONSUMABLE MATERIALS

7.1 SOLVENTS -- High purity, distilled-in-glass hexane and methylene chloride. For precise injections with splitless injectors and capillary columns, all samples and standards should be contained in the same solvent. Effects of minor variations in solvent composition (i.e., small percentage of another solvent remaining in hexane extracts) are minimized with the use of internal standards. (External standard calibration is not acceptable.)

7.2 SODIUM SULFATE -- ACS, granular, anhydrous. Purify by heating at 400°C for 4 h in a shallow tray.

7.3 SODIUM THIOSULFATE -- ACS, granular.

7.4 TETRABUTYLAMMONIUM SULFITE REAGENT -- Dissove 3.39 g of tetrabutylammonium hydrogen sulfate in 100 mL distilled water. To remove impurities extract solution three times with 20-mL portions of hexane. Discard the hexane extracts, and add 25 g sodium sulfite to the water solution. Store the resulting solution in an amber bottle with a Teflon-lined screw cap. The solution can be stored at room temperature for at least one month.

7.5. MS PERFORMANCE CHECK SOLUTION -- Prepare a 10 ng/uL solution of decafluorotriphenylphosphine (DFTPP) in an appropriate solvent.

7.6 INTERNAL STANDARDS -- Chrysene-d_{12} and phenanthrene-d_{10} are used as internal standards. They are added to each sample extract just before analysis and are contained in all calibration/performance check solutions.

7.7 SURROGATE COMPOUNDS -- $^{13}C_{12}$-4,4'-DDT and $^{13}C_6$-gamma-BHC are added to every sample before extraction and are included in every calibration/performance check solution.

7.8 PCB CONCENTRATION CALIBRATION CONGENERS -- The nine individual PCB congeners listed in Table 2 are used as concentration calibration compounds for PCB determinations. One isomer at each level of chlorination is used as the concentration calibration standard for all other isomers at that level of chlorination, except that decachlorobiphenyl (Cl_{10}) is used for both Cl_9

and Cl_{10} isomer groups. The basis for selection of these calibration congeners has been reported (7).

7.9 PCB RETENTION TIME CONGENERS FOR SIM DATA ACQUISITION OPTION -- Knowledge of the retention times of certain congeners is necessary to determine when to acquire data with each ion set. Two concentration calibration congeners also serve as retention time congeners; the first eluting Cl_1-PCB indicates the time when data acquisition must have been initiated for ion set #1, and the Cl_{10}-PCB indicates when all PCBs have eluted. Two or three additional PCB congeners are used to establish times to initiate data acquisition with other ion sets (Sect. 9.4).

7.10 PESTICIDE SOLUTIONS

7.10.1 Pesticide Stock Solutions -- Prepare from pure standard materials. Weigh approximately 25.0 mg (with accuracy of 0.1 mg) of each surrogate compound and each pure pesticide analyte, except Endosulfan I and Endosulfan II. For those two pesticides, prepare a stock solution twice as concentrated as that prepared for other pesticide analytes. Dissolve each compound in hexane and dilute to volume in a 10-mL (5-mL for the two Endosulfans) volumetric flask. (Concentration of each component = 2.5 mg/mL, except Endosulfans, which should be 5 mg/mL.) Smaller or larger volumes of stock solution may be used if desired. If compound purity is certified at $\geq$96%, the weight can be used without correction to calculate the concentration of the stock standard solution. Commercially prepared stock standards in hexane can be used at any concentration if they are traceable to USEPA-supplied standards.

7.10.2 Pesticide Primary Dilution Solutions -- A convenient approach to solution preparation is to prepare two pesticide primary dilution solutions that are twice the concentration of the highest concentration calibration solution required. These solutions can then be diluted as necessary to prepare all needed calibration solutions. One solution contains endrin aldehyde and one does not, because the medium level calibration solution does not contain endrin aldehyde. Place 1 mL of each pesticide analyte/surrogate compound stock solution in a 25-mL volumetric flask. (Total volume for all 22 pesticide analytes and 2 surrogate compounds = 24 mL.) Make to volume with hexane and mix well. (Concentration of endosulfan sufate, endosulfan I and endosulfan II = 200 ng/uL; concentration of each other component = 100 ng/uL.)

7.11 PCB SOLUTIONS

7.11.1 Stock Solutions of PCB Calibration Congeners -- Prepare a stock solution of each of the nine PCB concentration calibration congeners at a concentration of 1 ug/uL in hexane. (If SIM data are to be acquired, prepare a 1 ug/uL stock solution of each of the three retention time congeners also.) Place each solution in a clean glass vial with a Teflon-lined screw cap and store at 4°C if solutions are not to be used right away. Solutions are stable indefinitely if solvent evaporation is prevented.
CAUTION: Each time a vial containing small volumes of solutions is warmed to room temperature and opened, a small volume of solvent in the vial headspace evaporates, significantly affecting concentration.

Solutions should be stored with the smallest possible volume of headspace, and opening vials should be minimized.

7.11.2 PCB Primary Dilution Standard -- Take aliquots of the stock solutions of the nine PCB concentration calibration congeners and mix together in the proportions of one part of each solution of the Cl_1 (#1), Cl_2 (#5), and Cl_3 (#29) congeners, two parts of each solution of the Cl_4 (#50), Cl_5 (#87), and Cl_6 (#154) congeners, three parts of each solution of the Cl_7 (#188) and Cl_8 (#200) congeners, and five parts of the Cl_{10} (#209) congener solution. (Note: The retention time congeners described in Sect. 7.9 are not included in the PCB primary dilution standard because they are not needed for full-range data acquisition.) This will provide a primary dilution standard solution of the composition shown in Table 3. Calculate the concentration in ug/uL; use three significant figures. Place each solution in a clean glass vial with a Teflon-lined screw cap and store at 4°C. Mark the meniscus on the vial wall to monitor solution volume during storage; solutions are stable indefinitely if solvent evaporation is prevented.

7.12 INTERNAL STANDARD (IS) SOLUTIONS -- Two solutions are needed to prepare concentration calibration solutions (CALs).

7.12.1 IS solution #1 (for full-range CALS) -- Weigh 7.5 mg $\pm$ 0.1 mg each of phenanthrene-d_{10} and chrysene-d_{12}; dissolve in hexane and dilute to 10 mL in a volumetric flask. (Concentration of each IS = 750 ng/uL)

7.12.2 IS solution #2 (for SIM CALS) -- Take 1 mL of IS solution #1 and dilute to 10 mL in a volumetric flask. (Concentration of each IS = 75 ng/uL)

7.13 CALS FOR FULL-RANGE DATA ACQUISITION -- Five hexane solutions are required. The solutions contain constant concentrations of the ISs (chrysene-d_{12} and phenanthrene-d_{12}) and varying concentrations of individual pesticide analytes, the nine PCB calibration compounds, and the two surrogate compounds ($^{13}C_{12}$-4,4'-DDT and $^{13}C_6$-gamma-BHC). (Composition and approximate concentrations are given in Table 4.) Four solutions (high and low concentrations) contain both ISs, both surrogate compounds, the nine PCB concentration calibration congeners, and each of the single-compound pesticide analytes. The fifth solution, the medium level concentration solution, contains all the above compounds except endrin aldehyde, which is not present for reasons described in Sect. 8. The lowest concentration solution contains each individual pesticide analyte and each PCB calibration congener at a concentration near but greater than its anticipated detection limit. (Because MS response to PCBs decreases with increasing level of chlorination, PCB congener concentrations in CALs increase with level of chlorination.) Components of the highest concentration solution (High CAL) are present at a concentration that allow injections of 2-uL aliquots without MS saturation or GC column overloading.

7.13.1 The Full-Range High CAL can be prepared by mixing equal portions of the PCB primary dilution solution and the pesticide primary dilution solution that contains endrin aldehyde and then adding an appropriate volume of IS solution #1. For example, 1 mL of each

primary dilution solution and 20 uL of IS solution #1 provide the appropriate concentration for High CAL.

7.13.2 Other full-range CALS are prepared by diluting the primary dilution standard solutions and adding the appropriate amount of IS solution #1. CAUTION: The pesticide primary dilution standard that does not contain endrin aldehyde must be used for the medium level full-range CAL.

7.14 CALS FOR SIM DATA ACQUISITION OPTION -- Two sets of solutions are needed, one set of five solutions for determinations of pesticide analytes, and one set of five solutions for PCB determinations. Appropriate concentrations of SIM CALs are given in Tables 5a and 5b. Solutions are prepared by diluting appropriate primary dilution standards and adding an appropriate volume of IS solution #2.
CAUTION: The Pesticide SIM Medium CAL does not contain endrin aldehyde; the PCB SIM CALS must include the three PCB retention time congeners. that are used to establish conditions for SIM data acquisition.

7.15 Prepare a solution of surrogate compounds in a water miscible solvent to provide a concentration in the sample/blank extract that is near the concentration anticipated for analytes when an aliquot of $\geq$20 uL is added to the sample before extraction.

7.15 Calculate the concentration (two significant figures if <100 and three significant figures if $\geq$100 ng/uL) of each component in each solution. Note: Concentrations presented in tables are only approximate.

7.16 LABORATORY PERFORMANCE CHECK SOLUTION - For both full-range data acquisition, and the SIM data acquisition option, the Medium CAL is used as the laboratory performance check solution (LPC) to verify response factors and to demonstrate adequate GC resolution and MS performance.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1 WATER SAMPLES

8.1.1 Samples must be collected in clean (Sect. 4.2) glass containers. Note: When samples are anticipated to contain low concentrations of method analytes, a sample larger than 1-L may be needed. An effective sample collection procedure to minimize losses of hydrophobic analytes is to add a portion of extracting solvent to each sample container when the sample is collected. When a 1-gal sample is collected, an appropriate solvent volume is approximately 100 mL. (The entire sample must be used as one sample aliquot, and blank sample/solvent volumes must be adjusted also.)

8.1.2 Samples must be iced or refrigerated at 4°C from time of collection until extraction. If samples will not be extracted within 72 h after collection, use either sodium hydroxide or sulfuric acid to adjust sample pH to within a range of 5 to 9. Record the volume of acid or base used. If aldrin is to be determined, add sodium thiosulfate when residual chlorine is present. Field test kits are available for measurement of residual chlorine.

8.1.3 Samples should be extracted within 7 days after collection and analyzed within 40 days after extraction.

8.2 SOIL/SEDIMENT SAMPLES -- Appropriate procedures will be specified when results are obtained from ongoing experiments.

9. CALIBRATION

Demonstration and documentation of acceptable initial calibration is required before any samples are analyzed and is required intermittently throughout sample analyses as dictated by results of continuing calibration checks. After initial calibration is successfully performed, a continuing calibration check is required at the beginning and end of each 12-h period during which analyses are performed. The Medium CALs for pesticide determinations do not include endrin aldehyde. This allows the Medium CAL to be used for continuing calibration checks, including a check to ensure that endrin decomposition is $\leq$10%. During initial calibration a separate Medium CAL containing endrin aldehyde and the internal standard is analyzed to determine the response factor for endrin aldehyde. Thereafter, if endrin aldehyde is a component of any sample and endrin decomposition is not a problem, the response factor for endrin aldehyde is verified by analyzing a calibration solution containing it.

9.1 DATA ACQUISITION OPTIONS -- Either full-range or SIM data acquisition may be used.

9.1.1 Full-range data acquisition is recommended if sample extract components are anticipated to be at sufficiently high concentrations.

9.1.2 SIM data acquisition will provide an increase in sensitivity by at least a factor of five for pesticide determinations and by at least a factor of three for PCB determinations.

9.2. INITIAL CALIBRATION

9.2.1 Calibrate and tune the MS with standards and procedures prescribed by the manufacturer with any necessary modifications to meet USEPA requirements.

9.2.2 Inject a 1- uL or 2-uL aliquot of the 10 ng/uL DFTPP solution and acquire a mass spectrum that includes data for m/z 45-450. If the spectrum does not meet all criteria (Table 6), the MS must be hardware tuned to meet all criteria before proceeding with calibration.

9.2.3 Full-Range Calibration -- Inject a 1- or 2-uL aliquot of the Medium CAL and acquire data from m/z 45 to 510. Acquire $\geq$5 spectra during elution of each GC peak. Total cycle time should be $\geq$0.5 s and $\leq$1.5 s. Note: Either a 1- or 2-uL aliquot should be used consistently for CALs and sample/blank extracts.

9.2.4 SIM Calibration -- Acquire at least five data points for each ion during elution of each GC peak. Total cycle time should be $\geq$0.5 s and $\leq$1.5 s.
CAUTION: When acquiring SIM data, GC operating conditions must be carefully reproduced for each analysis to provide reproducible retention times; if not, ions will not be monitored at the appropriate times.

9.2.4.1 SIM Calibration for PCB determinations

9.2.4.1.1 Two options for SIM data acquisition are provided. Data can be acquired with four sets of ≤six mass ranges (≤35 ions each as shown in Table 7a) or with the five ion sets (≤20 ions each) shown in Tables 7b and 7c.

9.2.4.1.2 The time (scan number) for initiation of data acquisition with each ion set must be carefully determined from the retention times (scan numbers) of the retention time congeners. Approximate relative retention times of calibration congeners and approximate relative retention time windows for PCB isomer groups are shown in Table 8. (Also see Figures 1 and 2.)

9.2.4.1.3 SIM data acquisition with four ion sets. Begin data acquisition with Ion Set #1 before elution of PCB congener #1, the first eluting Cl_1-PCB. Stop acquisition with Ion Set #1 and begin acquisition with Ion Set #2 just (approximately 10 s) <u>before</u> elution of PCB congener #104, the first eluting Cl_5-PCB. Stop acquisition with Ion Set #2 and begin acquisition with Ion Set #3 just (approximately 10 s) <u>after</u> elution of PCB congener #77, the last eluting Cl_4-PCB. Stop acquisition with Ion Set #3 and begin acquisition with Ion Set #4 just (approximately 10 s) <u>after</u> elution of $^{13}C_{12}$-4,4'-DDT.

9.2.4.1.4 SIM data acquisition with five ion sets. Acquire data with the four Ion Sets described in Sect. 9.2.4.1.3 and add a fifth Ion Set beginning data acquisition with that set just (approximately 10 s) <u>before</u> elution of PCB congener #208, the first eluting Cl_9-PCB.

9.2.4.2 SIM Calibration for Pesticide Determinations -- Three sets of ≤15 ions each are used (Tables 9-10). Begin data acquisition with Ion Set #1 before elution of alpha-BHC, the first eluting pesticide analyte. Begin data acquisition with Ion Set #2 after elution of aldrin and before elution of heptachlor epoxide. Stop acquisition with Ion Set #2 and begin acquisition with Ion Set #3 after elution of endosulfan II and before 4,4'-DDD.

9.2.5 Performance Criteria

9.2.5.1 Full-Range Data from Analysis of Medium CAL

9.2.5.1.1 GC performance -- baseline separation of beta-BHC and gamma-BHC; baseline separation of endrin ketone and chrysene-d_{12}; height of Cl_1-PCB peak ≥80% beta-BHC peak height; height of chrysene-d_{12} peak ≥60% of the peak height of methoxychlor, which may partially coelute with the Cl_8-PCB congener.

9.2.5.1.2 MS sensitivity -- Signal/noise ratio of ≥5 for m/z 499 of PCB congener #209, Cl_{10}-PCB.

9.2.5.1.3 MS calibration -- Abundance of $\geq$40% and $\leq$60% of m/z 502 relative to m/z 498 for PCB congener #209.

9.2.5.1.4 Lack of degradation of endrin. Examine an extracted ion current profile (EICP) for m/z 67 in the retention time window between 4,4'-DDE and endosulfan sulfate; confirm that the abundance of m/z 67 at the retention time of endrin aldehyde is <10% of the abundance of m/z 67 produced by endrin.

9.2.5.1.5 Lack of degradation of $^{13}C_{12}$-4,4'-DDT. Examine EICPs for m/z 258 and m/z 247 in the retention time window that includes 4,4'-DDD, 4,4'-DDE and 4,4'-DDT; m/z 258 would be produced by $^{13}C_{12}$-4,4'DDE, and m/z 247 by $^{13}C_{12}$-4,4'-DDD. Confirm that the total abundance of both ions is <5% of m/z 247 produced by $^{13}C_{12}$-4,4'-DDT.

9.2.5.2 SIM PCB Data

9.2.5.2.1 GC separation -- Baseline separation of PCB congener #87 from congeners #154 and #77, which may coelute.

9.2.5.2.2 MS sensitivity -- Signal/noise ratio of $\geq$5 for m/z 499 of PCB congener #209, Cl_{10}-PCB, and for m/z 241 of chrysene-d_{12}.

9.2.5.2.3 MS calibration -- Abundance of $\geq$70% and $\leq$95% of m/z 500 relative to m/z 498 for congener #209, Cl_{10}-PCB.

9.2.5.3 SIM Pesticide Data

9.2.5.3.1 GC separation -- Baseline separation of endrin ketone and chrysene-d_{12}; baseline separation of beta-BHC and gamma-BHC; baseline separation of endrin ketone and chrysene-d_{12}; height of chrysene-d_{12} peak $\geq$60% of methoxychlor peak height.

9.2.5.3.2 MS sensitivity -- Signal/noise ratio of >5 for m/z 241 of chrysene-d_{12}.

9.2.5.3.3 MS calibration -- Abundance of m/z 241 relative to that of m/z 240 produced by chrysene-d_{12} is >15% and <25%.

9.2.5.3.4 Lack of degradation of endrin. Examine an SICP for m/z 67 in the retention time window between 4,4'-DDE and endosulfan sulfate; confirm that the abundance of m/z 67 at the retention time of endrin aldehyde is <10% that of m/z 67 produced by endrin.

9.2.5.3.5 Lack of degradation of $^{13}C_{12}$-4,4'-DDT. Examine SICPs for m/z 258 and m/z 247 in the retention time window that includes 4,4'-DDD, 4,4'-DDE, and 4,4'-DDT; m/z 258 would be produced by $^{13}C_{12}$-4,4'-DDE, and m/z 247 by $^{13}C_{12}$-4,4'-DDD. Confirm that the total abundance of both ions is <5% of m/z 247 produced by $^{13}C_{12}$-4,4'-DDT.

9.2.6 Replicate Analyses of CALs -- If all performance criteria are met, analyze one 1- or 2-uL aliquot of each of the other four CALs.

9.2.7 Response Factor Calculation

9.2.7.1 Calculate five response factors (RFs) for each pesticide analyte, PCB calibration congener, and surrogate compound relative to both ISs (See Sect. 12.3.2), phenanthrene-d_{10} and chrysene-d_{12}:

$$RF = A_x Q_{is} / A_{is} Q_x$$

where A_x = integrated ion abundance of quantitation ion for a pesticide, a PCB calibration congener or a surrogate compound,

A_{is} = integrated ion abundance of m/z 240, the quantitation ion when chrysene-d_{12} is used as the internal standard or m/z 188, the quantitation ion when phenanthrene-d_{10} is used as the internal standard,

Q_{is} = injected quantity of chrysene-d_{12} or phenanthrene-d_{10},

Q_x = injected quantity of pesticide analyte, PCB calibration congener or surrogate compound.

RF is a unitless number, units used to express quantities must be equivalent. Note: The Cl_2-PCB calibration congener may not be resolved from alpha-BHC. If not, alpha-BHC will contribute to the ion abundance measured for Cl_2-PCB. To correct for this contribution, subtract 6.7% of the ion abundance of m/z 219 measured for alpha-BHC from the ion abundance measured for m/z 222 for Cl_2-PCB.

9.2.8 Response Factor Reproducibility -- For each pesticide analyte, PCB calibration congener and surrogate compound, calculate the mean RF from analyses of each of the five CALS. When the RSD exceeds 20%, analyze additional aliquots of appropriate CALS to obtain an acceptable RSD of RFs over the entire concentration range, or take action to improve GC/MS performance.

9.2.9 SIM Analyte Retention Time Reproducibility

9.2.9.1 PCB determinations - Absolute retention times of PCB congeners #77 and #104 should not vary by more than ±10 s from one analysis to the next. (Retention time reproducibility is not as critical for congeners #1 and #209 as for #77 and #104, which are used to determine when ion sets are changed.)

9.2.9.2 Pesticide determinations -- Absolute retention times of gamma-chlordane, endosulfan I, and endosulfan II should not vary by more than ±10 s from one analysis to the next.

9.2.10 Record a spectrum of each CAL component.

9.3. CONTINUING CALIBRATION CHECK

9.3.1 With the following procedures, verify initial calibration at the beginning and end of each 12-h period during which analyses are to be performed.

9.3.2 Calibrate and tune the MS with standards and procedures prescribed by the manufacturer.

9.3.3 Analyze a 1-uL or 2-uL aliquot of the DFTPP solution and ensure acceptable MS calibration and performance (Table 6).

9.3.4 Inject a 1-uL or 2-uL aliquot of the Medium CAL and analyze with the same conditions used during Initial Calibration.

9.3.5 Demonstrate acceptable performance for criteria described in Sect. 9.2.5.

9.3.6 Determine that neither the area measured for m/z 240 for chrysene-d_{12} nor that for m/z 188 for phenanthrene-d_{10} has decreased by more than 30% from the area measured in the most recent previous analysis of a calibration solution or by more than 50% from the mean area measured during initial calibration.

9.3.7 Response Factor Reproducibility -- For an acceptable Continuing Calibration Check, the measured RF for each analyte/surrogate compound must be within ±20% of the mean value calculated (Sect. 9.2.7) during Initial Calibration. If not, remedial action must be taken; recalibration may be necessary.

9.3.8 SIM Analyte Retention Time Reproducibility -- Demonstrate and document acceptable (Sect. 9.2.9) reproducibility of absolute retention times of appropriate pesticide analytes and PCB retention time congeners.

9.3.9 Remedial actions must be taken if criteria are not met; possible remedies are:

9.3.9.1 Check and adjust GC and/or MS operating conditions.

9.3.9.2 Clean or replace injector liner.

9.3.9.3 Flush column with solvent according to manufacturers instructions.

9.3.9.4 Break off a short portion (approximately 0.33 m) of the column; check column performance by analysis of performance check solution.

9.3.9.5 Replace GC column; performance of all initial calibration procedures then required.

9.3.9.6 Adjust MS for greater or lesser resolution.

9.3.9.7 Calibrate MS mass scale.

9.3.9.8 Prepare and analyze new concentration/calibration/performance check solution.

9.3.9.9 Prepare new concentration calibration curve(s).

10. QUALITY CONTROL

10.1 LABORATORY REAGENT BLANK (LRB) -- Perform all steps in the analytical procedure (Section 11) using all reagents, standards, surrogate compounds, equipment, apparatus, glassware, and solvents that would be used for a sample analysis; but omit an aliquot of sample (water or soil/sediment). For water samples, substitute 1 L of reagent water. If available, substitute EPA-provided reagent blank solid material for an aliquot of soil/sediment.

10.1.1 An LRB must contain the same amount of surrogate compounds and internal standards that is added to each sample. This amount will vary with sample type and with the type of data acquisition (full-range or SIM).

10.1.2 Analyze an LRB before any samples are extracted and analyzed.

10.1.3 Before a new batch of solvents or reagents is used for sample extraction or for column chromatographic procedures, analyze an LRB. In addition, analyze a laboratory solvent blank (LSB), which is the same as an LRB except that no surrogate compounds or internal standards are added; this demonstrates that reagents contain no impurities producing an ion current above the level of background noise for quantitation ions for those compounds.

10.1.4 Analyze an LRB along with each batch of $\leq$20 samples.

10.1.5 An acceptable LRB contains no method analyte at a concentration greater than one half of its MDL and contains no additional compounds with elution characteristics and mass spectral features that would interfere with identification and measurement of a method analyte at its MDL. If the LRB that was extracted along with a batch of samples is contaminated, the entire batch of samples must be reextracted and reanalyzed.

10.1.6 Corrective action for unacceptable LRB -- Check solvents, reagents, apparatus and glassware to locate and eliminate the source of contamination before any samples are extracted and analyzed. Purify or discard contaminated reagents and solvents.

10.2 CALIBRATION -- Included among initial and continuing calibration procedures are numerous quality control checks to ensure that valid data are acquired (See Sect. 9). Continuing calibration checks are accomplished with results from analysis of one solution, the medium level calibration solution for the appropriate type of data acquisition, either full-range or SIM.

10.2.1 If some criteria are not met for a Continuing Calibration Check after a 12-h period during which samples were analyzed, those samples must be reanalyzed. Those criteria are: GC performance (Sect. 9.2.5), MS calibration as indicated by DFTPP spectrum, and MS sensitivity as indicated by area of internal standards.

10.2.2 When other criteria in Sect. 9.2 are not met, results for affected analytes must be labeled as suspect to alert the data user of the observed problem. Included among those criteria are: response factor check for each analyte or PCB calibration congener, degradation of DDT and endrin, and retention time reproducibility for SIM data acquisition.

10.3 INITIAL DEMONSTRATION OF LABORATORY CAPABILITY FOR WATER ANALYSES (Insufficient information is currently available for demonstration for soil/ sediment analyses.)

10.3.1 Until appropriate Quality Control Check Samples are available, each laboratory should prepare one or more solutions containing each method analyte at a concentration corresponding to that anticipated in samples. Until accuracy and precision limits have been established for PCB isomer groups in appropriate samples, a solution containing an Aroclor mixture may be used; compare total measured PCB concentration to the total Aroclor concentration. Report Aroclor concentration and measured concentrations of PCB isomer groups and total measured PCB concentration.

10.3.2 Add an appropriate volume of a solution of method analytes to each of four 1-L aliquots of reagent water. Extract and analyze according to procedures in Sect. 11.

10.3.2 For each analyte, calculate measured concentrations, relative standard deviation of the four measurements, and method bias (Sect. 12.6).

10.4 LABORATORY PERFORMANCE CHECK SOLUTION -- In this method, the medium level concentration calibration solution also serves the purpose of a laboratory performance check solution.

10.5 LABORATORY SURROGATE SPIKE

10.5.1 Measure the concentration of both surrogate compounds in every sample and blank.

10.5.2 Until performance based acceptance limits have been established for surrogate compounds, the following guidelines are provided: measured bias with LRB = -30% to +10%; measured bias with water or soil/sediment extract = -50% to +25%.

10.6 QUALITY CONTROL CHECK SAMPLE -- Not yet available; anticipate need for analysis of one for each batch of $\leq$20 samples. If full-range data are acquired, both pesticide and PCB analytes can be determined with one analysis. If SIM data are acquired, one extraction and two GC/MS analyses will be needed to determine both PCBs and pesticides.

10.7 LABORATORY SPIKED DUPLICATE SAMPLE -- Select one sample from each batch of $\leq$20 samples of similar type and fortify (spike) two aliquots of that sample with a solution containing appropriate concentrations of pesticide analytes and at least one Aroclor mixture. After addition of surrogate compounds, extract and analyze (Sect. 11) these two fortified aliquots along with an additional unfortified sample aliquot. Relative difference (RD) of duplicate results for surrogate compound concentrations should be $\leq$40%.

($RD = [C_1 - C_2 / 0.5 (C_1 + C_2)] 100$) Calculate bias (Sect. 12.6) for each analyte and surrogate compound. Insufficient data are currently available to provide guidance for acceptable bias and RD of measured analyte concentrations.

10.8 PERFORMANCE EVALUATION SAMPLE -- Not yet available; to be analyzed periodically when available.

11. PROCEDURES

11.1 SAMPLE EXTRACTION

11.1.1 Water Samples

11.1.1.1 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Pour entire sample into a 2-L separatory funnel. (If a sample larger than 1-L or 1-qt is extracted, the funnel size and solvent volume for samples and blanks must be adjusted also.)

11.1.1.2 Add an appropriate volume of surrogate compound solution.

11.1.1.2 Add 60 mL of methylene chloride to the sample bottle, seal, and shake 30 s to rinse the inner surface. Transfer the solvent to the separatory funnel and extract the sample by shaking the funnel for 2 min with periodic venting to release excess pressure. Wait at least 10 min to allow the organic layer to separate from the water phase. If the emulsion interface between layers is more than one-third the volume of the solvent layer, use mechanical techniques (such as stirring, filtration of emulsion through glass wool, or centrifugation) to complete phase separation. Collect the methylene chloride extract in a 250-mL Erlenmeyer flask. Add a second 60-mL volume of methylene chloride to the sample bottle and repeat the extraction procedure a second time, combining the extracts in the Erlenmeyer flask. Perform a third extraction in the same manner.

11.1.1.3 Assemble a Kurderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporative flask.

11.1.1.4 Pour the combined extract into a solvent-rinsed drying column containing about 10 cm of anhydrous sodium sulfate. Rinse the Erlenmeyer flask with a 20 to 30 mL portion of methylene chloride, and add the rinse to the drying column. Collect the combined extract in the K-D concentrator.

11.1.1.5 Add one or two clean boiling chips to the evaporative flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 mL of methylene chloride to the top. Place the K-D apparatus on a hot water bath (60-65°C) so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus

and the water temperature as required to complete the concentration in 15-20 min. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 min.

11.1.1.6 Momentarily remove the Snyder column, add 50 mL of hexane and a new boiling chip, and reattach the Snyder column. Increase the temperature of the hot water bath to about 80°C. Concentrate the extract to approximately 10 mL as in Sect. 11.1.1.5, except use hexane to prewet the column. Elapsed time of concentration should be 5-10 min.

11.1.1.7 Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1-2 mL of hexane. A 5-mL syringe is recommended for this operation. Stopper the concentrator tube and store refrigerated if further processing will not be performed within a few hours. If the extract will be stored longer than two days, transfer it to a Teflon-sealed screw-cap vial.

11.1.1.8 Determine the original sample volume by refilling the sample bottle to the mark and transferring the liquid to a 1000-mL graduated cylinder. Record the sample volume to the nearest 5 mL.

11.1.2 Soil/Sediment Samples -- Appropriate extraction procedures to be specified when results of ongoing experiments are obtained.

11.2 Sulfur Removal -- Elemental sulfur can be removed by the procedure described below. (Sulfur is not expected to be a problem in water sample extracts but sulfur removal is recommended for soil/sediment sample extracts.)

11.2.1 Transfer the extract to a 50-mL clear glass bottle or vial with a Teflon-lined screw cap. Rinse the extract container wtih 1.0 mL of hexane, adding the rinse to the 50-mL bottle.

11.2.2 Add 1 mL of Tetrabutylammonium-sulfite reagent and 1 mL 2-propanol, cap the bottle, and shake for at least 1 min. If the sample is colorless or if the initial color is unchanged, and if clear crystals (precipitated sodium sulfite) are observed, sufficient sodium sulfite is present. If the precipitated sodium sulfite disappears, add more crystalline sodium sulfite in approximately 100-mg portions until a solid residue remains after repeated shaking.

11.2.3 Add 5 mL of distilled water and shake for at least 1 min. Allow the sample to stand for 5-10 min and remove the hexane layer (top) for analysis. Dry the extract by passing it through a 10-cm column containing hexane-washed sodium sulfate. Rinse the sodium sulfate with about 30 mL of hexane and add this hexane to the extract. Concentrate the extract to approximately 10 mL with a K-D apparatus. Store in a refrigerator if GC/MS analysis is not to be performed within a few hours.

11.3 GC/MS ANALYSIS

11.3.1 Remove the sample extract or blank from storage and allow it to warm to ambient laboratory temperature if necessary. With a stream of dry, filtered nitrogen, reduce the extract/blank volume to the appropriate volume, depending on anticipated analyte concentrations. Add an appropriate volume of the appropriate internal standard stock solution.

11.3.1.1 Internal standard concentration for full-range data acquisition = 7.5 ng/uL of extract.

11.3.1.2 Internal standard concentration for SIM data acquisition = 0.75 ng/uL of extract.

11.3.2 Inject a 1-uL or 2-uL aliquot of the blank/sample extract into the GC operated under conditions used to produce acceptable results during calibration.

11.3.3 Acquire mass spectral data with either full-range data acquisition conditions or SIM conditions, as appropriate. Use the same data acquisition time and MS operating conditions previously used to determine response factors.

11.3.4 Examine data for saturated ions in mass spectra of target compounds, if saturation occurred, dilute and reanalyze the extract after the quantity of the internal standards is adjusted appropriately.

11.3.5 For each internal standard, determine that the area measured in the sample extract has not decreased by >30% from the area measured during the most recent previous analysis of a calibration solution or by >50% from the mean area measured during initial calibration. If either criterion is not met, remedial action must be taken to improve sensitivity, and the sample extract must be reanalyzed.

11.4 IDENTIFICATION PROCEDURES

11.4.1 Using the ions shown in Tables 7a-7c for PCBs or Table 9 for pesticides, examine ion current profiles (ICPs) to locate internal standards, surrogate compounds, pesticide analytes, and PCBs for each isomer group. Use the RRT data in Table 9 as guidelines for location of pesticide analytes and the RRT window data in Table 8 as guidelines for location of PCB isomers. (A reverse search software routine can be used to locate compounds of concern.)

11.4.2 Full-Range Data

11.4.2.1 Examine each pesticide and PCB candidate spectrum after background correction routines have been applied. Compare the candidate spectrum with the appropriate standard spectrum measured during calibration. Verify the absence of any ions with mass greater than the highest mass possible for the compound of concern. (Ions in PCB M^+ ion clusters are shown in Table 12.)

11.4.2.2 Obtain integrated abundance areas for quantitation and confirmation ions.

11.4.3 SIM Data -- Obtain appropriate selected ion current profiles (SICPs) for IS quantitation and confirmation ions, for each ion monitored to detect pesticides and the surrogate compounds (Table 9), and for the quantitation and confirmation ions for each PCB isomer group.

11.4.4 PCB Analytes

11.4.4.1 For all PCB candidates, confirm the presence of an $(M-70)^+$ ion cluster by examining ICPs or spectra for at least one of the most intense ions in the appropriate ion cluster.

11.4.4.2 For Cl_3-Cl_7 isomer groups, examine ICPs or spectra for intense $(M+70)^+$ ions that would indicate a coeluting PCB containing two additional chlorines. (GC retention time data show that this is not a potential problem for other PCB isomer groups; see Figure 2.) If this interference occurs, a correction can be made. Obtain and record the area for the appropriate ion (Table 12) for the candidate PCB isomer group. Use the information in Table 13 to correct the measured abundance of M^+. For example, if a Cl_7-PCB and a Cl_5-PCB candidate coelute, the Cl_7-PCB will contribute to the ion measured for m/z 326 and m/z 324, the quantitation and confirmation ions, respectively, for a Cl_5-PCB. Obtain and record the area for m/z 322 (the lowest mass ion in the $(M+-70)^+$ ion cluster of a Cl_5-PCB fragment produced by a Cl_7-PCB). To determine the m/z 326 and m/z 324 areas produced by the Cl_5 PCB, calculate the Cl_7-PCB contribution to each and subtract it from the measured area. In this example, 164% of the area measured for m/z 322 should be subtracted from the area measured for m/z 324, and 108% of the m/z 322 area should be subtracted from the area measured for m/z 326 (Table 13).

11.4.4.3 For Cl_2-Cl_8-PCB candidates, examine ICPs or spectra for intense $(M+35)^+$ ions that would indicate a coeluting PCB containing one additional chlorine. This coelution causes interferences because of the natural abundance of ^{13}C. (This interference will be small and can be neglected except when measuring the area of a small amount of a PCB coeluting with a large amount of another PCB containing one more chlorine.) To correct for this interference, obtain and record the area for the appropriate ion (Table 14) from the $(M-1)^+$ ion cluster, and subtract 13.5% of the area measured for the $(M-1)^+$ ion from the measured area of the quantitation ion. For example, for Cl_5-PCB candidates, obtain and record the area for m/z 325; subtract 13.5% of that area from the measured area of m/z 326.

11.4.5 All Analytes -- Use ICP data to calculate the ratio of the measured peak areas of the quantitation ion and confirmation ion(s), and compare to the acceptable ratio (Table 9 for pesticides and Table 12 for PCBs). If acceptable ratios are not obtained, a coeluting or partially coeluting compound may be interfering. Examination of data from several scans may provide information that will allow application of additional background corrections to improve the ion ratio.

11.5. IDENTIFICATION CRITERIA

11.5.1 Internal Standards

11.5.1.1 Chrysene-d_{12} -- the abundance of m/z 241 relative to m/z 240 must be $\geq$15% and $\leq$25%, and these ions must maximize simultaneously. The area measured for m/z 240 must be within 30% of the area measured during the most recent calibration.

11.5.1.2 Phenanthrene-d_{10} -- the abundance of m/z 189 relative to m/z 188 must be $\geq$10% and $\leq$22%, and these ions must maximize simultaneously. The area measured for m/z 188 must be within 30% of the area measured during the most recent acceptable calibration.

11.5.1.3 Retention time must be within $\pm$10 s of that observed during the most recent acceptable calibration.

11.5.2 Full-Range Data for Pesticide Analytes and Surrogate Compounds

11.5.2.1 Retention time of the sample component must be within $\underline{t}$ s of the time observed for that same compound when a calibration solution was analyzed. Calculate the value of $\underline{t}$ with the equation, $t = (RT)^{1/3}$, where RT = observed retention time (in seconds) of the compound during the last previous acceptable calibration.

11.5.2.2 All ions with relative abundance >10% in the mass spectrum must be present in the mass spectrum of the candidate sample component; a molecular ion with relative abundance >2% in the standard spectrum must be present in the candidate spectrum.

11.5.2.3 The ion that was the most abundant (base peak) in the standard spectrum must also be the base peak in the candidate spectrum.

11.5.2.4 For all ions with relative abundance >20% in the standard spectrum, the relative abundance in the candidate spectrum must not vary by more than $\pm$15% in percentage units (i.e., if 50% in standard, must be $\geq$35% and $\leq$65%).

11.5.2.5 Ions with relative abundance >10% in the candidate spectrum but not present in the standard spectrum must be considered and accounted for by the analyst. When data processing software is used to obtain candidate spectra, both processed and unprocessed spectra must be evaluated.

11.5.3 SIM Data for Pesticide Analytes and Surrogate Compounds

11.5.3.1 Absolute retention time of each surrogate compound and pesticide candidate must be within 10 s of that measured during the last previous acceptable calibration.

11.5.3.2 All ions monitored for each compound (Table 9) must be present and must maximize simultaneously.

11.5.3.3 In a spectrum averaged across a GC peak and with background correction, if necessary, the most abundant ion must correlate with Table 9 data.

11.5.3.4 Observed relative abundances of the monitored ions must meet the following criteria:

Aldrin -- m/z 263 = >20% and m/z 265 = >13%
BHC (each isomer) -- m/z 183 = 70-95% of m/z 181
$^{13}C_6$-gamma-BHC -- m/z 189 = 75-90% of m/z 187
Chlordane (alpha and gamma) -- m/z 375 = 75-99%
4,4'-DDE -- m/z 248 = 45-85%
4,4'-DDD and 4,4'-DDT -- m/z 237 = 45-85%
$^{13}C_{12}$-4,4'-DDT -- m/z 249 = 45-85%
Dieldrin -- m/z 263 = >3% and m/z 108 = >8%
Endosulfan I and II -- m/z 339 = >30% and m/z 341 = >20%
Endosulfan sulfate -- m/z 274 = 60-95%
Endrin -- m/z 263 = $\geq$50%
Endrin aldehyde -- m/z 345 = $\geq$10%
Endrin ketone -- m/z 317 = $\geq$30%
Heptachlor -- m/z 272 = >30% and m/z 274 = >20%
Heptachlor epoxide -- m/z 353 = >60%
Methoxychlor -- m/z 228 = 3-30%
Nonachlor -- m/z 407 = 65-95%

11.5.4 Full-Range and SIM Data for PCBs

11.5.4.1 Absolute retention times of surrogate compounds must be within $\pm$10 s of that measured during the last previous continuing calibration check.

11.5.4.2 Quantitation and confirmation ions for each PCB isomer group must maximize within $\pm$1 scan of each other.

11.5.4.3 The integrated ion current for each quantitation and confirmation ion must be at least three times background noise and must not have saturated the detector.

11.5.4.4 For each PCB isomer group candidate, the ratio of the quantitation ion area to the confirmation ion area must be within limits shown in Table 12; at least one ion in the $(M-70)^+$ ion cluster must be present.

12. CALCULATIONS

12.1 From appropriate ICPs of quantitation ions, obtain and record the spectrum number of the chromatographic peak apex and the area of the entire chromatographic peak.

12.2 For PCBs, sum the areas for all isomers identified at each level of chlorination (e.g., sum all quantitation ion areas for Cl_4-PCBs).

12.3 Calculate the concentration of each surrogate compound, pesticide candidate, and PCB isomer group using the formula:

$$C_x = (A_x \cdot Q_{is})/(A_{is} \cdot RF \cdot W)$$

where C_x = concentration (micrograms per kilogram or micrograms per liter) of surrogate compound, individual pesticide or a PCB isomer group,

A_x = the area of the quantitation ion for each pesticide analyte/surrogate compound <u>or</u> the sum of quantitation ion areas for all PCB isomers at a particular level of chlorination,

A_{is} = the area of the internal standard quantitation ion, m/z 240 for chrysene-d_{12} or m/z 188 for phenanthrene-d_{10},

Q_{is} = quantity (micrograms) of internal standard added to the extract before GC/MS analysis,

RF = calculated response factor for the surrogate compound, the pesticide standard, or the PCB calibration compound for the isomer group (level of chlorination), and

W = weight (kilograms) of sample extracted. If a liquid sample was extracted, W becomes V, the volume (liters) of water extracted, and concentration units become micrograms per liter.

12.3.1 Use the grand mean RF calculated during Initial Calibration. CAUTION: For PCB analyses with automated data interpretation a linear fit algorithm will produce erroneous concentration data.

12.3.2 For pesticides eluting before heptachlor epoxide, use the RF relative to phenanthrene-d_{10}; for heptachlor expoxide and later eluting pesticides, use the RF relative to chrysene-d_{12}. For PCBs, use the RF relative to chrysene-d_{12} unless an interference makes the use of the RF relative to phenanthrene-d_{10} necessary.

12.4 Estimation of the Concentration of Technical Chlordane. Technical chlordane is a mixture that contains alpha-chlordane (about 13% by weight), gamma-chlordane (about 18% by weight), heptachlor (about 8%), chlordene (three isomers; about 19%) and a variety of side reaction products (including nonachlor isomers) from chlorination of chlordene. Alpha-chlordane is readily converted to gamma-chlordane, which is persistent in environmental samples. Another persistent component is trans-nonachlor. The presence of gamma-chlordane and trans-nonachlor, with or without alpha-chlordane and heptachlor) indicates that technical chlordane was once present in the sample. Therefore the sum of measured concentrations of alpha-chlordane and gamma-chlordane can be used to estimate the original concentration of technical chlordane.

$$C_{tc} = (C_a + C_g)/0.31$$

where C_a = measured concentration of alpha-chlordane,
C_g = measured concentration of gamma-chlordane, and
C_{tc} = estimated concentration of technical chlordane.

12.5 Report calculated values to two significant figures.

12.6 When samples of known composition or fortified samples are analyzed, calculate the percent method bias using the equation:

$$B = 100\ (C_s - C_t)/\ C_t$$

where C_s = measured concentration (in micrograms per kilogram or micrograms per liter),
C_t = theoretical concentration (i.e., the quantity added to the sample aliquot/weight or volume of sample aliquot).

Note: The bias value retains a positive or negative sign.

13. AUTOMATED IDENTIFICATION AND MEASUREMENT

Special software can be used for automated identification and measurement of PCBs (8) and pesticides. Unprocessed GC/MS data are handled without human interaction with the software operating on the dedicated computer. A concentration for each pesticide and each PCB isomer group is calculated automatically. Contact EMSL-Cincinnati for further information.

14. METHOD PERFORMANCE

To obtain single laboratory accuracy and precision data for method analytes, replicate 1-L aliquots of reagent water and river water fortified with known amounts of analytes were extracted and analyzed. Automated procedures were used to identify and measure method analytes in 2-uL aliquots of 1-mL extracts. Because a sufficient quantity of individual PCB congeners was not available, Aroclor mixtures were used to fortify water samples. This is not desirable, because individual PCBs in Aroclors vary in concentration. As Aroclor concentrations decrease in a sample extract, an increasing number of components will fall below the detection limit and will not be identified and measured. In addition, insufficient data are available about Aroclor composition to assess accuracy of isomer group measurements or to assess MDLs for PCBs when Aroclors are used to fortify samples.

14.1 Medium Level Reagent Water Extracts -- Five aliquots of reagent water fortified with each individual pesticide at a concentration of 10 ug/L and Aroclors 1221, 1242, 1254, and 1268 at concentrations of 5 ug/L, 50 ug/L, 50 ug/L and 25 ug/L, respectively, were extracted and analyzed. Method bias for individual pesticides ranged from -10% to +18% with a mean method bias of +2% for all 21 pesticides (Table 15). For individual pesticides, RSDs of measured concentration ranged from 0.61% for endrin ketone to 9.8% for endrin aldehyde. No true values are known for concentrations of PCB isomer groups in Aroclors, but the mean measured total PCB concentration was 110 ug/L (RSD 2.9%), which indicated a method bias of -15%. For individual isomer groups, RSDs of mean measured concentrations ranged from 3.9% to 16%.

14.2 Low Level Reagent Water Extract -- Reagent water was fortified with each pesticide at a concentration of 3 ug/L and a total PCB concentration of 27 ug/L (Aroclors 1221, 1 ug/L; 1242, 10 ug/L; 1254, 10 ug/L; and 1268,

6 ug/L). When seven replicate extracts were analyzed, method bias for individual pesticides ranged from -17% to +20% with a mean method bias of -2% (Table 15). An MDL was calculated for each pesticide using the equation relating the standard deviation of the seven replicate measurement and Student's t value for a one-tailed test at the 99% confidence level with n-1 degrees of freedom (1). With this calculation, MDL is defined as the minimum concentration that can be measured and reported with 99% confidence that the value is above zero. The excellent precision achieved with these measurements resulted in unrealistically low MDLs ranging from 0.2 to 0.8 ug/L for pesticide analytes (Table 15). A PCB MDL is an individual congener characteristic and cannot be determined with samples fortified with Aroclor mixtures. Estimates of MDLs for individual components of PCB isomer groups were obtained by proportioning the total quantity measured for each isomer group among individual measured isomers. The estimated MDL values for individual PCBs also were unrealistically low (0.01-0.1 ug/L) because of the excellent precision of measurements. A more realistic statement of detection limits for pesticides and PCBs can be found in Sect. 1.2.

14.3 River Water Extracts -- Five aliquots of river water fortified with each pesticide at a concentration of 5 ug/L and total PCB concentration of 70 ug/L (Aroclors 1221, 2 ug/L; 1242, 30 ug/L; 1254, 30 ug/L; and 1268, 8 ug/L) were extracted and analyzed. Method bias for individual pesticides ranged from -30% to +8% with a mean of -8% (Table 15). The excellent precision of measured pesticide PCB isomer group concentrations was indicated by RSDs ranging from 1.6% to 7.5%. The mean measured total PCB concentration of 51 ug/L (RSD 2.5%) indicated a method bias of -27%.

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Table 1. Recommended GC Operating Conditions

Column Type:	SE-54 or DB-5
Film Thickness:	0.25 um
Column Dimensions:	30 m X 0.32 mm
Helium Linear Velocity:	28-29 cm/sec at 250°C
Temperature Program for Splitless Injection:	
o Full-range data acquisition for PCBs and pesticides (Analysis time = approx. 50 min)	Inject at 80°C and hold 1 min; increase at 30°/min to 160°C and hold 1 min; increase at 3°/min to 310°C. or Inject at 80°C and hold 1 min; heat rapidly to 160°C and hold 1 min; increase at 3°/min to 310°C.
o SIM data acquisition for PCBs (Analysis time = approx. 25 min)	Inject at 45°C and hold 1 min; increase at 20°/min to 150°C and hold 1 min; increase at 10°/min to 310°C.
o SIM data acquisition for pesticides (Analysis time = approx. 30 min)	Inject at 80°C and hold 1 min; increase at 30°/min to 160°C and hold 1 min; increase at 3°/min to 250°C; hold past elution time of methoxychlor.

Table 2. PCB Congeners Used as Calibration Standards

PCB Isomer Group	Congener Number[a]	Chlorine Substitution
Concentration Calibration Standard		
Monochlorobiphenyl	1	2
Dichlorobiphenyl	5	2,3
Trichlorobiphenyl	29	2,4,5
Tetrachlorobiphenyl	50	2,2',4,6
Pentachlorobiphenyl	87	2,2',3,4,5'
Hexachlorobiphenyl	154	2,2',4,4',5,6'
Heptachlorobiphenyl	188	2,2',3,4',5,6,6'
Octachlorobiphenyl	200	2,2',3,3',4,5',6,6'
Nonachlorobiphenyl[b]	-	---
Decachlorobiphenyl	209	2,2',3,3',4,4',5,5',6,6'
Retention Time Calibration Standards		
Tetrachlorobiphenyl	77	3,3',4,4'
Pentachlorobiphenyl	104	2,2',4,6,6'
Nonachlorobiphenyl	208	2,2',3,3',4,5,5',6,7'

[a] Numbered according to the system of Ballschmiter and Zell (2).

[b] Decachlorobiphenyl is used as the calibration congener for both nona- and decachlorobiphenyl isomer groups.

Table 3. Scheme for Preparation of PCB Primary Dilution Standard

PCB Cong.	Isomer Group	Stock Sol. Conc. mg/mL	Proportion for Primary Dil. Sol.	Primary Dil. Std. Conc. ng/uL
#1	Cl_1	1.0	1 part	50
#5	Cl_2	1.0	1 part	50
#29	Cl_3	1.0	1 part	50
#50	Cl_4	1.0	2 parts	100
#87	Cl_5	1.0	2 parts	100
#154	Cl_6	1.0	2 parts	100
#188	Cl_7	1.0	3 parts	150
#200	Cl_8	1.0	3 parts	150
#209	Cl_{10}	1.0	5 parts	250
			Total 20 parts	

Table 4. Composition and Approximate Concentrations of Calibration Solutions for Full-Range Data Acquisition

Analyte/Int. Std./ Surrogate Compound	Concentration (ng/uL)				
	CAL 1	CAL 2	CAL 3	CAL 4	CAL 5
PCB Cal. Congeners					
Cl_1 (#1)	0.5	2.5	5	10	25
Cl_2 (#5)	0.5	2.5	5	10	25
Cl_3 (#29)	0.5	2.5	5	10	25
Cl_4 (#50)	1	5	10	20	50
Cl_5 (#87)	1	5	10	20	50
Cl_6 (#154)	1	5	10	20	50
Cl_7 (#188)	1.5	7.5	15	30	75
Cl_8 (#200)	1.5	7.5	15	30	75
Cl_{10} (#209)	2.5	12.5	25	50	125
Pesticides					
Aldrin	1	5	10	20	50
BHC, each isomer	1	5	10	20	50
Chlordane, each isomer	1	5	10	20	50
4,4'-DDD	1	5	10	20	50
4,4'-DDE	1	5	10	20	50
4,4'-DDT	1	5	10	20	50
Dieldrin	1	5	10	20	50
Endosulfan I	2	10	20	40	100
Endosulfan II	2	10	20	40	100
Endosulfan sulfate	2	10	20	40	100
Endrin	1	5	10	20	50
Endrin aldehyde	1	5	--	20	50
Endrin ketone	1	5	10	20	50
Heptachlor	1	5	10	20	50
Heptachlor epoxide	1	5	10	20	50
Methoxychlor	1	5	10	20	50
Nonachlor, each isomer	1	5	10	20	50
Internal Standards					
Chrysene-d_{12}	7.5	7.5	7.5	7.5	7.5
Phenanthrene-d_{10}	7.5	7.5	7.5	7.5	7.5
Surrogate Compounds					
$^{13}C_6$-gamma BHC	1	5	10	20	50
$^{13}C_{12}$-4,4'-DDT	1	5	10	20	50

Table 5a. Composition and Approximate Concentrations of Calibration Solutions for SIM Data Acquisition for PCB Determinations

Compound	Concentration (ng/uL)				
	CAL 1	CAL 2	CAL 3	CAL 4	CAL 5
Cal. Congeners					-
Cl_1 (#1)	0.1	0.5	1	2	5
Cl_2 (#5)	0.1	0.5	1	2	5
Cl_3 (#29)	0.1	0.5	1	2	5
Cl_4 (#50)	0.2	1.0	2	4	10
Cl_5 (#87)	0.2	1	2	4	10
Cl_6 (#154)	0.2	1	2	4	10
Cl_7 (#188)	0.3	1.5	3	6	15
Cl_8 (#200)	0.3	1.5	3	6	15
Cl_{10} (#209)	0.5	2.5	5	10	25
All congeners	.2	.5	1	2	4ng/ul
RT Congeners					
Cl_4 (#77)	0.2	1	2	4	10
Cl_5 (#104)	0.2	1	2	4	10
Cl_9 (#208)	0.4	2	4	8	20
Internal Standards					
Chrysene-d_{12}	0.75	0.75	0.75	0.75	0.75
Phenanthrene-d_{10}	0.75	0.75	0.75	0.75	0.75
Surrogate Compounds					
$^{13}C_6$-gamma-BHC	0.2	1	2	4	10
$^{13}C_{12}$-4,4'-DDT	0.2	1	2	4	10

not added

4ng/ul

Stock	.2	.5	1.0	2.0	4.
4.0ng/ul	.05	.125	.25	.5	1.

Table 5b. Composition and Approximate Concentrations of Calibration Solutions for SIM Data Acquisition for Pesticide Determinations

Analyte/Internal Std/ Surrogate Compound	Concentration (ng/uL)				
	CAL 1	CAL 2	CAL 3	CAL 4	CAL 5
Pesticide Analytes					
Aldrin	0.2	1	2	5	10
BHC, each isomer	0.2	1	2	5	10
Chlordane, each isomer	0.2	1	2	5	10
4,4'-DDD	0.2	1	2	5	10
4,4'-DDE	0.2	1	2	5	10
4,4'-DDT	0.2	1	2	5	10
Dieldrin	0.2	1	2	5	10
Endosulfan I	0.4	2	4	10	20
Endosulfan II	0.4	2	4	10	20
Endosulfan sulfate	0.2	1	2	5	10
Endrin	0.2	1	2	5	10
Endrin aldehyde	0.2	1	-	5	10
Endrin ketone	0.2	1	2	5	10
Heptachlor	0.2	1	2	5	10
Heptachlor epoxide	0.2	1	2	5	10
Methoxychlor	0.2	1	2	5	10
Nonachlor, each isomer	0.2	1	2	5	10
Internal Standards					
Chrysene-d_{12}	0.75	0.75	0.75	0.75	0.75
Phenanthrene-d_{10}	0.75	0.75	0.75	0.75	0.75
Surrogate Compounds					
$^{13}C_6$-gamma-BHC	0.2	1	2	5	10
$^{13}C_{12}$-4,4'-DDT	0.2	1	2	5	10

Table 6. Criteria for DFTPP Spectrum

m/z	Relative Abundance
127	40-60%
197	<1%
198	100% (Base Peak)
199	5-9%
275	10-30%
365	>1%
441	Present and <m/z 443
442	>40%
443	17-23% of m/z 442

Table 7a. Ions for Selected Ion Monitoring to Determine PCBs by Acquiring Data for Four Sets of ≤35 Ions Each

PCB Isomer Group/ Int.Std./Surr.Cmpd.	Nominal Mol. Wt.	Mass or Range to be Monitored	No. of Ions	Ion Sets #1	#2	#3	#4
Monochlorobiphenyls	188	152; 186-190	6	6			
Dichlorobiphenyls	222	220-224	5	5			
Trichlorobiphenyls	256	254-260	7	7	7	1[a]	
Tetrachlorobiphenyls	290	288-294	7	7	7	1[b]	
Pentachlorobiphenyls	324	322-328	7		7	7	
Hexachlorobiphenyls	358	356-362	7		6[c]	7	7
Heptachlorobiphenyls	392	390-396	7			6[d]	7
Octachlorobiphenyls	426	424-430	7				7
Nonachlorobiphenyls	460	460-466	7				7
Decachlorobiphenyl	494	496-500	5				5
Chrysene-d_{12}	240	240-241	2				2
Phenanthrene-d_{10}	188	188-189	2	2[e]			
$^{13}C_6$-gamma-BHC	294	187,189	2	2[f]			
$^{13}C_{12}$-4,4'-DDT	364	247; 249	2			2	
		Total # ions		25	27	24	35

[a]Monitor m/z 254 to confirm presence of $(M-70)^+$ for Cl_5-PCBs.

[b]Monitor m/z 288 to confirm presence of $(M-70)^+$ for Cl_6-PCBs.

[c]Begin range at m/z 357 in Ion Set #2.

[d]Begin range at m/z 391 in Ion Set #3.

[e]M/z 188 and 189 included among ions used to detect and measure monochlorobiphenyls.

[f]M/z 187 and 189 included among ions used to detect and measure monochlorobiphenyls.

Table 7b. Ions for Selected Ion Monitoring to Determine PCBs by Acquiring Data for Five Sets of ≤20 Ions Each

Ion Set	Isomer Group/ IS/Surrogate	Quant. Ion	Confirm. Ions	M-70 Ions	M+70 Ions	M+35 Ions	Ion Measured[a] for Correction	
1	Cl_1	188	190	152,153[b]	256,258	222,224	-	-
	Cl_2	222	224	152,153,186,188[c]	290,292,294	256,258	-	221
	Cl_3	256	258	186,188	-	290,292,294	-	255
	Cl_4	292	290,294	220,222	-	-	-	-
	$^{13}C_6$-gamma-BHC	187	189	-	-	-	-	-
	Phenanthrene-d_{10}	188	189	-	-	-	-	-
2	Cl_3	256	258	186,188	324,326,328	290,292,294	254	255
	Cl_4	292	290,294	220,222	360,362	324,326,328	288	289
	Cl_5	326	324,328	254,256,258	-	360,362	-	323
	Cl_6	360	358,362	288,290,292	-	-	-	-
3	Cl_5	326	324,328	254,256	392,394,396,398	360,362	322	323
	Cl_6	360	358,362	288,290	-	392,394,396,398	-	357
	Cl_7	394	392,396	322,324,326	-	-	-	-
	$^{13}C_{12}$-4,4'-DDT	247	249	-	-	-	-	-
4	Cl_6	360	358,362	288,290	426,428,430,432	392,394,396	356	357
	Cl_7	394	392,396,398	322,324	-	428,430,432	-	391
	Cl_8	430	428,432	356,358,360	-	-	-	-
	Chrysene-d_{12}	240	241	-	-	-	-	-
5	Cl_8	430	426,428,432	356,358,360	494,496,498,500	462,464,466	-	425
	Cl_9	464	460,462,466	390,392,394	-	496,498,500	-	-
	Cl_{10}	498	494,496,500	424,426,428,430	-	-	-	-

[a] See Tables 12-13.
[b] Cl_1-PCBs lose HCl.
[c] Some Cl_2-PCBs lose Cl_2 and some lose HCl.

Table 7c. Ions for Selected Ion Monitoring to Determine PCBs by Acquiring Data for Five Ion Sets of ≤20 Ions

Ion Set No. 1[a]	Ion Set No. 2[b]	Ion Set No. 3[c]	Ion Set No. 4[d]	Ion Set No. 5[e]
152	186	247	240	356
153	188	249	241	358
186	220	254	288	360
187	222	256	290	390
188	254	288	322	392
189	255	290	324	394
190	256	322	326	424
220	258	323	356	425
221	288	324	357	426
222	289	326	358	428
224	290	328	360	430
255	292	357	362	432
256	294	358	391	462
258	323	360	392	464
290	324	362	394	466
292	326	392	396	496
294	328	394	398	498
	358	396	428	499
	360	398	430	500
	362		432	502
17 ions	20 ions	19 ions	20 ions	20 ions

[a] Ions to identify and measure Cl_1-Cl_4-PCBs, phenanthrene-d_{10}, and $^{13}C_6$-gamma-BHC.

[b] Ions to identify and measure Cl_3-Cl_6-PCBs.

[c] Ions to identify and measure Cl_5-Cl_7-PCBs and $^{13}C_{12}$-4,4'-DDT.

[d] Ions to identify and measure Cl_6-Cl_8-PCBs and chrysene-d_{12}.

[e] Ions to identify and measure Cl_8-Cl_{10}-PCBs.

Table 8. Retention Time Data for PCB Isomer Groups and Calibration Congeners

Isomer Group	Approximate RRT Range[a]	Cal. Cong. Number	Cal. Cong. RRT[a]
Monochlorobiphenyls	0.30-0.35	1	0.30
Dichlorobiphenyls	0.38-0.50	5	0.43
Trichlorobiphenyls	0.46-0.64	29	0.54
Tetrachlorobiphenyls	0.55-0.82	50	0.56
Pentachlorobiphenyls	0.64-0.92	87	0.80
Hexachlorobiphenyls	0.75-1.1	154	0.82
Heptachlorobiphenyls	0.88-1.2	188	0.88
Octachlorobiphenyls	0.99-1.21	200	1.03
Nonachlorobiphenyls	1.16-1.28	-	-
Decachlorobiphenyl	1.3	209	1.3

[a] Retention time relative to chrysene-d_{12} with a 30 m X 0.31 mm ID SE-54 fused silica capillary column and the following GC conditions: splitless injection at 80°C; hold for 1 min; heat rapidly to 160°C and hold 1 min; increase at 3°C/min to 310°C.

Table 9. Ions for Selected Ion Monitoring Data Acquisition for Pesticide Analytes, Internal Standards and Surrogate Compounds (Ordered by Retention Time)

Ion Set	Analyte/Internal Std/ Surrogate Compound (MW)		Approx. RRT	Quant. Ion	Ions (Approximate Relative Abundance)
1	Alpha-BHC	(288)	0.43	219	181 (100), 183 (90), 219 (70)
	Beta-BHC	(288)	0.47	219	181 (100), 183 (90), 219 (70)
	Gamma-BHC	(288)	0.48	219	181 (100), 183 (90), 219 (75)
	$^{13}C_6$-gamma-BHC	(294)	0.48	225	187 (100), 189 (90) 225 (80), 227 (40
	Phenanthrene-d_{10}	(188)	0.49	188	188 (100), 189 (15)
	Delta-BHC	(288)	0.51	219	181 (100), 183 (90), 219 (70)
	Heptachlor	(370)	0.58	272	100 (100), 272 (60), 274 (40)
	Aldrin	(362)	0.64	263	66 (100), 263 (40), 265 (25)
2	Heptachlor epoxide	(386)	0.70	353	81 (100), 353 (80), 355 (65)
	Gamma-chlordane	(406)	0.74	373	373 (100), 375 (95)
	Endosulfan I	(404)	0.76	195	195 (100), 339 (50), 341 (35)
	Alpha-chlordane	(406)	0.76	373	373 (100), 375 (95)
	Trans-nonachlor	(440)	0.77	409	409 (100), 407 (85)
	Dieldrin	(378)	0.80	79	79 (100), 263 (10), 108 (15)
	4,4'-DDE	(316)	0.81	246	246 (100), 248 (65)
	Endrin	(378)	0.83	81	81 (100), 263 (75)
	Endosulfan II	(404)	0.85	195	195 (100), 339 (50), 341 (35)
3	4,4'-DDD	(318)	0.87	235	235 (100), 237 (65), 165 (65)
	Endrin aldehyde	(378)	0.88	67	67 (100), 345 (30)
	Endosulfan sulfate	(420)	0.92	272	272 (100), 274 (80), 387 (50)
	4,4'-DDT	(352)	0.93	235	235 (100), 237 (65), 165 (65)
	$^{13}C_{12}$-4,4'-DDT	(364)	0.93	247	247 (100), 249 (65)
	Endrin ketone	(378)	0.99	67	67 (100), 317 (50)
	Chrysene-d_{12}	(240)	1.00	240	240 (100), 241 (20)
	Methoxychlor	(344)	1.03	227	227 (100), 228 (15)

Table 10. Ion Sets for Selected Ion Monitoring of Pesticide Analytes, Internal Standards and Surrogate Compounds (Ordered by Retention Time)

Ion Set No. 1	Monitored Compounds	Ion Set No. 2	Monitored Compounds	Ion Set No. 3	Monitored Compounds
66	Alpha-BHC	79	Heptachlor	67	4,4'-DDD
100	Beta-BHC	81	epoxide	165	Endrin aldehyde
181	Delta-BHC	108	Alpha-chlordane	227	Endosulfan sulfate
183	Gamma-BHC	195	Gamma-chlordane	228	4,4'-DDT
187	$^{13}C_6$-gamma-BHC	246	Endosulfan I	235	$^{13}C_{12}$-4,4'-DDT
188	Phenanthrene-d_{10}	248	Trans-nonachlor	237	Endrin ketone
189	Heptachlor	263	Dieldrin	240	Chrysene-d_{12}
219	Aldrin	339	4,4'-DDE	241	Methoxychlor
225		341	Endrin	247	
227		353	Endosulfan II	249	
263		355		272	
265		373		274	
272		375		317	
274		407		345	
		409		387	
14 ions, 8 compounds		15 ions, 9 compounds		15 ions	8 compounds

Table 11. Known Relative Abundances of Ions in PCB Molecular Ion Clusters[a]

m/z	Relative Intensity
Monochlorobiphenyls	
188	100
189	13.5
190	33.4
192	4.41
Dichlorobiphenyls	
222	100
223	13.5
224	66.0
225	8.82
226	11.2
227	1.44
Trichlorobiphenyls	
256	100
257	13.5
258	98.6
259	13.2
260	32.7
261	4.31
262	3.73
263	0.47
Tetrachlorobiphenyls	
290	76.2
291	10.3
292	100
293	13.4
294	49.4
295	6.57
296	11.0
297	1.43
298	0.95
Pentachlorobiphenyls	
324	61.0
325	8.26
326	100
327	13.5
328	65.7
329	8.78
330	21.7
331	2.86
332	3.62
333	0.47
334	0.25
Hexachlorobiphenyls	
358	50.9
359	6.89
360	100
361	13.5
362	82.0
363	11.0
364	36.0
365	4.77
366	8.92
367	1.17
368	1.20
369	0.15
Heptachlorobiphenyls	
392	43.7
393	5.91
394	100
395	13.5
396	98.3
397	13.2
398	53.8
399	7.16
400	17.7
401	2.34
402	3.52
403	0.46
404	0.40
Octachlorobiphenyls	
426	33.4
427	4.51
428	87.3
429	11.8
430	100
431	13.4
432	65.6
433	8.76
434	26.9
435	3.57
436	7.10
437	0.93
438	1.18
439	0.15
440	0.11
Nonachlorobiphenyls	
460	26.0
461	3.51
462	76.4
463	10.3
464	100
465	13.4
466	76.4
467	10.2
468	37.6
469	5.00
470	12.4
471	1.63
472	2.72
473	0.35
474	0.39
Decachlorobiphenyl	
494	20.8
495	2.81
496	68.0
497	9.17
498	100
499	13.4
500	87.3
501	11.7
502	50.0
503	6.67
504	19.7
505	2.61
506	5.40
507	0.71
508	1.02
509	0.13

[a]Source: Rote and Morris (9)

Table 12. Quantitation, Confirmation, and Interference Check Ions for PCBs, Internal Standards, and Surrogate Compounds

Analyte/ Internal Std.	Nom. MW	Quant. Ion	Confirm. Ion	Expected Ratio[a]	Accept. Ratio[a]	M-70 Confirm. Ion	Interference Check Ions M+70	Interference Check Ions M+35
PCB Isomer Group								
Cl_1	188	188	190	3.0	2.5-3.5	152[b]	256	222
Cl_2	222	222	224	1.5	1.3-1.7	152	292	256
Cl_3	256	256	258	1.0	0.8-1.2	186	326	290
Cl_4	290	292	290	1.3	1.1-1.5	220	360	326
Cl_5	324	326	324	1.6	1.4-1.8	254	394	360
Cl_6	358	360	362	1.2	1.0-1.4	288	430	394
Cl_7	392	394	396	1.0	0.8-1.2	322	464	430
Cl_8	426	430	428	1.1	0.9-1.3	356	498	464
Cl_9	460	464	466	1.3	1.1-1.5	390	-	498
Cl_{10}	494	498	500	1.1	0.9-1.3	424	-	-
Internal standards								
Chrysene-d_{12}	240	240	241	5.1	4.3-5.9	-	-	-
Phenanthrene-d_{10}	188	188	189	6.6	6.0-7.2	-	-	-
Surrogate compounds								
$^{13}C_6$-gamma-BHC	294	187	189	1.0	0.8-1.2	-	-	-
$^{13}C_{12}$-4,4'-DDT	364	247	249	1.5	1.3-1.7	-	-	-

[a] Ratio of quantitation ion to confirmation ion

[b] Monodichlorobiphenyls lose HCl to produce an ion at m/z 152.

Table 13. Correction for Interference of PCB Containing Two Additional Chlorines

Candidate Isomer Group	Quant. Ion	Confirm. Ion	Ion Measured to Determine Interference	% of Meas. Ion Area to be Subtracted from	
				Quant Ion Area	Confirm. Ion Area
Trichlorobiphenyls	256	258	254	99% -	33%
Tetrachlorobiphenyls	292	290	288	65%	131%
Pentachlorobiphenyls	326	324	322	108%	164%
Hexachlorobiphenyls	360	362	356	161%	71%
Heptachlorobiphenyls	394	396	390	225%	123%

Table 14. Correction for Interference of PCB Containing One Additional Chlorine

Candidate Isomer Group	Quant. Ion	Ion Measured to Determine Interference	% of Meas. Ion Area to be Subtracted from Quant. Ion Area
Dichlorobiphenyls	222	221	13.5%
Trichlorobiphenyls	256	255	13.5%
Tetrachlorobiphenyls	292	289	17.4%
Pentachlorobiphenyls	326	323	22.0%
Hexachlorobiphenyls	360	357	26.5%
Heptachlorobiphenyls	394	391	30.9%
Octachlorobiphenyls	430	425	40.0%

Table 15. Accuracy and Precision of Automated Measurements of PCBs and Pesticides in Fortified Water Extracts

Analyte (Meas. Ion)	Medium Level Reagent Water[a]				Low Level Reagent Water[b]					Ohio River Water[a]			
	True Conc. ug/L	Mean Meas. Conc., ug/L	(RSD, %)	Bias %	True Conc. ug/L	Mean Meas. Conc., ug/L	(RSD, %)	Bias %	MDL ug/L	True Conc. ug/L	Mean Meas. Conc., ug/L	(RSD, %)	Bias %
Aldrin (263)	10	9.6	(3.6)	-4	3	2.5	(7.2)	-17	0.6	5	4.7	(3.0)	-6
BHC, alpha (219)	10	9.8	(4.3)	-2	3	2.8	(5.0)	-7	0.4	5	4.7	(1.6)	-6
BHC, beta (219)	10	10.5	(3.6)	+5	3	3.0	(2.5)	0	0.2	5	5.1	(2.5)	+2
BHC, gamma (219)	10	10.2	(4.7)	+2	3	2.9	(5.3)	-3	0.5	5	4.8	(3.0)	-4
BHC, delta (219)	10	9.9	(4.2)	-1	3	2.9	(4.8)	-3	0.4	5	4.8	(2.4)	-4
Chlordane, alpha (373)	10	9.6	(3.9)	-4	3	2.9	(4.0)	-3	0.4	5	4.6	(4.2)	-8
Chlordane, gamma (373)	10	9.6	(4.6)	-4	3	2.7	(4.8)	-10	0.4	5	4.4	(3.5)	-12
4,4'-DDD (235)	10	10.4	(3.0)	+4	3	2.9	(3.8)	-3	0.4	5	4.8	(2.5)	-4
4,4'-DDE (246)	10	9.8	(3.2)	-2	3	2.8	(5.4)	-7	0.5	5	4.5	(4.5)	-10
4,4'-DDT (235)	10	10.9	(3.0)	+9	3	2.9	(4.5)	-3	0.4	5	4.7	(3.9)	-6
Dieldrin (79)	10	10.6	(3.2)	+6	3	2.9	(7.6)	-3	0.7	5	4.5	(4.3)	-10
Endosulfan I (195)	10	9.6	(5.8)	-4	3	3.1	(4.8)	+3	0.5	5	4.4	(5.0)	-12
Endosulfan II (195)	10	10.2	(4.5)	+2	3	3.3	(6.3)	+10	0.7	5	3.5	(4.1)	-30
Endosulfan sulf. (272)	10	10.6	(2.3)	+6	3	3.2	(4.4)	+7	0.4	5	4.8	(1.7)	-4
Endrin (81)	10	11.8	(2.8)	+18	3	3.6	(7.0)	+20	0.8	5	5.4	(7.5)	+8
Endrin aldehyde (67)	10	9.0	(9.8)	-10	3	2.8	(8.4)	-7	0.7	5	4.4	(4.8)	-12
Endrin ketone (67)	10	11.5	(0.61)	+15	3	3.2	(1.9)	+7	0.2	5	4.7	(3.0)	-6
Heptachlor (272)	10	10.6	(5.1)	+6	3	2.6	(5.3)	-13	0.4	5	4.9	(3.5)	-2
Heptachlor epox. (353)	10	10.0	(2.5)	0	3	3.0	(5.9)	0	0.6	5	4.8	(3.9)	-4
Methoxychlor (227)	10	11.4	(1.6)	+14	3	3.1	(2.3)	+3	0.2	5	4.8	(3.8)	-4
Nonachlor, trans (409)	10	9.5	(4.6)	-5	3	2.8	(2.4)	-7	0.2	5	4.4	(4.3)	-12
All pesticides	10	10.2	(7.1)	+2	3	2.9	(8.6)	-2		5	4.6	(7.7)	-8

Table 15. (Cont.) Accuracy and Precision of Automated Measurements of PCBs and Pesticides in Fortified Water Extracts

Analyte (Meas. Ion)	Medium Level Reagent Water[a]			Low Level Reagent Water[b]				Ohio River Water[a]		
	True Conc. ug/L	Mean Meas. Conc., ug/L (RSD, %)	Mean Bias %	True Conc. ug/L	Mean Meas. Conc., ug/L (RSD, %)	Mean Bias %	Method Detect. Limit	True Conc. ug/L	Mean Meas. Conc., ug/L (RSD, %)	Mean Bias %
PCBs	130	110 (2.9)	-15	27	21.2 (2.8)	-21	c	70	51.3 (2.5)	-27
Cl_1 (188)	-	3.6 (9.9)	-		0.7 (15)	-			1.83 (4.8)	
Cl_2 (222)	-	6.5 (5.7)	-		1.2 (10)	-			3.42 (3.9)	
Cl_3 (256)	-	17.2 (5.3)	-		3.1 (10)	-			10.1 (3.0)	
Cl_4 (292)	-	21.7 (4.1)	-		4.1 (3.8)	-			11.0 (4.5)	
Cl_5 (326)	-	28.8 (3.6)	-		5.6 (2.8)	-			15.4 (3.6)	
Cl_6 (360)	-	9.8 (5.7)	-		1.6 (3.1)	-			4.86 (6.4)	
Cl_7 (394)	-	1.3 (4.3)	-		- -	-			0.335(4.8)	
Cl_8 (428)	-	7.1 (3.5)	-		1.6 (2.7)	-			1.56 (4.3)	
Cl_9 (466)	-	12.6 (5.3)	-		2.7 (4.6)	-			3.00 (1.8)	
Cl_{10} (500)	-	2.0 (16.0)	-		0.6 (12)	-			0.442 (1.8)	
Surrogate Compounds										
$^{13}C_6$-gamma-BHC (187)	-	- -	-	3	3.0 (3.4)	0	0.3	5	4.9 (1.4)	-2
$^{13}C_{12}$-4,4'-DDT (247)	-	- -	-	-	- -	-	-	5	4.4 (7.0)	-12

[a] Results of analysis of five replicate extracts of 1-L aliquots of fortified water.

[b] Results of analysis of seven replicate extracts of 1-L aliquots of fortified water.

[c] PCB method detection limits cannot be determined because Aroclor mixtures were used to fortify samples.

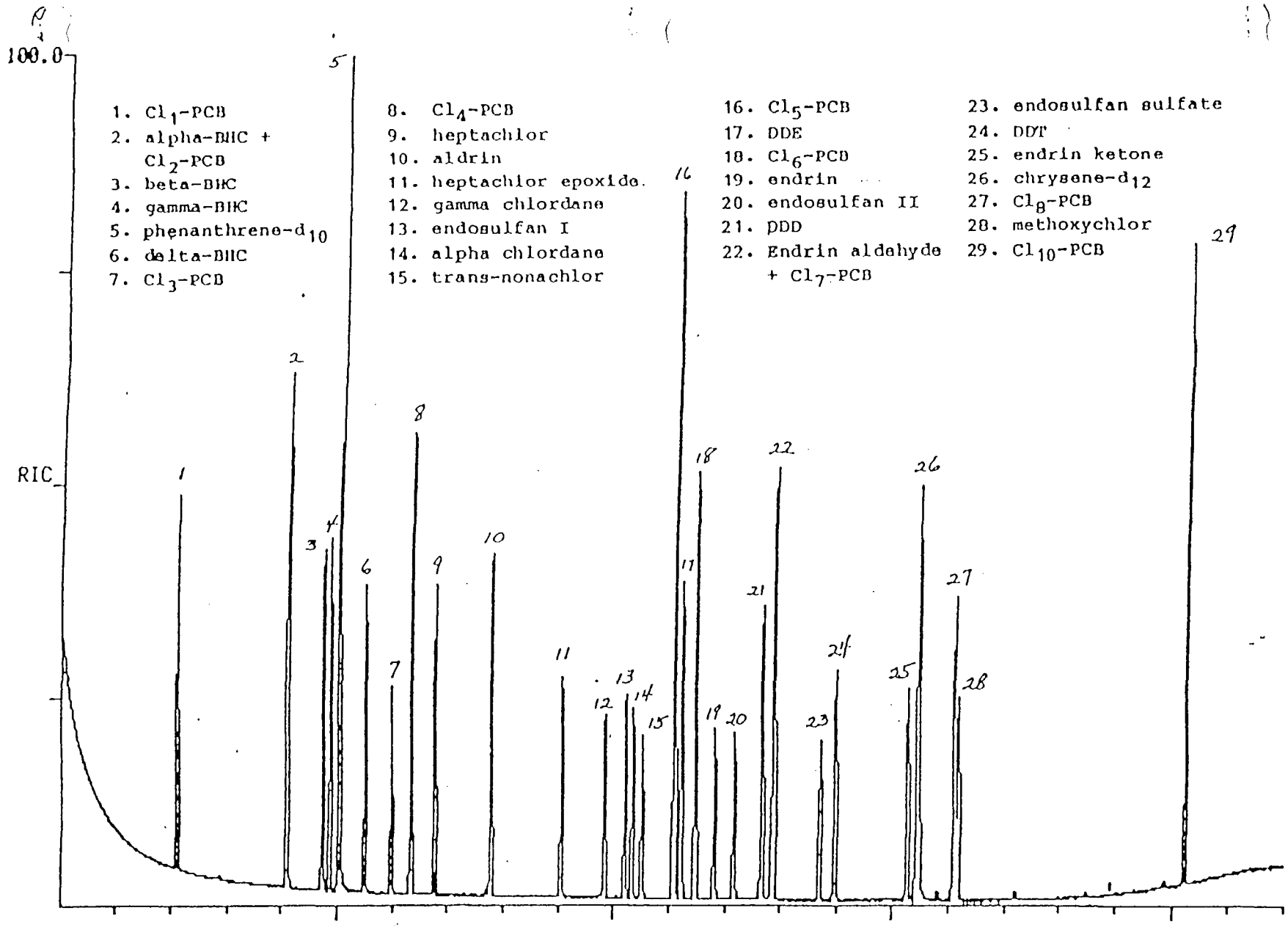

Figure 1. Total Ion Current Profile of PCB Calibration Congeners and Pesticide Analytes.

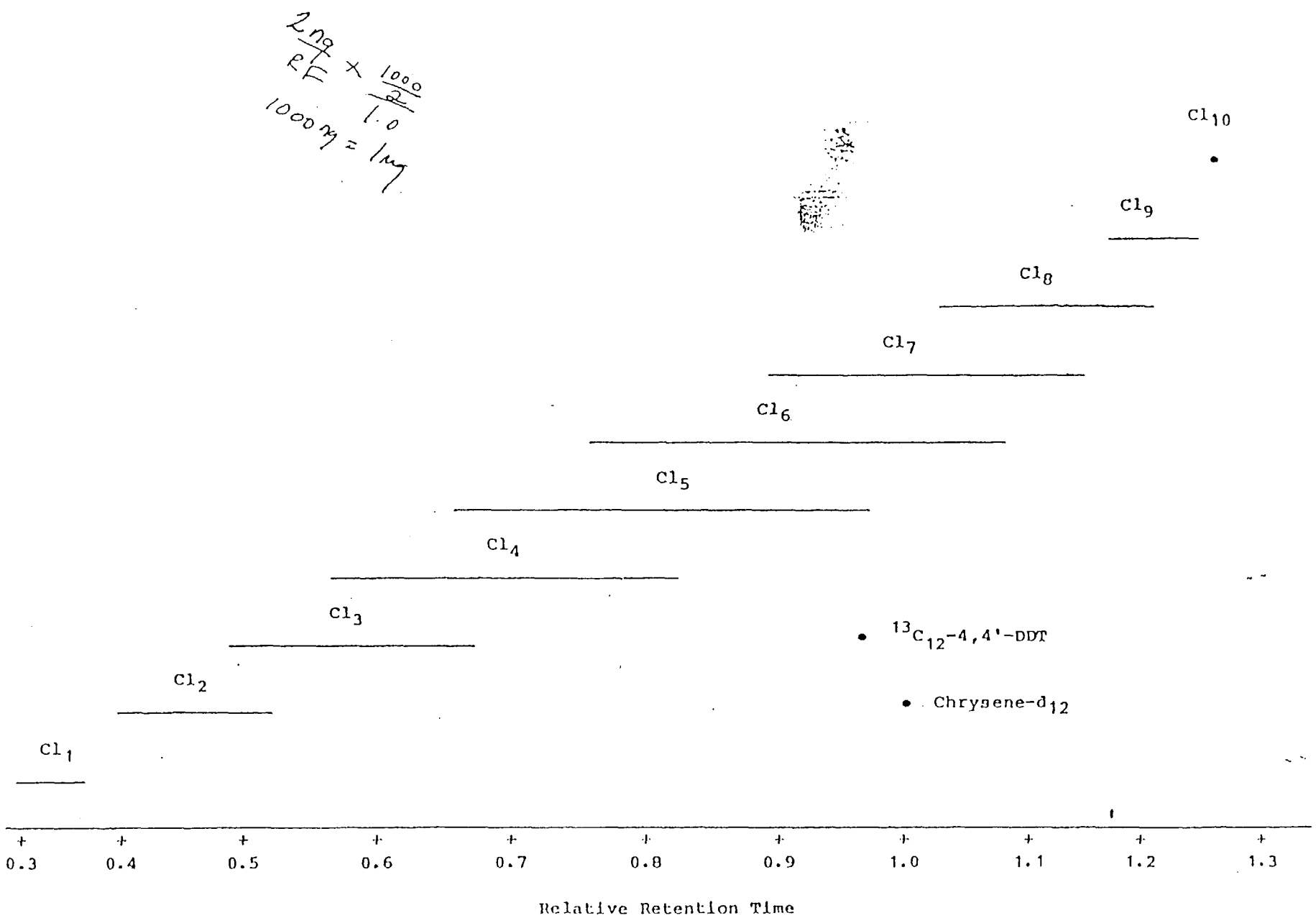

Figure 2. Diagram indicating approximate relative retention times (DB-5 GC column; chrysene-d_{12} internal standard) of PCB isomer groups and retention time marker compounds (for PCB SIM data acquistion option).

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CHANGE -IN-PROGRESS ATTACHMENT

SOP Document No: SM07:07.12.99:1

SOP Description: Polychlorinated Biphenyls (PCBs) by GC/MS (Method 680)

Approval Signature: R. Wayne Robbins 6 Sept 2001
Date

Title: Technical Manager, QA

STL X Savannah __ Tallahassee __ Mobile __ Tampa West

The following revisions or additions have been made to the referenced SOP.

The following attachments are for a specific project and will be effective from the date of approval until the date that the project is completed. The purpose of this CIPA is to document changes or additions to the standard operating procedures requested for the Sauget Area 2 Sites Group and EPA Region V.

The attachments are tables of the project RLs and MDLs, including the QC limits, and an excerpt from the Sauget Area 2 Sites Group QAPP.

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PCBs by GC/MS (Method 680) Water

PARAMETER	METHOD	%REC	%RPD	MDL(ug/L)	RL(ug/L)
Monochlorobiphenyls	680	30-130	<=50	0.018	0.10
Dichlorobiphenyls	680	30-130	<=50	0.015	0.10
Trichlorobiphenyls	680	30-130	<=50	0.016	0.10
Tetrachlorobiphenyls	680	40-140	<=50	0.034	0.20
Pentachlorobiphenyls	680	40-140	<=50	0.023	0.20
Hexachlorobiphenyls	680	40-140	<=50	0.027	0.20
Heptachlorobiphenyls	680	40-140	<=50	0.039	0.30
Octachlorobiphenyls	680	40-140	<=50	0.033	0.30
Nonachlorobiphenyls	680	30-130	<=50	0.028	0.50
Decachlorobiphenyl	680	30-130	<=50	0.028	0.50
Surrogate					
Decachlorobiphenyl-13C10	680	30-130	NA	NA	NA

PCBs by GC/MS (Method 680) Soils

PARAMETER	METHOD	%REC	%RPD	MDL(ug/kg)	RL(ug/kg)
Monochlorobiphenyls	680/(3550)	30-130	<=50	0.62	3.3
Dihlorobiphenyls	680/(3550)	30-130	<=50	0.70	3.3
Trichlorobiphenyls	680/(3550)	30-130	<=50	0.69	3.3
Tetrachlorobiphenyls	680/(3550)	40-140	<=50	1.3	6.7
Pentachlorobiphenyls	680/(3550)	40-140	<=50	0.88	6.7
Hexachlorobiphenyls	680/(3550)	40-140	<=50	0.95	6.7
Heptachlorobiphenyls	680/(3550)	40-140	<=50	1.4	10
Octachlorobiphenyls	680/(3550)	40-140	<=50	1.3	10
Nonachlorobiphenyls	680/(3550)	30-130	<=50	2.6	17
Decachlorobiphenyl	680/(3550)	30-130	<=50	2.6	17
Surrogate					
Decachlorobiphenyl-13C12	680/(3550)	30-130	NA	NA	NA

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Table 7D. *PCBs Method 680 by Selected Ion Monitoring (SIM) Mode Quality Control Requirements and Corrective Actions.**

Audit	Frequency	Control Limits	Corrective Action
Holding Times	Samples must be extracted and analyzed within holding time.	Extract within 7 days for aqueous and 14 days for soil samples from collection. Analyze extracts within 40 days of extraction.	If holding times are exceeded for initial or any re-analyses required due to QC excursions, notify the QAO* immediately since re-sampling may be required.
MS Tuning	At the beginning of the 12 hour sequence. Prior to calibration, blank, sample and QC sample analysis.	1. Tune instrument in accordance with Method 680. 2. Size of DFTPP peak should be within instrument specific established area window.	1. Identify and correct problem. 2. Re-tune the mass spectrometer; samples must not be analyzed until tuning criteria are met.
Initial Calibration	Prior to start up after tuning and when criteria are exceeded for continuing calibration.	1. Minimally five concentrations, one calibration standard must be at concentration less than or equal to the PQL. 2. Toxaphene, technical chlordane require a single point calibration. If detected in samples, the samples are re-analyzed behind a five point calibration for each detected analyte. 3. If RSD <20% the average RRF may be used for quantitation. If RSD >20% a first or second order calibration curve with a correlation coefficient >0.99 must be used for quantitation.	1. Identify and correct problem. 2. Recalibrate instrument; samples must not be analyzed until initial calibration criteria are met.
Calibration Verification	Calibration standards must contain target compounds at mid-range concentration. Minimally, analyze calibration standards prior to sample analysis and at the end of the sample sequence, and every 12 hours.	1. %D <20% for water, 30% for soil. 2. Mass abundance ratio of all calibration congeners within acceptable range. 3. Baseline separators of PCB congener #87 from #154 and #77. 4. Signal to noise ratio of ≥5 for decachlorobiphenyl ion #499 and chrysene-d12 ion #241. 5. Decachlorobiphenyl mass abundances for mass 500 ≥70% and ≤95% for mass 498.	1. Reanalyze. 2. If criteria are still not met, identify and correct problem, recalibrate; re-analyze samples back to last compliant calibration standard. Samples must be bracketed by compliant calibration standards.
Identification	Samples, blanks, and QC data.	1. The retention time must be within the corresponding retention time established by the window defining mixture for each chlorination level. 2. The ion current response for both ions must reach a maximum with ±1 scan. 3. Ion abundance rations specified in SOP must be met. 4. The area of the ions must by >3 times the background noise. 5. At least one ion in the M-70 cluster must be present. 6. Evaluate PCBs in the CI-3 to CI-7 range for coeluting PCBs. See SOP Section 11.1.3. 7. Examine data for presence of PCB of higher chlorination level if both ions and M-70 ions are present and the ratio does not fall within acceptable limits.	1. If identification criteria are not all met, but in the judgment of the operator the target compound is present, proceed with quantitation and document reasoning in the data package.

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Table 7D. *PCBs Method 680 by Selected Ion Monitoring (SIM) Mode Quality Control Requirements and Corrective Actions.**

Audit	Frequency	Control Limits	Corrective Action
Equipment Blank Analysis	1 per sampling equipment and after collection of 10 samples.	Compounds concentration must be < reporting limit.	1. Investigate problem; re-analyze to verify laboratory cross contamination is not a factor. 2. Notify QAO Officer since resampling may be necessary.
Field Duplicate Analysis	Collected every 10 samples	Aqueous: RPD ≤50% for results >5xCRQL. Soils: RPD ≤100% for results >5xCRQL. For Results <5xCRQL must agree with ±2xCRQL for aqueous and soils.	No corrective action required of the laboratory since the laboratory will not know the identity of the field duplicate samples. If these criteria are not met, sample results will be evaluated on a case by case basis during the validation process..

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EPA RESPONSE

ATTACHMENT H

ELEMENTS BY ICP (200.7 and 6010B)

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Approved by:

R. Wayne Robbs — 21 March 2001
Date

Title: Technical Manager, QA

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1.0 SCOPE AND APPLICATION

1.1 This SOP describes the procedures to determine the concentration of various elements by inductively coupled plasma (ICP) atomic emission spectroscopy. This method contains the analytical procedures for the determination of metals in surface and ground water, wastewater, soil, sediment, leachate (EP or TCLP), and waste samples after digestion.

1.2 Table 1 lists the elements that may be determined by ICP and the characteristic wavelength used for each element. The reporting limit (RL) for each element, the method detection limit (MDL) for each element, and the accuracy and precision criteria for each element are in the Laboratory Quality Manual (LQM) prepared by and for STL Savannah, STL Tallahassee, STL Mobile, and STL Tampa West.

2.0 SUMMARY OF METHOD AND DEFINITIONS

2.1 Prior to analysis by ICP, the sample must be solubilized or digested using the sample preparation method appropriate to the matrix. Sample digestates are aspirated and nebulized into a spray chamber. A stream of argon gas carries the sample aerosol through the innermost of three concentric tubes and injects it into the middle of the donut-shaped plasma. The sample elements are dissociated, atomized, and exited to a higher energy level. As the elements fall to a lower energy level, radiation characteristic of the elements present in the plasma is emitted. The light is directed through an entrance slit, dispersed by the diffraction grating, and projected on to the photomultiplier tube (PMT). The PMTs, located behind the exit slits, convert the light energy to an electrical current. This signal is then digitized and processed by the data system. Background correction is required for trace element determination.

2.2 Definitions

ICP -inductively coupled (argon) plasma; sometimes referred to a "ICAP"
TCLP-toxicity compound leaching procedure
EP (tox)-extraction procedure (toxicity)
Analytical Spike or Post-Digestion Spike - addition of a known concentration of analyte to an aliquot of sample after the preparation steps have been performed
RL - reporting limit, the lowest calibration standard or the sample equivalent of the lowest calibration standard; published in LQM or project-specific quality assurance plan (QAPP); sometimes referred to as the "practical quantitation limit(PQL).
MDL - method detection limit, the concentration that can be reported with 99% confidence that the result is greater than zero; published in LQM

2.3 This method is based on EPA Method 200.7 and SW-846 Method 6010B. Note that EPA has promulgated two versions of method 200.7-one for NPDES samples and one for drinking water. The calibration sequence for drinking water by 200.7 requires a multi-point curve with a minimum of three standards and a calibration blank.

3.0 SAFETY

3.1 Use good common sense when working in the lab. Do not perform any procedures that you do not understand or that will put you or others in potentially dangerous situations.

3.2 Each digestion lab must have acid spill kits. These kits must be located in a highly accessible area of the lab. Each digestion lab must be equipped with a properly working shower.

3.3 The standards and reagents used to prepare the standards in this method should be treated as potential hazards. Lab coats, gloves, and other protective equipment should be used when preparing and using the standards and reagents.

3.4 The Material Safety Data Sheets (MSDS) for each reagent and standard are located in each laboratory. These sheets denote the type of hazard that each reagent poses, the safe handling instructions for these compounds, and first aid instructions.

4.0 INTERFERENCES

4.1 Spectral interferences are caused by (1) the overlap of a spectral line from another element, (2) unresolved overlap of molecular band spectra, (3) background contribution from continuous phenomena, and (4) stray light from the line emissions of highly concentrated elements.

4.1.1 Spectral overlap may be compensated for by the use of inter-element correction factors.

4.1.2 Background contribution and stray light can be compensated for by a background correction adjacent to the analyte line.

4.2 Physical interferences are effects associated with the sample nebulization and transport processes. Changes in viscosity can cause significant inaccuracies, especially in samples containing high concentrations of dissolved solids or high acid concentrations. If physical interferences are present, they must be reduced by diluting the sample digestate, by using a peristaltic pump, or by using the method of standards additions(MSA), or use of an internal standard

4.3 Contamination of the sample can occur when the preparation glassware and/or reagents contain the target elements. Reagent blanks (method blanks) must be analyzed as a check on contamination due to the sample digestion.

5.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

5.1 Aqueous Samples

5.1.1 Liquid samples are routinely collected in 250-mL or 500-mL plastic containers. The sample is preserved with HNO_3 to a pH <2. The sample must be digested and analyzed within 6 months of collection. Samples may be stored at room temperature.

5.1.2 Samples for dissolved metals should be filtered in the field before acid is added to the sample. If the sample is to be filtered in the lab, no preservative is added to the sample until the sample is filtered.

5.2 Soil/Sediment Samples
Soil and sediment samples are routinely collected in 500-mL plastic containers. The sample is iced at the time of collection and is stored in the lab at 4C (less than 6C but not frozen) until time of digestion and analysis. The sample must be digested and analyzed within 6 months of collection.

5.3 TCLP or EP Toxicity Leachate Samples
The leachate is transferred to a plastic container after the extraction procedure. The sample is preserved with HNO_3 to a pH <2. The leachate sample must be digested and analyzed within 6 months of completion of the leaching procedure.

5.4 Waste Samples
Waste samples are routinely collected in 500-mL plastic containers. The sample must be digested and analyzed within 6 months of collection.

6.0 APPARATUS AND MATERIALS

6.1 Thermo Jarrell Ash TJA ICAP61E-trace, or other suitable inductively coupled plasma emission spectrometer with data system

6.2 Argon gas supply and appropriate fittings

6.3 Cooling water supply

6.4 Peristaltic pump

6.5 Volumetric flasks

6.6 Pipettes

7.0 REAGENTS

Reagents are tracked in accordance with STL SOP AN44:*Reagent Traceability.*

7.1 Reagent water-lab generated deionized water, ASTM Type I or Type II. The conductivity is monitored in accordance with STL SOP AN35.

7.2 Nitric acid (HNO_3)-reagent grade. The assay sheet of each lot of acid received into the lab must be reviewed to make sure that the quality of the acid is sufficient for trace analysis of metals.

7.4 Hydrochloric acid (HCl)-reagent grade. The assay sheet of each lot of acid received into the lab must be reviewed to make sure that the quality of the acid is sufficient for trace analysis of metals.

8.0 STANDARDS

Calibration and spike solutions are prepared from either certified stock solutions or from stock solutions purchased from vendors. Certificates of analysis or purity must be received with all neat compounds or stock solutions. All preparation steps must be in accordance with STL SOP AN41: *Standard Materials Traceability*. SOP AN43 contains guidance for the preparation of standards.

8.1 Recommended concentrations for the calibration standards are given in Table 1. Appendix A contains examples for the preparation of the initial calibration and calibration verification standards for both 6010 and 200.7. if the laboratory uses "recipes' other than those listed in Appendix A, the recipe must be documented in the standard material traceability logbook or as controlled posting. All standards must have be prepared in 5% hydrochloric acid and 1% nitric acid by volume.

NOTE: Standards must be prepared every six months "or sooner if needed or required." "If needed" means the standard has been exhausted; "if required" means that the standard does not meet the QC criteria.

8.2 Preparation of the Linearity Check Solutions

The linearity check solutions are prepared individually according to the following equation:

$$Vs = \frac{Vlc \otimes Clc}{Cs}$$

where
Vs = volume of stock standard (mL)
Cs = concentration of stock standard (mg/L)
Vlc = volume of linearity check standard to prepare (mL)
Clc = concentration of linearity check standard to prepare (mg/L)

The linearity check solutions are prepared at the concentrations specified in Table 1. Prepare sufficient volume to perform the linearity check, maintaining the hydrochloric acid concentration at 5% by volume and the nitric acid concentration at 1% by volume.

9.0 SAMPLE PREPARATION

The sample preparation and digestion procedures are listed in the following SOPs:

MATRIX	SOP
Aqueous and leachate samples	ME50
Soils and Sediments	ME51
Wastes and oils	ME51

10.0 ANALYSIS PROCEDURE

The analytical sequence, including standardization and calibration verification, is included in the SOP Summary in Appendix A. The SOP Summary also included the acceptance criteria for QC, including recommended corrective actions.

10.1 Initial Calibration/Standardization

10.1.1 Turn the ICP on and allow it to become thermally stable before beginning to analyze the calibration standards. It will take about an hour for the instrument to warm up. If optics were turned off, allow 2 hours warm up time.

10.1.2 Run the "Automatic Profile" program. The "automatic profile" of the instrument should be checked twice a day to compensate for changes in air pressure, humidity, and temperature. If the environment of the instrument is such that daily changes in the instrument profile are extreme, the instrument should be "profiled" every few hours.

10.1.3 Analyze the calibration standards and calibrate the ICP. ***If using a multi-point calibration, use the Calibration/Analysis and Curvefit programs to calibrate the instrument.***

10.1.4 The highest concentration calibration standard is reanalyzed after the instrument is standardized as an "unknown". The results for the re-analysis of the highest concentration calibration standard must be within +/- 5% of the true value for each target analyte. If the result for any target analyte is outside of this range, the ICP may need to be "profiled" and the standardization/calibration repeated.

10.1.5 The QC Check standards (ICV) and the Calibration Blank (ICB) are analyzed as a check on the instrument calibration.

10.1.5.1 (EPA Method 6010) The results for the target compounds in the initial calibration verification (ICV) must be within the +/- 10 % of the true value.

10.1.5.2 (EPA Method 200.7) The results for the target compounds in the initial calibration verification (ICV) must be within the +/-5.0 % of the true value. **When performing 200.7 work, note that this solution should be prepared fresh weekly.**

10.1.5.3 (EPA 6010/200.7) The results for the target compounds in the initial calibration blank (ICB) must be less than the RL.

10.1.6 The RL/PQL Check Solution is analyzed to demonstrate that the ICP is capable of detecting the target compounds at or near the reporting limit (RL). The determined concentration must within +/- 50% of the true concentration.

10.1.7 The ICP Interference Check Sample is analyzed. The concentrations of the target analytes must be within 20% of the true concentrations. Pay particular attention to false positives and false negatives for elements not present in the interference check solutions.

10.2 Continuing Calibration Verification (CCV)

10.2.1 The calibration of the ICP must be verified every 10 samples by the analysis of the analysis of the QC Check Solutions (CCV) and the Calibration Blank (CCB).

10.2.1.2 (EPA Method 6010/200.7-DW) The results for the target compounds in the continuing calibration verification (CCV) must be within the +/- 10 % of the true value.

10.2.1.2 (EPA Method 200.7-NPDES) The results for the target compounds in the continuing calibration verification (CCV) must be within the +/-5.0 % of the true value.

10.2.1.3 (EPA 6010/200.7) The results for the target compounds in the continuing calibration blank (CCB) must be less than the Reporting Limit (RL).

10.2.2 ICP Interference Check Solution and the RL check solution are analyzed at the beginning and end of each analytical sequence.

10.3 Sample Analysis

10.3.1 The samples are analyzed only after the ICB/CCB and ICV/CCV criteria are met.

10.3.2 The samples are analyzed in a sequence as follows:

INSTRUMENT WARM-UP
PROFILE
INITIAL CALIBRATION (STANDARDIZATION/CALIBRATION OF THE ICP)
REANALYSIS OF HIGH CONCENTRATION CALIBRATION STANDARD AS A SAMPLE
INITIAL CALIBRATION VERIFICATION (ICV)
INITIAL CALIBRATION BLANK (ICB)
DETECTION LIMIT CHECK SOLUTION
ICP INTERFERENCE CHECK SOLUTION A (ICSA)
ICP INTERFERENCE CHECK SOLUTION AB (ICSAB)
CONTINUING CALIBRATION VERIFICATION (CCV)
CONTINUING CALIBRATION BLANK (CCB)
10 SAMPLES
CONTINUING CALIBRATION VERIFICATION (CCV)
CONTINUING CALIBRATION BLANK (CCB)
10 SAMPLES
CCV
CCB
10 SAMPLES
CCV
CCB
10 SAMPLES
CCV
CCB

The analytical sequence must end with the analysis of the detection limit check standard, ICSA, ICSAB, CCV and CCB. The 10 samples include all QC samples/standards with the exception of CCVs and CCBs.

10.3.3 Determine the concentration of the samples and QC items using the procedures of Section 11.

10.3.3.1 If the concentration of a sample is above the linear range of the ICP, the sample digestate must be diluted and reanalyzed.

10.3.3.2 The amount of sample digestate needed to prepare the desired dilution is determined form the following equation:

$$V_{digest} = \frac{Vf_{vol}}{DF}$$

where
Vf_{vol} = final volume of diluted sample (mL)
V_{digest} = volume of sample digestate used to make the dilution (mL)

10.3.3.3 The dilution factor is calculated as follows:

$$DF = \frac{Vf_{vol}}{V_{digest}}$$

where
Vf_{vol} = final volume of diluted sample extract (mL)
V_{digest} = volume of sample extract used to make the dilution (mL)

NOTE: The following examples are based on a final volume of 100mL. It may be more convenient to prepare dilutions at smaller final volumes.

EXAMPLE
A sample digestate is analyzed and one of the target analytes exceeds the linear range of the ICP. 1.0mL of the digestate is added to a 100mL volumetric flask and the extract brought up to volume with reagent water. What is the dilution factor?

$$DF = \frac{100mL}{1.0mL} = 100$$

Dilutions must be prepared in reagent water containing 5% hydrochloric acid and 1% nitric acid by volume.

Some samples may require multiple dilutions; that is, a dilution of a dilution will have to be made. In this case, the final dilution factor is the product of the individual dilutions.

10.4 Dilution QC Check
A dilution is prepared and analyzed on one sample per batch to determine if matrix interferences are present.

10.4.1 Select a sample digestate that contains one or more target analytes at a concentrations greater than 10X the reporting limit.

10.4.2 Dilute the digestate by a factor of 5 (DF=5) and analyze the dilution using the same procedures used for the un-diluted aliquot.

10.4.3 Compare the results of the diluted and un-diluted aliquots of sample digestate.

10.4.4 If the results of the dilution are within ± 10% of the results of the undiluted sample, no matrix interference is present. If the results differ by greater than ± 10%, a matrix interference should be suspected and the sample digestate should be subjected to a post-digestion spike (see section 10.4).

If the concentration of the analyte in the sample is not at least 50 times the instrument detection limit, evaluate the post-digestion spike.

10.5 Post-digestion Spike QC Check
A post-digestion spike is performed on one sample per analytical batch to determine if matrix interferences are present. This post-digestion spike is evaluated if the serial dilution fails or if the analyte concentration is not at least 50 times the instrument detection limit. This should be the same sample selected for dilution in 10.3, above.

10.5.1 Transfer 10mL of a digestate to a suitable vial.

10.5.2 Spike the sample with 0.10mL of ICP Matrix Spike I and 0.10mL of ICP Matrix Spike II. The theoretical concentration of the post digestion spike is the same as the LCS or MS if the volume of spiking solution is discounted.

10.5.3 Analyze the spiked aliquot and an un-spiked aliquot (the un-spiked may have been analyzed previously and does not need to be reanalyzed).

10.5.4 Calculate the percent recovery of the post digestion spike:

$$\%REC = \frac{C_{ps} - C_s}{C_2} \times 100$$

where

Cps = concentration of post digestion spike (ug/L)
Cs = concentration of un-spiked sample (ug/L)
C2 = theoretical concentration of spike (ug/L)
(See 10.2.5.2)

10.5.5 Evaluate the recovery using the following decision matrix. Limits for post digestion spikes are 75-125% recovery.

Result of Post Digestion Spikes	Action
Within 75-125% limits	None
>125% recovery	Repeat analysis. Remake spiking solutions, re-spike, and reanalyze. Reanalyze un-spiked sample
<75% recovery but >50% recovery	1) Dilute and re-spike. Elevate RL accordingly (for all associated samples). 2) Spike and evaluate all associated samples. 3) Spike and evaluate all associated samples by single point MSA 4) Qualify all associated samples
<50% recovery	Dilute digestate and repeat spike. Treat all samples associated with spike in the same manner as the spiked sample (i.e., spike or dilute samples) If recoveries are not 75-125%, analyze all associated samples by single point MSA. Note – high level of target analytes may inhibit spike recovery. Consult the supervisor in events where high levels of targets appear to be interfering

Note: The >50% recovery of the post digestion spike is a benchmark below which samples may be biased high if corrected for spike recovery.

10.5.6 The post digestion spike and the method of standard additions must not be applied to samples analyzed at a dilution that produces a significant negative response. The analyst must use good judgement when evaluating data where the sample response is negative. Where a significant negative response is present, the digestate should be diluted and reanalyzed to determine the extent of the matrix interferences.

10.6 Single Point Method of Standard Additions

Two identical aliquots of the sample digest, Vx, are taken. One aliquot is spiked with a solution of known concentration, Cs. The second aliquot is analyzed un-spiked (the small volume of standard added to the spiked sample should be disregarded). The concentration of both aliquots are measured and the sample concentration, Cx, is calculated:

$$C_x = \frac{S_2 V_s C_s}{(S_1 - S_2) V_x}$$

where

S_1 = absorbance or concentration of the spiked aliquot
S_2 = absorbance or concentration of the un-spiked aliquot
Vs = Volume of spike solution

Example:	Sample concentration (S_2):	523 ug/L.
	Spike solution concentration (C_s):	50,000 ug/L
	Volume of spike solution (V_s):	0.10mL
	Volume of sample aliquots (V_x):	10mL
	Spiked sample concentration (S_1):	951 ug/L

C_x = [(523)*(0.10)*(50,000)]/[(951-523)*10)] = [2,615,000]/[4280] = 611 ug/L

10.7 Determination of Linear Range of the ICP

The linear range must be determined a minimum of once per year. Divisions performing CLP analyses are required to determine and document the linear range quarterly. Documentation of the linear range study must be kept on hand and be available for inspection. A summary of the linear range study must be available to the bench analyst.

10.7.1 Profile and calibrate the ICP as described in Section 10.1

10.7.2 Prepare individual standards at concentrations that are expected to define the linear range of the instrument. Use the concentrations in Table 1 for guidance. The calibration standards and the linear range standards should be matrix matched; that is, they have the same percentage of hydrochloric and nitric acids.

10.7.3 Analyze the standards following the analytical sequence described in Section 10.3. Verify the calibration after every 10 analyses.

10.7.4 Compare the concentration of the linear range standard with its true concentration.

$$PercentDifference = \left| \frac{Ccal - Ctrue}{Ctrue} \right| \otimes 100$$

where
Ccal = concentration determined from analysis
Ctrue = true concentration of the standard

If the percent difference is less than or equal to 5%, the linear range is confirmed at that concentration. If the percent difference is greater than 5%, repeat the analysis with a lower concentration.

The linear range may be extended by analyzing higher standards and evaluating the results against the 5% difference criterion. The linear range of the ICP for an analyte is the highest standard of that analyte that meets this criterion.

11.0 DATA ANALYSIS/CALCULATIONS

11.1 Aqueous and Leachate Samples

Aqueous samples are routinely reported in mg/L while the ICP is routinely calibrated in ug/L. If the results are reported in ug/L, the conversion factor is omitted from the calculation.

11.1.1 The concentration of the target analyte in liquid samples is calculated as follows:

$$Concentration\,(mg/L) = ug/L(from\ printout) \otimes \frac{F}{V} \otimes DF \otimes \frac{1mg}{1000ug}$$

where
F = final volume of the sample digestate (L)-usually 50mL (0.050L)
V = volume of sample digested (L)
DF = dilution factor

11.1.2 The Reporting Limit (RL) of the target analyte in liquid samples is calculated as follows:

$$Concentration(mg/L) = RLqap \otimes \frac{F}{V} \otimes DF \otimes \frac{1mg}{1000ug}$$

where
RLqap = reporting limit from STL LQM (ug/L)
F = final volume of the sample digestate (L)
V= volume of sample digested (L)
DF = dilution factor

The LQM Reporting Limits assumes:
F = 50mL, V = 50mL, and DF = 1

11.2 Soil/Solid Samples

Soils and solids are routinely reported in mg/kg while the ICP is routinely calibrated in ug/L. If the results are reported in ug/kg, the conversion factor is omitted from the calculation.

11.2.1 The concentration of the target analyte in soil and solid samples is calculated as follows:

$$Concentration(mg/kg,dw) = ug/L(from\ printout) \otimes \frac{F}{W \otimes solids} \otimes DF \otimes \frac{1mg}{1000ug}$$

where
F = final volume of the sample digestate (L)
W = volume of sample digested (kg)
DF = dilution factor
solids = decimal equivalent of the percent solids (percent solids/100)
(for example, if the percent solids is 85%, the decimal equivalent is 0.85; if the %solids is 100%, the decimal equivalent is 1.0.)

11.2.2 The Reporting Limit (RL) of the target analyte in soil/solid samples is calculated as follows:

$$Concentration(mg/kg,dw) = RL_{qap} \otimes \frac{0.0010kg}{W \otimes solids} \otimes \frac{F}{0.100L}\ x\ DF$$

where
RL(qap) = reporting limit from LQM
W = weight of sample digested (kg)
F = final volume of the sample digestate (L)
V = volume of sample digested (L)
DF = dilution factor
solids = decimal equivalent of the percent solids (percent solids/100)

The LQM Reporting Limits assumes F = 0.100L (100mL), DF = 1, W = 0.0010kg (1.0g), and solids = 1.0

12.0 QUALITY ASSURANCE /QUALITY CONTROL

12.1 STL SOP AN02: *Analytical Batching* and the SOP Summary provide guidance on evaluating QC and sample data, including recommended corrective actions.

12.2 The method detection limit (MDL) is determined annually in accordance with STL SOP CA90. The concentrations of the IDL and MDL solutions are given in Section 8 of this SOP.

12.3 Determination of the Instrument Detection Limit (IDL)

The difference between the MDL and the IDL is the *digestion step*. The MDL samples are prepared and digested prior to analysis. The IDL is defined as three times the standard deviation of seven replicate analyses analyzed over three non-consecutive days. The concentrations of the IDL and MDL solutions are given in Section 8 of this SOP. See SOP CA91 for the procedures for the determination of the IDL.

12.4 The linear range of the ICP must be determined at least annually. The procedure for the determination is given in Section 10.7 of this SOP. If any calibration regression fit, other than linear, is utilized for the calibration of the ICP (i.e., Curvilinear or Full Fit), the upper limit of the linear range is the concentration of the High Standard.

12.5 Interelement correction factors (IEC) for all elements must be determined annually. Use the manufacturer's guidance for determination of the IECs. The IECs must be verified at the beginning and end of each analytical sequence.

13.0 TROUBLESHOOTING AND PREVENTIVE MAINTENANCE

LABORATORY EQUIPMENT PREVENTIVE MAINTENANCE SCHEDULE								
EQUIPMENT ITEM	Service Interval							SERVICE LEVEL
	D	W	M	Q	SA	A	AN	
ICAP								
Pump Tubing	X							Change.
Nebulizer							X	Clean.
Filters			X					Inspect monthly, clean or replace as needed.
Spray Chamber							X	Clean.
Quartz Torch							X	Clean and realign.

D = daily W = Weekly M = monthly Q = Quarterly SA = semi-annually A = annually AN = as needed

14.0 WASTE MANAGEMENT AND POLLUTION PREVENTION

Excess samples, reagents, and digests must be disposed of in accordance with SOP CA70:*Waste Management.*

15.0 REFERENCES

15.1 *Methods for Chemical Analysis of Water and Waste*; U.S EPA Office of Research and Development: Cincinnati, OHIO, March 1983.

15.2 *Test Methods for Evaluating Solid Waste, Third Edition*; U.S. EPA Office of Solid Waste and Emergency Response: Washington, D.C., November 1986.

15.3 *Methods for the Determination of Metals in Environmental Samples*; US EPA Office of Research and Development. Washington, DC.

TABLE 1

Element	Wavelength (nm)	Calibration Conc. (mg/L)	ICV/CCV Conc. (mg/L)	RL Std. Conc. (mg/L)	Linear Range Std. Conc. (mg/L)*	MATRIX SPIKE CONC. (mg/L)	
						Water (mg/L)	Soil (mg/kg)
Aluminum (Al)	308.215	10	1.0/5.0	0.20	800	2.0	200
Antimony (Sb)	206.838	10	1.0/0.50	0.020	10	0.50	50
Arsenic (As)	189.042 193.696	1.0	1.0/0.50	0.010	25	2.0	200
Barium (Ba)	493.409	10	1.0/5.0	0.010	10	2.0	200
Beryllium (Be)	313.042	1.0	1.0/0.50	0.0040	10	0.050	5.0
Boron (B)	249.678	10	1.0/5.0	0.050	100	1.0	100
Cadmium (Cd)	226.502 228.802	1.0	1.0/5.0	0.0050	10	0.050	5.0
Calcium (Ca)	317.933 315.887	10	1.0/5.0	0.50	800	5.0	500
Chromium (Cr)	267.716	10	1.0/5.0	0.010	25	0.20	20
Cobalt (Co)	228.616	1.0	1.0/0.50	0.010	25	0.50	50
Copper (Cu)	324.754	10	1.0/5.0	0.020	50	0.25	25
Iron (Fe)	259.940 271.441	10	1.0/5.0	0.050	800	1.0	100
Lead (Pb)	220.353	1.0	1.0/0.50	0.0050	5	0.50	50
Magnesium (Mg)	279.079	10	1.0/5.0	0.50	1000	5.0	500

TABLE 1

Element	Wavelength (nm)	Calibration Conc. (mg/L)	ICV/CCV Conc. (mg/L)	RL Std. Conc. (mg/L)	Linear Range Std. Conc. (mg/L)*	MATRIX SPIKE CONC. (mg/L)	
						Water (mg/L)	Soil (mg/kg)
Manganese (Mn)	257.610	10	1.0/5.0	0.010	50	0.50	50
Molybdenum (Mo)	202.030	1.0	1.0/0.50	0.010	50	0.50	50
Nickel (Ni)	231.604	5.0	1.0/2.5	0.040	10	0.50	50
Potassium (K)	766.491	20	10/5.0	1.0	50	5.0	500
Selenium (Se)	196.026	10	1.0/5.0	0.010	25	2.0	200
Silver (Ag)	328.068	1.0	1.0/5.0	0.010	5.0	0.050	5.0
Sodium (Na)	588.995 330.231	10	1.0/5.0	0.50	20	5.0	500
Strontium (Sr)	421.552	10	1.0/5.0	0.010	100	0.50	50
Thallium (Tl)	189.042 190.801 377.572	10	1.0/5.0	0.010	30	2.0	200
Tin (Sn)	189.989	10	1.0/5.0	0.050	50	1.0	100
Titanium (W)	334.941	10	1.0/5.0	0.010	10	1.0	100
Vanadium (V)	292.402	10	1.0/5.0	0.010	50	0.50	50
Zinc (Zn)	213.856 206.200+	5.0	1.0/2.5	0.020	20	0.50	50

*For guidance only-instrument sensitivity will vary.

APPENDIX A
SOP SUMMARY

METHOD SUMMARY - ICP ANALYSIS

HOLD/STORAGE

Container	Minimum 250mL plastic bottle with plastic or Teflon-lined lid
Preservative	HNO3 to pH <2 in the field. If dissolved metals are required, filter the samples before preservation.
Storage	Liquids preserved to pH <2 may be stored at room temperature until preparation. Solid samples must be stored at 4C (less than 6C but not frozen) until preparation.
Hold Time	Samples must be analyzed within six months from the time of collection.

SAMPLE PREPARATION

Samples should be prepared with the appropriate matrix-specific procedure.

ANALYTICAL SEQUENCE

Ignite Plasma	Follow instrument manufacturer's guidelines and allow instrument to stabilize for at least 60 minutes.
Profile Instrument	Follow manufacturer's guidelines.
Initial Calibration	Calibrate with a blank and a high standard or a blank and three standards. Verify calibration by reanalyzing highest concentration standard for each element.
Initial Calibration Verification (ICV/ICB)	Analyze an initial calibration verification solution at the beginning of the run. ICV solution must come from a source other than the calibration standard source. Analyze a calibration blank after the ICV.
Continuing Calibration Verification (CCV/CCB)	Analyze a standard with concentrations at or near mid-range levels of the calibration. The CCV should be analyzed every 10 samples and at the end of the analysis run Analyze a continuing calibration blank after every CCV.
Interference Check Solutions	At the beginning and the end of an analysis run, verify the inter-element and background corrections by analyzing the interferent check solutions (ICSA & ICSAB).
Detection limit check solution	At the beginning and the end of an analysis run and verify the accuracy at the RL by analyzing a solution at the SL RL
Serial Dilution	Perform serial dilution (1/5) on a representative sample from each batch..
Post Digestion Spike Recovery.	To check for possible matrix interference, analyze a post digestion spike on a representative sample (minimum of 1 per batch). The post-digestion spike is evaluated if the serial dilution fails or if the analyte concentration in the sample is not at least 50 times the instrument detection limit.

QC Item	Frequency	Criteria	Corrective Action
Initial Calibration	Daily	1 std. and 1 blank	
Initial Calibration: Multi-point-minimum 3 stds and 1 blank	Daily	Correlation ≥0.995	Recalibrate
Highest Standard	Immediately after every calibration	Recoveries within ± 5% of expected values	New initial calibration
Initial Calibration Verification Standard (ICV)	At the beginning of the analysis	SW846 = within ±10% 200.7 = within ± 5%	Recalibrate
Continuing Calibration Verification Standard (CCV)	At the beginning and end of the analysis, and every 10 samples	Within ±10% of the true value, 200.7-NPDES - within ± 5% 200.7-Drinking Water – within ±10%	Terminate the analysis, fix the problem and reanalyze the previous 10 samples.
Calibration Blank (ICB/CCB)	After ICV and every CCV	Absolute value of the calibration blank must be less that the RL/CRDL	Terminate the analysis, correct the problem and reanalyze the previous 10 samples
Interference check standards (ICSA/ICSAB)	At the beginning and end of an analysis run	Determined values must be within ± 20% of the true values. Pay attention to false positives and false negatives for elements not present in the solutions.	Terminate the analysis, correct the problem, recalibrate, and reanalyze all samples since the last ICS that was in control.
Lab control sample	One per batch of twenty samples or less	6010B: STL LQM 200.7: 85-115%	Redigest and reanalyze batch
Preparation blank - SW846	One per batch of twenty samples or less	|result| <RL or result <5% of the analyte level in the sample.	Redigest and reanalyze batch
Preparation blank - 200.7	One per batch of twenty samples or less	|result| <RL or result <10% of the analyte level in the sample	Redigest and reanalyze batch
MS/MSD - SW846	One set per batch of twenty samples or less	STL LQM	Flag and report data
Serial Dilution (1/5 Dilution)	One per batch of twenty samples or less	See section 10.3.4	
Post Digestion Spike	One per batch of twenty samples or less	See section 10.4.5	
Detection Limit Check Solution	At the beginning and end of an analysis run	Recovery +/-50% of the true concentration.	Stop the analysis, fix the problem and reanalyze the affected samples.

APPENDIX B
EXAMPLES OF STANDARD PREPARATION

GENERAL INSTRUCTIONS

All calibration standards must contain 5% hydrochloric acid and 1% nitric acid by volume. The following table lists the volume of each acid needed to prepare the desired final volume of standard.

Final Volume of Standard (mL)	Volume of Hydrochloric acid (mL)	Volume of Nitric Acid (mL)
100	5.0	1.0
200	10	2.0
500	25	5.0
1000	50	10

For example, to prepare 500mL of a standard:

- Add 100mL to 200mL of reagent water to a clean 500mL volumetric flask.
- Add 5.0mL of concentrated nitric acid (HNO_3) and 25mL of hydrochloric acid (HCl) to the volumetric flask.
- Add the volumes of the stock standards given in the table to the volumetric flask:
- Dilute to a final volume of 500mL with reagent water. Store the standard at room temperature.

SINGLE POINT CALIBRATION STANDARDS FOR 6010

Calibration Standard 1-Calibration Blank (ICB, CCB)

Add 500mL to 600mL of reagent water to a clean 1-L volumetric flask. Add 10mL of concentrated nitric acid (HNO_3) and 50mL of hydrochloric acid (HCl) to the volumetric flask. Dilute to a final volume of 1.0-L with reagent water. Store the standard at room temperature. Other volumes may be prepared at the discretion of the lab. The nitric acid concentration must be 1% by volume and the hydrochloric acid concentration must be 5% by volume.

Calibration STANDARD 2

Element	Conc. of Stock Std	mL of Stock Std	Final Volume (ml)	Conc. of Cal Std (mg/L)
Silver(Ag)	1000	0.50	500	1.0
Arsenic(As)	1000	0.50		1.0
Molybdenum(Mo)	1000	0.50		1.0
Lead(Pb)	1000	0.50		1.0
Selenium(Se)	1000	5.0		10
Antimony(Sb)	1000	0.50		1.0
Thallium(Tl)	1000	5.0		10

Calibration STANDARD 3

Element	Conc. of Stock Std	mL of Stock Std	Final Volume (mL)	Conc. of Cal Std (mg/L)
Beryllium(Be)	1000	0.50	500	1.0
Barium(Ba)	1000	5.0		10
Cadmium(Cd)	1000	0.50		1.0
Cobalt(Co)	1000	0.50		1.0
Chromium(Cr)	1000	5.0		10
Copper(Cu)	1000	5.0		10
Manganese(Mn)	1000	5.0		10
Nickel(Ni)	1000	2.5		5.0
Zinc(Zn)	1000	2.5		5.0

Calibration STANDARD 4

Element	Conc. of Stock Std	mL of Stock Std	Final Volume (mL)	Conc. of Cal Std (mg/L)
Aluminum(Al)	10000	0.50	500	10
Iron(Fe)	10000	0.50		10
Boron(B)	1000	5.0		10
Strontium(Sr)	1000	5.0		10
Titanium (Ti)	1000	5.0		10

Calibration STANDARD 5

Element	Conc. of Stock Std	mL of Stock Std	Final Volume (mL)	Conc. of Cal Std (mg/L)
Calcium(Ca)	10000	0.50	500	10
Potassium(K)	10000	1.0		20
Magnesium(Mg)	10000	0.50		10
Sodium(Na)	10000	0.50		10
Tin(Sn)	1000	5.0		10
Vanadium(V)	1000	5.0		10

MULTI-POINT INSTRUMENT CALIBRATION-200.7

For all drinking water samples (EPA 200.7) the ICP must be calibrated with a minimum of three standards and a blank. The following standards may be used for this purpose. With the Thermo Jarrell Ash software the Calibration Analysis and Curve-fit programs must be used to be successful with the multi-point calibration of the ICP instruments.

High Standard.

Element	Conc. of Stock Std	mL of Stock Std	Final Volume (mL)	Conc. of Cal Std (mg/L)
Aluminum (Al)	10000	1.0	1000	10
Antimony (Sb)	1000	1.0		1.0
Arsenic (As)	1000	1.0		1.0
Boron (B)	1000	10		10
Barium (Ba)	1000	10		10
Beryllium (Be)	1000	1.0		1.0
Cadmium (Cd)	1000	1.0		1.0
Calcium (Ca)	10000	1.0		10
Cobalt (Co)	1000	1.0		1.0
Chromium (Cr)	1000	10		10
Copper (Cu)	1000	10		10
Iron (Fe)	10000	1.0		10
Lead (Pb)	1000	1.0		10
Magnesium (Mg)	10000	1.0		10
Manganese (Mn)	1000	10		10
Molybdenum Mo)	1000	1.0		1.0
Nickel (Ni)	1000	5.0		5.0
Potassium (K)	10000	1.0		10
Selenium (Se)	1000	10		10
Silver (Ag)	1000	1.0		1.0
Sodium (Na)	10000	1.0		10
Strontium (Sr)	1000	10		10
Thallium (Tl)	1000	10		10
Tin (Sn)	1000	10		10
Titanium (Ti)	1000	10		10
Vanadium (V)	1000	10		10
Zinc (Zn)	1000	5.0		5.0

Mid-Level Standard- Prepare as the CCV is prepared.

Low-Level Standard- Prepare as the RL/PQL Check Standard.

Initial Calibration Verification (ICV) Solution

Element/Stock	Conc. of Stock Std	mL of Stock Std	Final Volume (mL)	Conc. of CCV Std (mg/L)
SPEX QC19	(1)	5.0	500	(2)
SPEX QC 7	(1)	5.0		(2)
Tin(Sn)	1000	0.50		1.0
Strontium (Sr)	1000	0.50		1.0
Potassium (K)	10000	0.50		10(3)
Sodium (Na)	10000	0.45		10(3)

(1) SPEX QC19 and SPEX QC7 are solutions containing multiple elements. The concentrations are given on the certificate of analysis.
(2) The final concentrations of the various elements are the same as listed in Table 1. The SPEC QC solutions are diluted by a factor of 100 from the concentration listed on the certificate of analysis.
(3) These concentrations include the contribution from SPEX Solutions QC-7

Continuing Calibration Verification (CCV) Standard

(also used as midpoint of multi-point calibration for EPA 200.7)

Element	Conc. of Stock Std	mL of Stock Std	Final Volume (mL)	Conc. of CCV Std (mg/L)
Aluminum (Al)	10000	0.50	1000	5.0
Antimony (Sb)	1000	0.50		0.50
Arsenic (As)	1000	0.50		050
Boron (B)	1000	5.0		5.0
Barium (Ba)	1000	5.0		5.0
Beryllium (Be)	1000	0.50		0.50
Cadmium (Cd)	1000	0.50		0.50
Calcium (Ca)	10000	0.50		5.0
Cobalt (Co)	1000	0.50		0.50
Chromium (Cr)	1000	5.0		5.0
Copper (Cu)	1000	5.0		5.0
Iron (Fe)	10000	0.50		5.0
Lead (Pb)	1000	0.50		0.50
Magnesium (Mg)	10000	0.50		5.0
Manganese (Mn)	1000	5.0		5.0
Molybdenum (Mo)	1000	0.50		0.50
Nickel (Ni)	1000	2.5		2.5
Potassium (K)	10000	0.50		5.0
Selenium (Se)	1000	5.0		5.0
Silver (Ag)	1000	0.50		0.50
Sodium (Na)	10000	0.50		5.0
Strontium (Sr)	1000	5.0		5.0
Thallium (Tl)	1000	5.0		5.0
Tin (Sn)	1000	5.0		5.0
Titanium (Ti)	1000	5.0		5.0
Vanadium (V)	1000	5.0		5.0
Zinc (Zn)	1000	2.5		2.5

Reporting Limit (RL) Check Standard

(also used as low point in multi-point calibrations; e.g. EPA 200.7)

Preparation of RL/PQL Stock A-ICP

Element	Conc. of Stock Std	mL of Stock Std	Final Volume (mL)	Conc. Of Stock Std (mg/L)
Silver (Ag)	1000	0.10	100	1.0
Arsenic (As)	1000	0.10		1.0
Cadmium (Cd)	1000	0.050		0.50
Copper (Cu)	1000	0.20		2.0
Nickel (Ni)	1000	0.40		4.0
Lead (Pb)	1000	0.050		0.50
Selenium (Se)	1000	0.10		1.0
Thallium (Tl)	1000	0.10		1.0

Preparation of RL/PQL Stock B-ICP

Element	Conc. of Stock Std	mL of Stock Std	Final Volume (mL)	Conc. Of Stock Std (mg/L)
Aluminum (Al)	10000	0.20	100	20
Boron (B)	1000	0.50		5.0
Barium (Ba)	1000	0.10		1.0
Beryllium (Be)	1000	0.040		0.40
Calcium (Ca)	10000	0.50		50
Cobalt (Co)	1000	0.10		1.0
Chromium (Cr)	1000	0.10		1.0
Iron (Fe)	10000	0.050		5.0
Magnesium (Mg)	10000	0.50		50
Manganese (Mn)	1000	0.10		1.0
Molybdenum Mo)	1000	0.10		1.0
Sodium (Na)	10000	0.50		50
Antimony (Sb)	1000	0.20		2.0
Strontium (Sr)	1000	0.10		1.0
Tin (Sn)	1000	0.50		5.0
Titanium (Ti)	1000	0.10		1.0
Vanadium (V)	1000	0.10		1.0
Zinc (Zn)	1000	0.20		2.0

Preparation of RL/PQL Stock C-ICP

Element	Conc. of Stock Std	mL of Stock Std	Final Volume of Cal Std	Conc. Of Stock Std
Potassium(K)	10000	1.0	100	100

Preparation of the RL/PQL Check Solution-ICP

RL/PQL Stock	mL of RL/PQL Stock	Final Volume(mL)
Stock A-ICP	5.0	500
Stock B-ICP	5.0	
Stock C-ICP	5.0	

ICP Interference Check Solutions

Preparation of ICP Interference Check Solution A

Element	Conc. Of Stock(mg/L)	mL of Stock Std	Final Volume(mL)	Conc. (mg/L)
Aluminum (Al)	10000	25	500	500
Calcium (Ca)	10000	25		500
Magnesium (Mg)	10000	25		500
Iron (Fe)	10000	10		200

Preparation of ICP Interference Check Solution AB

Element	Conc. of Stock(mg/L)	mL of Stock	Final Volume (mL)	Conc. of Std (mg/L)
Aluminum (Al)	10000	25	500	500
Calcium (Ca)	10000	25		500
Magnesium (Mg)	10000	25		500
Iron (Fe)	10000	10		200
Silver (Ag)	1000	0.10		0.20
Arsenic (As)	1000	0.050		0.10
Barium (Ba)	1000	0.25		0.50
Beryllium (Be)	1000	0.25		0.50
Cadmium (Cd)	1000	0.50		1.0
Cobalt (Co)	1000	0.25		0.50
Chromium (Cr)	1000	0.25		0.50
Copper (Cu)	1000	0.25		0.50
Manganese (Mn)	1000	0.25		0.50
Nickel (Ni)	1000	0.50		1.0
Lead (Pb)	1000	0.025		0.050
Antimony (Sb)	1000	0.30		0.60
Selenium (Se)	1000	0.025		0.050
Thallium (Tl)	1000	0.050		0.10
Vanadium (V)	1000	0.25		0.50
Zinc (Zn)	1000	0.50		1.0
Molybdenum (Mo)	1000	0.50		1.0
Tin (Sn)	1000	0.50		1.0

ICP Matrix Spiking Solutions

ICP Matrix Spiking Solution 1 is a solution purchased from SPEX. The certificate of analysis will list the concentrations of the analytes. Store this solution at room temperature. Prepare this solution every six months or sooner if needed or required.

Preparation of the ICP Matrix Spiking Solution 2

Element	Conc. of Stock (mg/L)	mL of Stock	Final Volume (mL)	Conc. of Std. (mg/L)
Boron (B)	1000	10	100	100
Calcium (Ca)	10000	5.0		500
Magnesium (Mg)	10000	5.0		500
Molybdenum (Mo)	1000	5.0		50
Potassium (K)	10000	5.0		500
Sodium (Na)	10000	5.0		500
Strontium (Sr)	1000	5.0		50
Tin (Sn)	1000	10		100
Titanium (Ti)	1000	10		100

IDL/MDL Solution

The IDL/MDL solution is used in this procedure for two purposes:

1) To determine the Instrument Detection Limit (IDL) of each target compound on a quarterly basis (SOP CA91); and
2) To determine the Method Detection Limit (MDL) of each target compound on an annual basis (SOP CA90). MDLs should be digested straight and at 1:2 dilutions.

Preparation of IDL/MDL Stock A

Element	Conc. of Stock (mg/L)	mL of Stock	Final Volume (mL)	Conc. of Std. (mg/L)
Silver (Ag)	1000	0.040	100	0.40
Arsenic (As)	1000	0.20		2.0
Barium (Ba)	1000	0.020		0.20
Beryllium (Be)	100	0.050		0.050
Cadmium (Cd)	1000	0.040		0.40
Lead (Pb)	1000	0.10		1.0
Antimony (Sb)	1000	0.20		2.0
Selenium (Se)	1000	0.20		2.0
Thallium (Tl)	1000	0.20		2.0

Preparation of IDL/MDL Stock B

Element	Conc. Of Stock (mg/L)	mL of Stock	Final Volume (mL)	Conc. Of Std. (mg/L)
Cobalt (Co)	1000	0.030	100	0.30
Chromium (Cr)	1000	0.10		1.0
Copper (Cu)	1000	0.10		1.0
Manganese (Mn)	1000	0.020		0.20
Molybdenum (Mo)	1000	0.040		0.40
Nickel (Ni)	1000	0.10		1.0
Tin (Sn)	1000	0.20		2.0
Vanadium (V)	1000	0.060		0.60
Zinc (Zn)	1000	0.10		1.0

Preparation of IDL/MDL Stock C

Element	Conc. of Stock (mg/L)	mL of Stock	Final Volume (mL)	Conc. of Std. (mg/L)
Aluminum (Al)	10000	0.10	100	10
Calcium (Ca)	10000	0.10		10
Iron (Fe)	10000	0.10		10
Magnesium (Mg)	10000	0.10		10
Potassium (K)	10000	0.20		20
Sodium (Na)	10000	0.040		4.0

IDL/MDL Solution

Preparation of IDL/MDL Stock D

Element	Conc. Of Stock (mg/L)	mL of Stock	Final Volume (mL)	Conc. of Std. (mg/L)
Boron(B)	1000	0.40	100	4.0
Strontium (Sr)	1000	0.040		0.40
Titanium (Ti)	1000	0.050		0.50
Sodium (Na)	10000	2.0		200

Preparation of the IDL/MDL Check Solution

IDL/MDL Stock	mL of RL/PQL Stock	Final Volume(mL)
Stock A	5.0	1000
Stock B	5.0	
Stock C	5.0	
Stock D	5.0	

The IDL/MDL Check Solution contains the following elements at the given concentrations:

Element	Concentration(mg/L)
Be	0.00025
Ba, Mn	0.0010
Co	0.0015
Ag, Cd, Mo, Sr	0.0020
Ti	0.0025
V	0.0030
Cr, Cu, Ni, Pb, Zn	0.0050
As, Sb, Se, Sn, Tl	0.010
Na(1), B	0.020
Ca, Fe, Mg	0.050
Al, K	0.10
Na	1.0

(1) If the wavelength for sodium is 588.995, the lower concentration (0.020mg/L) is used for the IDL./MDL check solution. In this case, only stocks A,B, and C are used to make the IDL/MDL Check Solution. IDL/MDL Check Solutions for B, Sr, and Ti are prepared and evaluated separately.

SEVERN TRENT SERVICES

CHANGE -IN-PROGRESS ATTACHMENT

SOP Document No: ME70:0307.01:7

SOP Description: Elements by ICP (6010 and 200.7)

Approval Signature: R. Wayne Robbins 6 Sept 2001
Date
Title: Technical Manager, QA
STL X Savannah __ Tallahassee __ Mobile __ Tampa West

The following revisions or additions have been made to the referenced SOP.

The following attachments are for a specific project and will be effective from the date of approval until the date that the project is completed. The purpose of this CIPA is to document changes or additions to the standard operating procedures requested for the Sauget Area 2 Sites Group and EPA Region V.

The attachments are tables of the project RLs and MDLs, including the QC limits, and an excerpt from the Sauget Area 2 Sites Group QAPP.

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Target Analytes by ICP (SW846 6010) Aqueous

PARAMETER	METHOD	ACC (%REC)	PREC (%RPD)	MDL (mg/L)	RL (mg/L)
Aluminum	6010	75-125	<=20	0.0076	0.2
Antimony	6010	75-125	<=20	0.0043	0.02
Arsenic	6010	75-125	<=20	0.003	0.01
Barium	6010	75-125	<=20	0.00034	0.01
Beryllium	6010	75-125	<=20	0.00019	0.004
Cadmium	6010	75-125	<=20	0.00056	0.005
Calcium	6010	75-125	<=20	0.0086	0.5
Chromium	6010	75-125	<=20	0.0029	0.01
Cobalt	6010	75-125	<=20	0.00074	0.01
Copper	6010	75-125	<=20	0.00079	0.02
Iron	6010	75-125	<=20	0.021	0.05
Lead	6010	75-125	<=20	0.0026	0.005
Magnesium	6010	75-125	<=20	0.0064	0.5
Manganese	6010	75-125	<=20	0.00062	0.01
Nickel	6010	75-125	<=20	0.0041	0.04
Potassium	6010	75-125	<=20	0.023	1
Selenium	6010	75-125	<=20	0.0045	0.01
Silver	6010	75-125	<=20	0.0007	0.01
Sodium	6010	75-125	<=20	0.26	0.5
Thallium	6010	75-125	<=20	0.0036	0.01
Vanadium	6010	75-125	<=20	0.001	0.01
Zinc	6010	75-125	<=20	0.0032	0.02

Target Analytes by ICP (SW846 6010) Soils and Solids

PARAMETER	METHOD	ACC (%REC)	PREC (%RPD)	MDL (mg/kg)	RL (mg/kg)
Aluminum (ICP)	6010	75-125	<=20	1	20
Antimony (ICP)	6010	75-125	<=20	0.45	2
Arsenic (ICP)	6010	75-125	<=20	0.34	1
Barium (ICP)	6010	75-125	<=20	0.04	1
Beryllium (ICP)	6010	75-125	<=20	0.015	0.4
Cadmium (ICP)	6010	75-125	<=20	0.037	0.5
Calcium (ICP)	6010	75-125	<=20	1.8	50
Chromium (ICP)	6010	75-125	<=20	0.077	1
Cobalt (ICP)	6010	75-125	<=20	0.055	1
Copper (ICP)	6010	75-125	<=20	0.15	2
Iron (ICP)	6010	75-125	<=20	2.5	5
Lead (ICP)	6010	75-125	<=20	0.21	0.5
Magnesium (ICP)	6010	75-125	<=20	0.68	50
Manganese (ICP)	6010	75-125	<=20	0.11	1
Nickel (ICP)	6010	75-125	<=20	0.18	4
Potassium (ICP)	6010	75-125	<=20	1.3	100
Selenium (ICP)	6010	75-125	<=20	0.53	1
Silver (ICP)	6010	75-125	<=20	0.091	1
Sodium (ICP)	6010	75-125	<=20	16	50
Thallium (ICP)	6010	75-125	<=20	0.52	1
Vanadium (ICP)	6010	75-125	<=20	0.096	1
Zinc (ICP)	6010	75-125	<=20	1.4	2

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Table 7E. *Metals SW-846 Method 6010B, Zinc SW-846 Method 7951, Copper SW-846 Method 7211, Mercury SW-846 Method 7470A, 7471A, and Cyanide SW-846 Method 9010B/9012A Quality Control Requirements and Corrective Actions.*

Audit	Frequency	Control Limits	Corrective Action
Holding Times	Samples must be digested and analyzed within holding time.	Metals: Analyze 180 days from collection. Mercury: Analyze 28 days from collection. Cyanide: Analyze 14 days from collection.	If holding times are exceeded for initial or any re-analyses required due to QC excursions, notify the QAO immediately since re-sampling may be required.
Calibration Verification (ICV, CCV)	Two point calibration for ICP. Five point calibration for remaining methods. Calibrate according to method and each time instrument is set up; verify at more frequent of 10% or each 2 hours. Also verify at the end of each run. Analyze highest mix standard before sample analysis (ICP only). Standard at or below the PQL should be analyzed after initial calibration. Mercury standard should be less than or equal to 5 times the PQL.	90% to 110% of expected value for ICP AA, colorimeter, and spectrophotometer. 80% to120% of expected true value for Mercury. Highest standard mix ±5% of true value for ICP. Correlation coefficient for first or second order curve must be ≥0.995.	1. Re-analyze. 2. If criteria are still not met, identify and correct problem, recalibrate. 3. Document corrective action – samples cannot be analyzed until calibration control limit criteria have been met.
Calibration Blank	At the beginning and end of run and at a rate of 10% during run.	Less than PQL.	1. Identify and correct problem. 2. If criteria are still not met, recalibrate. 3. Document corrective action – samples cannot be analyzed until calibration control limit criteria have been met.

Audit	Frequency	Control Limits	Corrective Action
Preparation Blank Analysis	1 per batch of samples digested, or 1 in 20, whichever is greater.	Less than PQL.	1. Re-analyze blank. 2. If limits are still exceeded, clean instrument and recalibrate. 3. Document corrective action – samples cannot be analyzed until calibration control limit criteria have been met.

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EPA RESPONSE

ATTACHMENT I

DIGESTION PROCEDURES FOR ICP: TOTAL METALS AND TOTAL RECOVERABLE METALS IN LIQUID SAMPLES

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Approved by:

R. Wayne Robbins — 21 March 2001
Date

Title: Technical Manager, QA

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1.0 SCOPE AND APPLICATION

The purpose of this SOP is to describe the procedures used to digest water, drinking water, wastewater, and leachate samples prior to the analysis by ICP (SOP ME70).

2.0 SUMMARY OF METHOD AQND DEFINITIONS

2.1 Total metals and TCLP leachates: A known volume, usually 50mL, of sample is transferred to a digestion vessel. The sample is refluxed with nitric acid at approximately 95C. After sample has digested, as evidenced by a clear, pale yellow color, HCl is added and the sample is brought up to the original volume with reagent water.

2.2 Total recoverable metals: A known volume, usually 50mL, of sample is transferred to a digestion vessel. The sample is refluxed with dilute nitric acid and hydrochloric acid at approximately 95C. After sample has evaporated to approximately 10-20mL, the sample is brought up to the original volume with reagent water.

2.3 Drinking water samples with a turbidity concentration of less than 1 NTU can be analyzed with no digestion if the required quantitation limits can be achieved with no sample preconcentration. The exception to this rule is silver, which requires sample digestion prior to analysis.

2.4 Samples filtered for the determination of dissolved metals do not require digestion if the sample

1) has a low COD(<20mg/L);
2) has a turbidity <1 NTU ;
3) is colorless with no significant odor ; and
4) is of one liquid phase and free of suspended particulates or precipitates after acidification

(40 CFR Part 136 Table 1B-note 4)

2.5 Definitions

Digestate - the digested sample
ICP - inductively coupled (argon) plasma
HCl –hydrochloric acid
HNO3 – nitric acid
LQM – laboratory quality manual

2.6 The SOP is based on the guidance in SW-846 Methods 3005A and 3010A and EPA Method 200.7. Note that EPA has promulgated two procedures as EPA 200.7-one for drinking water and one for NPDES. The digestion procedures for both 200.7 methods are performed in the same manner as 3005A for total recoverable metals and 3010A for total metals.

3.0 SAFETY

3.1 Use good common sense when working in the lab. Do not perform any procedures that you do not understand or that will put you or others in potentially dangerous situations.

3.2 The samples are digested in strong acid solutions and contain acid concentrations of 10-20% by volume. The analyst must wear protective clothing such as a lab coat or apron. The acids used in this procedure will destroy unprotected clothing. The analyst must wear proper eye protection such as lab glasses or face shield. Acid can be splashed into the eyes from many sources. Gloves must be worn to protect hands from acid burns.

3.3 The acid digestion procedures must be performed under a properly functioning fume hood. The acid fumes from the digestion can cause mild to severe respiratory problems if breathed.

3.4 Each digestion lab must have acid spill kits. These kits must be located in a highly accessible area of the lab. Each digestion lab must be equipped with a properly working shower.

3.5 The standards and reagents used to prepare the standards in this method should be treated as potential hazards. Lab coats, gloves, and other protective equipment should be used when preparing and using the standards and reagents.

3.6 Each analyst should be familiar with the Material Safety Data Sheets (MSDS) for each reagent and standard used in this procedure. These sheets denote the type of hazard that each reagent poses and the safe handling instructions for these compounds.

3.7 Care must be taken when handling the digestion beakers. Before handling a vessel that has been in use, check the temperature to make sure that it is not hot. Make sure that the digestion vessels are placed on a stable platform during and after the digestion. Vibrations from the hood or an unstable platform can cause the beakers to move and possibly to fall and splatter an analyst with a hot acid solution. Hot acids can cause severe skin burns and destroy unprotected clothing.

4.0 INTERFERENCES

Contamination of the sample can occur when the preparation glassware and/or reagents contain the target elements. Reagent blanks (method blanks) must be analyzed as a check on contamination due to the sample digestion.

5.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

MATRIX	ROUTINE CONTAINER	PRESERVATIVE	STORAGE/HOLD TIME
Aqueous (water) and TCLP leachates	500-mL plastic	HNO3 to pH <2	Ambient

Samples for dissolved metals should be filtered in the field before acid is added to the sample. If the sample is to be filtered in the lab, no preservative is added to the sample until the sample is filtered.

The pH of all preserved samples must be checked and documented upon arrival in the lab. If the pH is not within the proper range, additional acid is added to the sample to bring the pH below 2.

- Place a piece of pH paper (wide range or narrow range can be used) on a watch glass or other inert surface.

- Transfer a few drops of the sample to the pH paper and note the color change. If the pH <2, record this in the log and transfer the sample to the storage area.

- If the pH is greater than 2, contact the Project Manager using an anomaly form (SOP 85) to get approval to adjust the pH. If the Project Manager approves the pH adjustment, move the sample under a hood. Add 1:1 nitric acid to the sample in 1mL aliquots, checking the sample pH after each addition, until the pH <2. The volume of 1:1 nitric acid added to the sample should not exceed 1% of the total volume of the sample. For a 500-mL sample, the maximum volume of 1:1 nitric is 5mL. If more acid is required, contact the supervisor for further guidance.

NOTE: Samples that are not at pH <2 upon arrival in the lab may contain cyanide or sulfide or may be highly buffered. Working under a hood minimizes the hazard that may be caused by the evolution of hydrogen cyanide or hydrogen sulfide upon acidification of the sample. Be aware that acid/base neutralization reaction may be violent and evolve a good deal of heat.

6.0 APPARATUS AND MATERIALS

6.1 Hot plate or digestion block-capable of maintaining a sample temperature of 95C+/-5C. The temperature of the hot plate or digestion block must be monitored and recorded each day samples are digested. The temperature is measured in a beaker or digestion vessel containing reagent water.

NOTE: The use of hot plates is listed in the preparation steps but a digestion block may be used if the same general procedures are employed. The hot plate or digestion block settings must be recorded in the maintenance log or other suitable log.

6.2 Digestion vessels: Teflon or Pyrex beakers, 150-mL and 250mL, or comparable digestion vessels (250-mL beakers are listed in the preparation steps but smaller digestion block vessels can be substituted)

6.3 Watch glasses, "ribbed", to fit over digestion vessels (not required for block digestion vessels)

6.4 Volumetric flasks- 100-mL or appropriate volume

6.5 Graduated cylinders-50mL

6.6 Pipettes

7.0 REAGENTS

Reagents must be tracked in accordance with SOP AN44: *Reagent Traceability*.

7.1 Reagent water-lab generated deionized water. ASTM Type I or Type II. The conductivity must be checked daily in accordance with SOP AN35: *Conductivity Checks for Laboratory Deionized Water*.

7.2 Nitric acid (HNO_3)-reagent grade.

7.3 Hydrochloric acid (HCl)-reagent grade.

8.0 STANDARDS

The preparation of the spiking solutions must be tracked in accordance with SOP AN41: *Standard Material Traceability*. General guidance on the preparation of standards is given in SOP AN43: *Standard Preparation*. The expiration date of the spiking solutions is 180 days from the date of preparation or the expiration date of the stock(s) used to prepare the spiking solution (if expiration date of the stock is less than 180 days).

The lab should purchase certified solutions from STL-approved vendors, if available. The lab should prepare standards from neat materials only if a certified solution is not available. See SOP AN43 for guidance for standard preparation.

8.1 Determine the volume of standard to be prepared and the volume of the stock standard needed to make the spiking solutions. The following equation can be used:

$$Vi = \frac{Cf \otimes Vf}{Ci}$$

where
Vi = volume of stock standard needed to prepare the spiking solution (mL)
Ci = concentration of stock solution (ug/mL)
Cf = concentration of spiking solution to prepare (ug/mL)
Vf = volume of spiking solution to prepare (mL)

The concentration can be expressed in whatever terms the analyst finds most convenient - ug/L, ug/mL, mg/L, etc. The units must be the same for *Ci* and *Cf*.

8.2 Preparation of the ICP Matrix Spiking Solutions

8.2.1 ICP Matrix Spiking Solution 1 is a solution purchased from SPEX (catalogue number SPIKE-1). The concentrations of the analytes in this solution are listed on the accompanying certificate of analysis. Store this solution at room temperature. Replace this solution every six months or sooner if needed or required.

8.2.2 Preparation of the ICP Matrix Spiking Solution 2

Element	*Ci(mg/L)*	*Vi(mL)*	*Vf(mL)*	*Cf(mg/L)*
Boron (B)	1000	10	100	100
Calcium (Ca)	10000	5.0		500
Magnesium (Mg)	10000	5.0		500
Molybdenum (Mo)	1000	5.0		50
Potassium (K)	10000	5.0		500
Sodium (Na)	10000	5.0		500
Strontium (Sr)	1000	5.0		50
Tin (Sn)	1000	10		100
Titanium (Ti)	1000	10		100

- Add 1mL of nitric acid and 5mL of hydrochloric acid to a 100mL volumetric flask containing about 50mL of reagent water.
- Add the appropriate volume of each element stock standard to the flask, dilute to volume with reagent water, and mix thoroughly.
- Transfer the spiking solution to a labeled storage container.
- Prepare this solution every 180 days or sooner as needed or required

8.3 Preparation of the ICP TCLP Matrix Spiking Solutions

8.3.1 ICP TCLP Spiking Solution I

Element	*Ci(mg/L)*	*Vi(mL)*	*Vf(mL)*	*Cf(mg/L)*
Arsenic (As)	1000	5.0	100	50
Barium (Ba)	1000	5.0		50
Cadmium (Cd)	1000	1.0		10
Chromium (Cr)	1000	5.0		50
Lead (Pb)	1000	5.0		50
Selenium (Se)	1000	1.0		10

- Add 1mL of nitric acid and 5mL of hydrochloric acid to a 100mL volumetric flask containing about 50mL of reagent water.
- Add the appropriate volume of each element stock standard to the flask, dilute to volume with reagent water, and mix thoroughly.
- Transfer the spiking solution to a labeled storage container.
- Prepare this solution every 180 days or sooner as needed or required

8.3.2 ICP TCLP Spiking Solution II

Element	*Ci(mg/L*	*Vi(mL)*	*Vf(mL)*	*Cf(mg/L)*
Silver (Ag)	1000	5.0	100	50

- Add 1mL of nitric acid and 5mL of hydrochloric acid to a 100mL volumetric flask containing about 50mL of reagent water.
- Add the appropriate volume of each element stock standard to the flask, dilute to volume with reagent water, and mix thoroughly.
- Transfer the spiking solution to a labeled storage container.
- Prepare this solution every 180 days or sooner as needed or required

9.0 SAMPLE PREPARATION

Unless otherwise requested, groundwater and surface waters will be prepared using the total recoverable metals procedure given in Section 9.1. TCLP samples must be digested for total metals (Section 9.3). Note that there are different spiking solutions for routine and TCLP samples.

Drinking water samples with a turbidity concentration of less than 1 NTU can be analyzed with no digestion if the required quantitation limits can be achieved with no sample preconcentration. The exception to this rule is silver, which requires sample digestion prior to analysis. The turbidity of drinking water samples can be checked using the procedures in SOP BA80: *Turbidity*. If the turbidity of the sample is not checked, the digestion procedure must be performed. If silver must be determined in a drinking water sample, the sample must be digested.

Samples filtered for the determination of dissolved metals do not require digestion if the sample
- has a low COD(<20mg/L);
- has a turbidity <1 NTU ;
- is colorless with no significant odor ; and
- is of one liquid phase and free of suspended particulates or precipitates after acidification

(40 CFR Part 136 Table 1B-note 4)

9.1 Total Recoverable Metals: Aqueous Samples

This digestion procedure is used for the preparation of aqueous samples for total recoverable metal determination by ICP (or flame AA). This digestion procedure is not suitable for most analytes that will be determined by graphite furnace atomic absorption (GFAA) because hydrochloric acid (HCl) can cause interferences during furnace atomization. The exception is antimony by GFAA, which must be digested using the procedures in this section.

9.1.1 Transfer a 50mL aliquot (or an appropriate volume diluted to 50mL with reagent water) of a well-mixed sample to a clean 250-mL Teflon beaker or other suitable digestion vessel.

NOTE: If there is not sufficient volume to use a 50mL aliquot, the lab can use a smaller volume of sample, proportional volumes of reagents, and adjust the final digestate volume back to the original volume of the sample used. For example, if 25mL of sample is digested, one half of the routine volumes of reagent are used and the final volume of the digestate is brought back to 25mL. When a smaller aliquot is used, the digestion analyst must be careful not to allow the sample digest to evaporate completely.

9.1.2 Add 50mL of reagent water to a beaker that has been designated as the method blank. This QC sample is taken through all digestion and sample preparation steps to monitor for contamination that may be due to glassware, reagents, or sample handling.

9.1.3 Add 0.50mL of the appropriate spiking solutions to a 50mL aliquot of reagent water designated as the laboratory control spike (LCS). If a duplicate laboratory control spike (LCSD) is required, spike a second 50mL aliquot of reagent water with 0.50mL of the appropriate spiking solutions.

Analytical Method	Matrix	QC	Spiking Solutions
6010	Liquids (aqueous)	LCS/MS	(Spex) ICP Spike I ICP Spike II

9.1.4 Add 0.50mL of the appropriate spiking solutions to each of two 50mL aliquots of the client sample designated as the matrix spikes sample(MS and MSD).

9.1.5 Record the following information on the digestion log:

- date
- analyst's initials
- beaker ID#
- sample identification
- the volume of sample digested
- batch identification
- fume hood #
- temperature of the digestion block (daily)
- the lot number of the acids used for the digestion
- the lot number of the ICP spiking solutions
- the time that the digestion was started
- the SOP/method number

NOTE: A DIGESTION BATCH CONSISTS OF TWENTY FIELD SAMPLES AND THE ASSOCIATED QC ITEMS. THE BATCH IS NOT TO EXCEED 20 FIELD SAMPLES. EVERY DIGESTION BATCH WILL HAVE A METHOD BLANK, A LABORATORY CONTROL SAMPLE (LCS), A MATRIX SPIKE AND A MATRIX SPIKE DUPLICATE (IF THERE IS SUFFICIENT SAMPLE FOR THE MS/MSD). IF THERE IS NOT SUFFICIENT SAMPLE FOR MS/MSD, THE LCS IS PREPARED IN DUPLICATE (LCSD).

9.1.6 Add 2.5mL of concentrated HCl and 1.0mL of concentrated HNO_3 to each sample. Cover each beaker with a watch glass (a watch glass is not required for the digestion block). Gently heat the beaker until the sample refluxes-the sample is not heated to boiling; that is, bubbles are not formed in the liquid in the bottom of the beaker. The sample/acid solution is refluxing when the liquid evaporates and drops of liquid condense on the watch glass and the sides of the beaker and fall back into the beaker. Evaporate the sample until the volume is approximately 15mL. Do not allow any portion of the vessel bottom to become dry at any time during the digestion.

NOTE: If a volume of sample smaller than 50mL is digested, the amount of acid should be reduced proportionately.

9.1.7 Wash down the inside of the beaker and the watchglass with reagent water. Dilute the sample digestate to 50mL with reagent water.

NOTE: The digestate may be diluted to a volume less than the original volume if sample concentration is required to meet lower reporting limits. The pre-concentration must be limited to a factor of four(4).

9.1.8 Record the analyst's initials, the final volume of the sample digestate, and the date and time that the digestion was completed in the digestion logbook. The sample is now ready for analysis by ICP.

9.2 Total Metals: Aqueous Samples

This digestion procedure is used for the preparation of aqueous samples for total metal determination by ICP (or flame AA). This digestion procedure is not suitable for samples that will be analyzed by graphite furnace atomic absorption (GFAA) because hydrochloric acid (HCl) can cause interferences during furnace atomization.

9.2.1 Transfer a 50-mL aliquot (or an appropriate volume diluted to 50-mL with reagent water) of a well-mixed sample to a clean 250-mL Teflon beaker or other suitable digestion vessel.

NOTE: If there is not sufficient volume to use a 50mL aliquot, the lab can use a smaller volume of sample, proportional volumes of reagents, and adjust the final digestate volume back to the original volume of the sample used. For example, if 25mL of sample is digested, one half of the routine volumes of reagent are used and the final volume of the digestate is brought back to 25mL. When a smaller aliquot is used, the digestion analyst must be careful not to allow the sample digest to evaporate completely.

9.2.2 Add 50mL of reagent water to a beaker that has been designated as the method blank. This QC sample is taken through all digestion and sample preparation steps to monitor for contamination that may be due to glassware, reagents, or sample handling.

9.2.3 Add 0.50mL of the appropriate spiking solutions to a 50-mL aliquot of reagent water designated as the laboratory control spikes(LCS). If a duplicate laboratory control spike (LCSD) is required, spike a second 50mL aliquot of reagent water with 0.50mL of the appropriate spiking solutions.

Analytical Method	Matrix	QC	Spiking Solutions
6010	Liquids (aqueous)	LCS/MS	(Spex) ICP Spike I ICP Spike II

9.2.4 Add 0.50mL of the appropriate spiking solutions to two 50mL aliquots of the client sample designated as the matrix spikes samples(MS and MSD).

Record the following information on the digestion log:

- date
- analyst's initials
- beaker ID#
- sample identification
- the volume of sample digested
- batch identification
- fume hood #
- temperature of the hot plate or digestion block (daily)
- the lot number of the acids used for the digestion
- the lot number of the ICP spiking solutions
- the time that the digestion was started
- the SOP/method number

NOTE:A DIGESTION BATCH CONSISTS OF TWENTY FIELD SAMPLES AND THE ASSOCIATED QC ITEMS. THE BATCH IS NOT TO EXCEED 20 FIELD SAMPLES. EVERY DIGESTION BATCH WILL HAVE A METHOD BLANK, A LABORATORY CONTROL SAMPLE (LCS), A MATRIX SPIKE AND A MATRIX SPIKE DUPLICATE (IF THERE IS SUFFICIENT SAMPLE FOR THE MS/MSD). IF THERE IS NOT SUFFICIENT SAMPLE FOR MS/MSD, THE LCS IS PREPARED IN DUPLICATE (LCSD).

9.2.5 Add 1.5mL of concentrated HNO_3 to each sample. Cover each beaker with a watch glass (a watch glass is not required for the digestion block). Gently heat the beaker until the sample refluxes-the sample is not heated to boiling; that is, bubbles are not formed in the liquid in the bottom of the beaker. The sample/acid solution is refluxing when the liquid evaporates and drops of liquid condense on the watch glass and the sides of the beaker and fall back into the beaker. Evaporate the sample until the volume is approximately 5-10mL. Do not allow any portion of the vessel bottom to become dry at any time during the digestion.

NOTE: If a volume of sample smaller than 50mL is digested, the amount of acid should be reduced proportionately.

9.2.6 Remove the beakers from the hot plate and cool the beakers to room temperature. Add another 1.5mL portion of concentrated HNO_3. Replace the watchglass and continue heating the sample on the hot plate. Again, at the proper temperature, the sample should gently reflux in the beaker-do not allow the sample to boil.

9.2.7 Continue heating the sample and adding additional 1.5mL portions of concentrated HNO_3 until the digestate is light in color or does not change in appearance after subsequent additions of HNO_3. If a sample requires more than 6mL of acid to digest, contact the digestion lab supervisor for guidance.

9.2.8 Evaporate the digestate (covered with the watch glass) until the volume is approximately 5-10mL.

9.2.9 Remove the watch glass and add a 2.5mL of concentrated HCl. Replace the watchglass on the beaker and warm the sample digestate for 15 minutes.

9.2.10 Wash down the inside of the beaker and the watchglass with reagent water. Dilute the sample digestate to 50mL with reagent water.

NOTE: The digestate may be diluted to a volume less than the original volume if sample concentration is required to meet lower reporting limits. The pre-concentration should be limited to a factor of four (4).

9.2.11 Record the analyst's initials, the final volume of the sample digestate, and the date and time that the digestion was completed in the digestion logbook. The sample is now ready for analysis by ICP.

9.3 Total Metals: TCLP Samples

This digestion procedure is used for the preparation of TCLP leachate samples for total metal determination by ICP. This digestion procedure is not suitable for samples that will be analyzed by graphite furnace atomic absorption (GFAA) because hydrochloric acid (HCl) can cause interferences during furnace atomization. Note that the LCS is spiked with the routine analytes to allow the TCLP samples to be digested along with aqueous samples. The MS for TCLP is performed only if requested.

9.3.1 Transfer a 5mL aliquot (diluted to 50 mL) of a well-mixed sample to a clean 50mL Teflon vial or other suitable digestion vessel. Larger volumes may be digested at the discretion of the lab. The volume of spike solution added should be adjusted proportionately.

9.3.2 Add 5mL of extraction fluid diluted to 50 mL to a beaker that has been designated as the method blank. This QC sample is taken through all digestion and sample preparation steps to monitor for contamination that may be due to glassware, reagents, or sample handling. A blank for each type of extraction fluid must be digested and analyzed.

9.3.3 Add 0.50mL of the appropriate spiking solutions to a 5.0-mL aliquot of extraction fluid diluted to 50 mL. This is designated as the laboratory control spike (LCS). If a duplicate laboratory control spike (LCSD) is required, spike a second 5-mL aliquot of extraction fluid diluted to 50 mL with 0.50mL of the appropriate spiking solutions. The routine ICP spiking solution is used for the TCLP LCS because of frequent client requests for reporting more analytes from the TCLP leachate than are currently regulated. Preparing an LCS with all of the target analytes eliminates re-digestion and provides QC for the requested analytes.

NOTE: If both extraction fluid I and extraction fluid II are included in the batch, use extraction fluid I for the LCS and LCSD.

Analytical Method	Matrix	QC	Spiking Solutions
6010	TCLP	MS	ICP TCLP Spike I ICP TCLP Spike II
6010	TCLP	LCS	(Spex) ICP Spike I ICP Spike II

9.3.4 If MS is requested, add 0.50 mL of each ICP TCLP spiking solution (I and II) to a separate 5.0-mL aliquot of the client sample (diluted to 50 mL) designated as the matrix spike.

Record the following information on the digestion log:

- date
- analyst's initials
- beaker ID#
- sample identification
- the volume of sample digested
- batch identification
- fume hood #
- temperature of the hot plate or digestion block (daily)
- the lot number of the acids used for the digestion
- the lot number of the ICP spiking solutions
- the time that the digestion was started
- the SOP/method number

NOTE: A DIGESTION BATCH CONSISTS OF TWENTY FIELD SAMPLES AND THE ASSOCIATED QC ITEMS. THE BATCH IS NOT TO EXCEED 20 FIELD SAMPLES. EVERY DIGESTION BATCH WILL HAVE A METHOD BLANK, A LABORATORY CONTROL SAMPLE (LCS), AND A MATRIX SPIKE IF REQUESTED.

9.3.5 Add 1.5 mL of concentrated HNO_3 to each sample. Cover each beaker with a watch glass (a watch glass is not required for the digestion block). Gently heat the beaker until the sample refluxes-the sample is not heated to boiling; that is, bubbles are not formed in the liquid in the bottom of the beaker. The sample/acid solution is refluxing when the liquid evaporates and drops of liquid condense on the watch glass and the sides of the beaker and fall back into the beaker. Evaporate the sample until the volume is approximately 5mL. Do not allow any portion of the vessel bottom to become dry at any time during the digestion.

NOTE: If a volume of sample smaller than 50 mL is digested, the amount of acid should be reduced proportionately.

9.3.6 Remove the beakers from the hot plate and cool the beakers to room temperature. Add another 1.5-mL portion of concentrated HNO_3. Replace the watchglass and continue heating the sample on the hot plate. Again, at the proper temperature, the sample should gently reflux in the beaker-do not allow the sample to boil.

9.3.7 Continue heating the sample and adding additional 1.5-mL portions of concentrated HNO_3 until the digestate is light in color or does not change in appearance after subsequent additions of HNO_3. If a sample requires more than 6mL of acid to digest, contact the digestion lab supervisor for guidance.

9.3.8 Evaporate the digestate (covered with the watch glass) until the volume is approximately 5-10 mL.

9.3.9 Remove the watch glass and add 2.5mL of concentrated HCl. Replace the watchglass on the beaker and warm the sample digestate for 15 minutes.

9.3.10 Wash down the inside of the beaker and the watchglass with reagent water. Dilute the sample digestate to 50 mL with reagent water.

9.3.11 Record the analyst's initials, the final volume of the sample digestate, and the date and time that the digestion was completed in the digestion logbook. The sample is now ready for analysis by ICP.

10.0 PROCEDURES

The digestion procedure is described in Section 9.0. The analytical procedure is given in SOP ME 70: *Elements by ICP.*

11.0 CALCULATIONS

Calculations for the determination of metals by ICP are given in SOP ME70:*Elements by ICP*

12.0 QUALITY CONTROL/QUALITY ASSURANCE

12.1 The analytical batch for aqueous samples consists of up to twenty (20) client samples and the associated quality control items. The quality control items consist of a method (reagent) blank, a lab control standard (LCS), a matrix spike (MS), and a matrix spike duplicate (MSD). If insufficient sample is available for the MS/MSD, the LCS is prepared in duplicate.

SOP AN02: *Analytical Batching* contains guidance for evaluating the QC in an analytical batch. The accuracy and precision limits are published in the current LQM.

12.2 The analytical batch for TCLP samples consists of up to twenty (20) client samples and the associated quality control items. The quality control items consist of a method (extraction fluid) blank, a lab control standard (LCS) spiked into the extraction fluid, and a matrix spike (MS) if requested. If both types of TCLP extraction have been used for samples in the batch, a method blank is processed for each extraction fluid and the LCS is prepared in extraction fluid I.

12.3 The lab must perform a method detection limit (MDL) study annually in each matrix in accordance with SOP CA90: *Procedure for the Determination of Method Detection Limit (MDL).*

13.0 PREVENTIVE MAINTENANCE AND TROUBLESHOOTING

The temperature of the hot plate or digestion block must be monitored daily. If the temperature required for sample preparation cannot be maintained the heating device must be removed from service and repaired or replaced.

14.0 WASTE MANAGEMENT AND POLLUTION PREVENTION

Excess samples, reagents, and digestates must be disposed in accordance with SOP CA70: *Waste Management.*

15.0 REFERENCES

Methods 3005 and 3010: *Test Methods for Evaluating Solid Waste*, Third Edition, SW-846; vs. EPA Office of Solid Waste and Emergency Response: Washington, DC.

Method 200.7 (Drinking Water): *Methods for the Determination of Metals in Environmental Samples*, May 1994, Supplement 1. (EPA 600/R-94/111).

Method 200.7 (NPDES): *Methods for Chemical Analysis of Water and Wastes*; USEPA Office of Research and Development, Cincinnati, Ohio, March 1982; (EPA 600/4-79-020) or latest 40CFR Part 136 citation.

DIGESTION PROCEDURES FOR ICP: TOTAL METALS IN SOILS, SEDIMENTS, WASTES, TISSUES, AND OILS

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1.0 SCOPE AND APPLICATION

The purpose of this SOP is to describe the procedures used to digest soil, sediment, waste, biological tissues, and oil samples prior to the analysis by ICP (SOP ME70).

2.0 SUMMARY OF METHOD AND DEFINTIONS

2.1 A known weight (approximately 1g) of the well-mixed sample is transferred to a suitable digestion vessel. The sample is digested with aliquots of nitric acid and hydrogen peroxide to break down the organics present in the sample. After sample has digested, as evidenced by a clear, pale yellow digestate, HCl is added to give an approximate acid concentration of 1% HCl and 5% HNO3 and the sample digest is diluted to 100mL with reagent water.

A smaller weight of sample may be digested and the sample brought to a final volume that is proportional to the 1g sample to 100mL final volume ratio. For example, if 0.50g is digested, the final volume of the digestate must be 50mL to achieve the same reporting limits.

2.2 Definitions

Digestate - the digested sample
ICP - inductively coupled (argon) plasma
HCl –hydrochloric acid
HNO3 – nitric acid
LQM – laboratory quality manual

2.3 The SOP is based on the guidance in SW-846 Method 3050B.

3.0 SAFETY

3.1 Use good common sense when working in the lab. Do not perform any procedures that you do not understand or that will put you or others in potentially dangerous situations.

3.2 The samples are digested in strong acid solutions and contain acid concentrations of 10-20% by volume. The analyst must wear protective clothing such as a lab coat or apron. The acids used in this procedure will destroy unprotected clothing. The analyst must wear proper eye protection such as lab glasses or face shield. Acid can be splashed into the eyes from many sources. Gloves must be worn to protect hands from acid burns.

3.3 The acid digestion procedures must be performed under a properly functioning fume hood. The acid fumes from the digestion can cause mild to severe respiratory problems if breathed.

3.4 Each digestion lab must have acid spill kits. These kits must be located in a highly accessible area of the lab. Each digestion lab must be equipped with a properly working shower.

3.5 The standards and reagents used to prepare the standards in this method should be treated as potential hazards. Lab coats, gloves, and other protective equipment should be used when preparing and using the standards and reagents.

3.6 The Material Safety Data Sheets (MSDS) for each reagent and standard are located in each laboratory. These sheets denote the type of hazard that each reagent poses and the safe handling instructions for these compounds.

3.7 Care must be taken when handling the digestion beakers. Before handling a vessel that has been in use, check the temperature to make sure that it is not hot. Make sure that the digestion vessels are placed on a stable platform during and after the digestion. Vibrations from the hood or an unstable platform can cause the beakers to move and possibly to fall and splatter an analyst with a hot acid solution. Hot acids can cause severe skin burns and destroy unprotected clothing.

4.0 INTERFERENCES

Contamination of the sample can occur when the preparation glassware and/or reagents contain the target elements. Reagent blanks (method blanks) must be analyzed as a check on contamination due to the sample digestion.

5.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

MATRIX	ROUTINE CONTAINER	PRESERVATIVE	STORAGE/ HOLD TIME
Soils and sediments, and biological tissues	500-mL plastic	None	<6C but not frozen
Wastes and Oils	500-mL plastic or glass*	None	ambient or <6C but not frozen
Biological Tissues	500-mL plastic or glass	None	Frozen until the time of sample preparation

*Some organic wastes may destroy plastic containers

6.0 APPARATUS AND MATERIALS

6.1 Hot plate or digestion block-capable of maintaining a sample temperature of 95C+/-5C. The temperature of the hot plate or digestion block must be monitored and recorded each day samples are digested. The temperature is measured in a beaker or digestion vessel containing reagent water.

6.2 Digestion vessels, appropriate volume for use with digestion block

6.3 Teflon or Pyrex beakers, appropriate volumes, Recommend 150mL or 250mL beakers for use with hot plates

6.4 Watch glasses, for use with beakers (block digestion vessels do not require watch glasses)

6.5 Teflon vials-25mL

6.5 Volumetric flasks- appropriate volumes

6.6 Graduated cylinder-appropriate volume

6.7 Pipettes

6.8 Analytical balance

6.9 Top-loading balance

7.0 REAGENTS

Reagents must be tracked in accordance with SOP AN44: *Reagent Traceability.*

7.1 Reagent water-lab generated deionized water. ASTM Type I or Type II. The conductivity must be checked daily in accordance with SOP AN35: *Conductivity Checks for Laboratory Deionized Water.*

7.2 Nitric acid (HNO_3)-reagent grade. The assay sheet of each lot of acid received into the lab must be reviewed to make sure that the quality of the acid is sufficient for trace analysis of metals. Each lot of acid must be assayed in the laboratory to ensure that each particular lot can be used for trace analysis.

7.3 Nitric acid solution (1:1)- Measure 500ml of reagent water into a 2-L beaker. Place the beaker on a magnetic stir plate and add a Teflon stir bar to the beaker. Carefully and slowly, add 500ml of concentrated nitric acid (HNO_3) to the reagent water in the beaker on the magnetic stir plate. Transfer the reagent to a labeled container suitable for storing acidic solutions. Do not store reagents in volumetric glassware. Prepare this reagent as needed.
CAUTION: HEAT WILL BE EVOLVED AS THE NITRIC ACID MIXES WITH THE WATER. THIS SOLUTION IS WILL CAUSE SKIN BURNS AND DESTROY UNPROTECTED CLOTHING.

7.4 Hydrochloric acid (HCl)-reagent grade. The assay sheet of each lot of acid received into the lab must be reviewed to make sure that the quality of the acid is sufficient for trace analysis of metals. Each lot of acid must be assayed in the laboratory to ensure that each particular lot can be used for trace analysis.

7.5 Hydrochloric acid solution (1:1)- Measure 500ml of reagent water into a 2-L beaker. Place the beaker on a magnetic stir plate and add a Teflon stir bar to the beaker. Carefully and slowly, add 500ml of concentrated hydrochloric acid (HCl) to the reagent water in the beaker on the magnetic stir plate. Transfer the reagent to a labeled storage container suitable for acidic solutions. Do not store reagents in volumetric glassware. Prepare this reagent as needed.
CAUTION: HEAT WILL BE EVOLVED AS THE HYDROCHLORIC ACID MIXES WITH THE WATER. HYDROCHLORIC ACID HAS A SUFFOCATING ODOR AND MUST BE USED UNDER THE HOOD. THIS SOLUTION IS WILL CAUSE SKIN BURNS AND DESTROY UNPROTECTED CLOTHING. PREPARE THIS SOLUTION UNDER A HOOD.

7.6 Hydrogen peroxide, 30%-reagent grade. Check for impurities by the analysis of a method blank.

8.0 STANDARDS

The preparation of the spiking solutions must be tracked in accordance with SOP AN41: *Standard Material Traceability*. General guidance on the preparation of standards is given in SOP AN43: *Standard Preparation*.

The lab should purchase certified solutions from STL-approved vendors, if available. The lab should prepare standards from neat materials only if a certified solution is not available. See SOP AN43 for guidance for standard preparation.

8.1 Determine the volume of standard to be prepared and the volume of the stock standard needed to make the spiking solutions. The following equation can be used:

$$Ci \otimes Vi = Cf \otimes Vf$$

$$Vi = \frac{Cf \otimes Vf}{Ci}$$

where
Vi = volume of stock standard needed to prepare the spiking solution (mL)
Ci = concentration of stock solution (ug/mL)
Cf = concentration of spiking solution to prepare (ug/mL)
Vf = volume of spiking solution to prepare (mL)

The concentration can be expressed in whatever terms the analyst finds most convenient - ug/L, ug/mL, mg/L, etc. The units must be the same for *Ci* and *Cf*.

8.2 Preparation of the ICP Matrix Spiking Solutions

8.2.1 ICP Matrix Spiking Solution 1 is a solution purchased from SPEX. The catalogue number is SPIKE-1. Store this solution at room temperature. Prepare this solution every six months or sooner if needed or required.

8.2.2 Preparation of the ICP Matrix Spiking Solution 2

Add 20-mL to 30-mL of reagent water to a clean100-mL volumetric flask. Add 1-mL of concentrated nitric acid (HNO_3) and 5-mL of hydrochloric acid (HCl) to the volumetric flask. The standard will have an acid concentration of 1% HNO_3 and 5% HCl when diluted to volume.

Add the volumes of the stock standards given in the following table to the volumetric flask:

Element	Conc. of Stock (mg/L)	mL of Stock	Final Volume (mL)	Conc. of std. (mg/L)
Boron (B)	1000	10	100	100
Calcium (Ca)	10000	5.0		500
Magnesium (Mg)	10000	5.0		500
Molybdenum (Mo)	1000	5.0		50
Potassium (K)	10000	5.0		500
Sodium (Na)	10000	5.0		500
Strontium (Sr)	1000	5.0		50
Tin (Sn)	1000	10		100
Titanium (Ti)	1000	10		100

Dilute to a final volume of 100-mL with reagent water. Store the standard at room temperature. Prepare this solution every six months or sooner if needed or required.

9.0 SAMPLE PREPARATION

This digestion procedure is used for the preparation of soil, sediment, waste, tissues, and oil samples for the determination of total metals ICP or flame atomic absorption (FLAA). This digestion procedure is not suitable for some analytes that will be analyzed by graphite furnace atomic absorption (GFAA) because HCl can cause interferences during furnace atomization.

9.1 Weigh 1g to 1.2g (wet weight) of a homogeneous sample into a 125-mL Teflon beaker or other suitable digestion vessel. The lab may weigh a larger aliquot equal to 1.0g of sample on a dry weight basis.

NOTE: A smaller weight of sample may be digested and the sample brought to a final volume that is proportional to the 1g sample to 100mL final volume ratio. For example, if 0.50g is digested, the final volume of the digestate must be 50mL to achieve the same reporting limits; if 0.1g is digested, the final volume of the digestate must be 10mL. If the sample weight: final volume ratio is greater than 1:100, the reporting limits will be higher than those listed in the LQM.

9.1.1 To homogenize a soil sample, the sample may be vigorously stirred in the sample container or transferred a plastic "baggie" and thoroughly mixed by kneading the container. After the sample is homogenized, return only enough sample to the original container to fill it three fourths full. This will allow the sample to be stirred and homogenized if additional aliquots of the sample are required. Place the discarded sample in a containerized waste receptacle for disposal.

9.1.2 If the sample is a solid material, break up the solid in the baggie by hitting the sample with a hammer or other suitable crushing device. Contact the immediate supervisor if the matrix is difficult to break up or is difficult to mix.

9.2 Add 1.0-mL of the appropriate spiking solution to the designated laboratory control spikes. The LCS/LCSD are prepared by weighing 1g aliquots of the "blank soil" into labeled beakers or digestion vessels.

9.3 Add 1.0mL of the appropriate spiking solution to the designated matrix spike samples. The MS/MSD are prepared by weighing 1g to 1.2g of the sample chosen for the matrix spike into labeled beakers or digestion vessels. The lab may weigh a larger aliquot equal to 1.0g of sample on a dry weight basis for the MS/MSD or may use a smaller weight if the final volume of the digestate is adjusted or if higher reporting limits are acceptable.

9.4 Record the following information on the digestion log:

- date
- analyst's initials
- beaker ID#
- sample identification
- the weight of sample digested
- batch identification
- fume hood #
- temperature of the hot plate or digestion block (daily)
- the lot number of the acids used for the digestion
- the lot number of the ICP spiking solutions
- the time that the digestion was started
- the SOP/method number

NOTE: THE DIGESTION BATCH CONSISTS OF TWENTY OR FEWER FIELD SAMPLES AND THE ASSOCIATED QC ITEMS. A DIGESTION BATCH IS NOT TO EXCEED 20 FIELD SAMPLES. EVERY DIGESTION BATCH WILL HAVE A METHOD BLANK, A LABORATORY CONTROL SAMPLE (LCS), A MATRIX SPIKE AND A MATRIX SPIKE DUPLICATE (IF THERE IS SUFFICIENT SAMPLE FOR THE MS/MSD). PERFORM THE LCS IN DUPLICATE IF THE MS/MSD CANNOT BE PERFORMED. THE METHOD BLANK IS PERFORMED WITH THE REAGENTS USED FOR THE DIGESTION. LAB SPIKES FOR SOIL MATRICES WILL BE PERFORMED USING 1-G ALIQUOTS OF BLANK SAND.

9.5 Add 5mL of reagent water and 5mL of concentrated HNO_3 to each beaker, mix, and cover the beaker with a watchglass. A watchglass is not used with the digestion block vessels.

9.6 Carefully heat the beaker until a gentle reflux is achieved-the sample is not heated to boiling; that is, bubbles are not formed in the liquid in the bottom of the beaker. The sample/acid solution is refluxing when the liquid evaporates and drops of liquid condense on the watch glass and the sides of the beaker and fall back into the beaker. Do not allow the samples to boil. Reflux for 10-15 minutes.

9.7 Remove the beakers from the hot plate or digestion block and allow the beakers to cool to room temperature. Add 5mL of concentrated HNO_3 to each sample. Replace the watchglass and return the beakers to the hot plate or digestion block. Carefully heat the beaker until a gentle reflux is achieved. Reflux the samples for 30 minutes. Do not allow the samples to boil.

9.8 Repeat the procedure in Step 9.7 with a second 5-mL portion of concentrated HNO_3 if brown fumes are given off. Repeat 9.7 until no brown fumes are given off.

9.9 Evaporate the sample digestate to approximately 10mL. Do not allow the bottom of the beaker to go dry during the evaporation. Allow the sample to cool to room temperature before continuing onto the next step.

NOTE: If the sample is still warm when the 30% H_2O_2 (hydrogen peroxide) is added in the next step, the sample may "boil over" and the entire process must be started over.

9.10 Add 2mL of reagent water to each beaker. Slowly and carefully add 3mL of 30% H_2O_2 to each beaker. It is very important to add the hydrogen peroxide slowly to prevent loss of sample due to vigorous effervescence. Return the beakers to the hot plate or digestion block and heat until the effervescence subsides. Cool the beaker after the effervescence subsides.

9.11 Continue to add 30% H_2O_2 in 1-3mL aliquots to the sample digestate until the effervescence is minimal or until the general appearance of the digestate is unchanged. Warm the sample digestate after each addition of H_2O_2 on the hot plate or digestion block.

NOTE: Do not add more than 10mL of hydrogen peroxide to each sample.

9.12 After the last addition of peroxide, reduce the volume of the digest to 5-10mL without boiling and without allowing the bottom of the beaker to go dry. Add 10mL of concentrated HCl to each sample digestate. Replace the watch glass, return the beakers to the hot plate or digestion block, and reflux the sample digestates for 10-15 minutes.

9.13 Wash down the inside of the beaker and the watchglass with reagent water. Dilute the sample digestate to 100mL with reagent water.

9.14 Record the analyst's initials, the final volume of the sample digestate, and the date that the digestion was completed in the digestion logbook. The sample is now ready for analysis.

10.0 PROCEDURES

The digestion procedure is described in Section 9.0. The analytical procedure is given in SOP ME 70: *Elements by ICP*.

11.0 CALCULATIONS

Calculations for the determination of metals by ICP are given in SOP ME70: *Elements by ICP*

12.0 QUALITY CONTROL/QUALITY ASSURANCE

12.1 The analytical batch consists of up to twenty (20) client samples and the associated quality control items. The quality control items consist of a method (reagent) blank, a lab control standard (LCS), a matrix spike (MS), and a matrix spike duplicate (MSD). If insufficient sample is available for the MS/MSD, the LCS is prepared in duplicate.

SOP AN02: *Analytical Batching* contains guidance for evaluating the QC in an analytical batch. The accuracy and precision limits are published in the current LQM.

12.2 The lab must perform a method detection limit (MDL) study annually in each matrix in accordance with SOP CA90: *Procedure for the Determination of Method Detection Limit (MDL).*

13.0 PREVENTIVE MAINTENANCE AND TROUBLESHOOTING

The temperature of the hot plate or digestion block must be monitored daily. If the temperature required for sample preparation cannot be maintained the heating device must be removed from service and repaired or replaced.

14.0 WASTE MANAGEMENT AND POLLUTION PREVENTION

Excess samples, reagents, and digestates must be disposed in accordance with SOP CA70: *Waste Management.*

15.0 REFERENCES

Test Methods for Evaluating Solid Waste, Third Edition, SW-846; EPA Office of Solid Waste and Emergency Response: Washington, DC. (including Update III)

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EPA RESPONSE

ATTACHMENT J

TOXICITY COMPOUND LEACHING PROCEDURE (TCLP): SEMIVOLATILE ORGANIC COMPOUNDS AND METALS

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Approved by:

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1.0 SCOPE AND APPLICATION

1.1 This method describes the procedures that are used to simulate the leaching that a waste will undergo when disposed of in a sanitary landfill. It can be used to determine the mobility of certain semivolatile organic compounds (SVOC) and inorganic compounds (metals) in liquid, solids, and multi-phase wastes.

1.2 Table 1 lists the target compounds that are amenable to this leaching procedure, the regulatory limit for each target compound, and the matrix spiking levels for each target compound. Table 1 also lists the appropriate methods for the extraction or digestion and analysis of the liquid phase or leachate. The reporting limit (RL), the method detection limit (MDL), and the accuracy and precision criteria for the target compounds are given in the Laboratory Quality Manual prepared by and for STL Savannah, STL Tallahassee, STL Mobile, and STL Tampa West.

2.0 SUMMARY OF METHOD AND DEFINITIONS

2.1 The waste sample is initially evaluated for percent solids. If a waste contains less than 0.5% solids, the liquid phase after filtration is defined as the TCLP leachate. If the percent solids is greater than 0.5%, the solid and liquid phases must be separated. The liquid phase (if present) is properly collected and refrigerated until time of extraction and analysis. The solid phase is extracted with twenty times the weight of the solid phase in extraction fluid for 18 hours. The leachate is collected, and if compatible, is combined with the liquid phase from the solids determination. If the leachate is not compatible with the liquid phase, the leachate is collected and refrigerated until time of extraction and analysis.

2.2 The leachate of combined leachate/liquid phase is solvent extracted or digested by the procedure appropriate to the target compounds. If the liquid phase from the solids determination is not compatible with the leachate, the samples (leachate and liquid phase) are analyzed individually and a weighted average is used to determine the total concentration of the contaminants. The extract or digestate is analyzed using the appropriate analytical procedure. The results from the analysis is compared to the regulatory limit to determine if the waste sample exhibits hazardous characteristics.

NOTE: It is unlikely that a sample that is a non-aqueous liquid or contains a non-aqueous liquid phase will be able to meet the regulatory threshold limits.

2.3 Definitions

TCLP – toxicity compound leaching procedure
Leachate – the liquid portion of the sample that passes through a 0.6um filter in the initial evaluation of the percent solids or the liquid that passes through a 0.6um filter after the sample has been subjected to the TCLP.
Percent solids – the percentage of sample remaining on the 0.6um filter after the sample is subjected to a pressure of 30psi. Oily or viscous materials, although they appear to be liquids, are part of the solids if they do not pass through the filter. **NOTE: This is not the same as the percent solids used to report samples on a "dry-weight basis".**
Regulatory Threshold Limit- the concentration of analyte in the TCLP leachate at which the sample is deemed hazardous.

2.4 This SOP is based on SW-846 Method 1311.

3.0 SAFETY

3.1 Use good common sense when working in the lab. Do not perform any procedures that you do not understand or that will put you or others in potentially dangerous situations.

3.2 The analyst must treat each waste sample as a potential hazardous waste. If possible, the waste should be evaluated in a hood or other well ventilated area until the nature of the waste can be determined. The analyst must not be allowed to work alone in a confined area with waste samples until it is determined that the waste poses no immediate threat. An immediate threat would be the release of a toxic gas when the waste container is opened or when the waste is treated with the buffer or acid solutions.

3.3 The analyst must wear a lab coat or an apron and gloves when handling all waste samples. A face mask should be worn and if the sample contains volatile materials, the sample should be handled under a ventilation hood.

3.4 If an MSDS (Material Safety Data Sheet) is included with a waste sample, the analyst must be made aware of the potential hazard that the waste poses.

3.5 The analyst must be aware of the potential hazard posed by the reagents used in this procedure. The analyst will have to prepare reagent using strong and weak acids and a strong base. The MSDS for each reagent is located at each lab division.

4.0 INTERFERENCES

4.1 Interferences encountered in the analysis of the leachate of liquid phase of the sample are discussed in the appropriate analytical method. (Table 1)

4.2 The extraction vessels must not be rinsed with acids or solvents that will interfere with the analysis of the target compounds. The extraction vessels must be stored in an area that is free from contamination and the extraction procedure must take place in an area that is free from contamination.

5.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

5.1 TCLP for SVOC or SVOC/Metals

5.1.1 Waste samples are collected in glass containers with minimum headspace and refrigerated at 4C (less than 6C with no frozen samples) until the time of the leaching procedure. The waste samples may contain very high levels of SVOC and should be segregated from the "normal" samples. The waste sample must undergo the toxicity compound leaching procedure within fourteen (14) days of collection.

5.1.2 The liquid phase (from the solids determination) or the leachate for SVOC are collected and stored in a 1.0-L glass container equipped with a Teflon-lined cap. The leachates are stored at 4C (less than 6C with no frozen samples) until preparation. The leachate or liquid phase must be extracted within 7 days of the leaching procedure.

5.1.3 The liquid phase (from the solids determination) or the leachate for metals analysis are collected and stored in a 500-mL plastic container. The leachate or liquid phase must be preserved with 1 mL of reagent grade nitric acid (HNO_3). The leachate or liquid phase must be digested and analyzed within six months of the leaching procedure. The analysis of the leachate or liquid phase for mercury (Hg) must be completed within 28 days of the leaching procedure.

5.2 TCLP for Metals Only

5.2.1 Waste samples are collected in glass or plastic containers with minimum headspace and refrigerated at 4C (less than 6C with no frozen samples) until the time of the leaching procedure. The waste sample must undergo the TCLP within six months of collection. If mercury (Hg) is to be determined, the leaching procedure must be completed within 28 days of collection.

5.2.2 The liquid phase (from the solids determination) of the leachate for metals analysis is collected and stored in a 500-mL plastic container. The leachate or liquid phase must be preserved with 1 mL of reagent grade nitric acid. The leachate or liquid phase must be digested and analyzed within six months of the leaching procedure. The analysis of the leachate or liquid phase for mercury must be completed within 28 days of the leaching procedure.

6.0 APPARATUS AND MATERIALS

6.1 Extractor: Capable of holding several TCLP extraction vessels and rotating samples continuously at a rate of 30 RPM ± 2 RPM. The extractor must be maintained at 23C ± 2C during the TCLP. Check the rotation device for the correct RPM at least annually by counting the rotations in one minute. Adjust to the proper range as required.

6.2 Extraction vessels

6.2.1 SVOC and SVOC/metals-borosilicate glass bottle with a volume of approximately 2 L. The glass container must be free from the target analytes when subjected to the TCLP.

6.2.2 Metals only-plastic bottle with a volume of approximately 2 L. The plastic container must be free from the target analytes when subjected to the TCLP.

6.3 Filtration device to determine percent solids and to filter the leachate after the TCLP.

6.4 Filter media: Binderless glass fiber filters, 0.6-0.8 um pore size. When the waste is to be evaluated for metals, the filters must be rinsed with 100mL of approximately 1.0 N nitric acid and rinsed with a minimum of three liters of reagent water. It is important that the filter and the filtration vessel not contribute to the pH of the sample. The filter and vessel must be thoroughly rinsed with reagent water.

6.5 pH meter: Accurate to 0.05 pH units

6.6 Laboratory balance: accurate to 0.01 g

6.7 Laboratory glassware: beakers

7.0 REAGENTS

Reagents must be tracked according to STL SOP AN44:*Reagent Traceability*.

7.1 Reagent water: Laboratory deionized water or other source of water that does not contain the target compounds above the reporting limit (RL).

7.2 Sodium hydroxide (NaOH): reagent grade

7.3 Sodium hydroxide (1N): Dissolve 40.0 grams of NaOH in 800 mL or reagent water contained in a 1-L volumetric flask. Dilute to volume with reagent water and mix thoroughly. Transfer the 1N NaOH to a glass container equipped with a Teflon-lined cap. Do not store basic solutions in volumetric glassware quipped with ground glass joints.

7.5 Extraction fluid # 1: Combine 5.7 mL of glacial acetic acid with 64.3 mL of 1.0 N NaOH in a 1-L volumetric flask and dilute to volume with reagent water. The pH of this solution should be 4.93 ± 0.05. The extraction fluid should be prepared as needed and stored to minimize contamination and pH change. The pH of each batch of extraction fluid must be verified prior to use. Sufficient volumes must be prepared so that there is enough extraction fluid for each sample and for the required QC.

7.6 Extraction fluid #2: Transfer 5.7 mL of glacial acetic acid to a 1.0-L volumetric flask and dilute to volume with reagent water. The pH of this fluid should be 2.88 ± 0.05. The extraction fluid should be prepared as needed and stored to minimize contamination and pH change. The pH of each batch of extraction fluid must be verified prior to use. Sufficient volumes must be prepared so that there is enough extraction fluid for each sample and for the required QC.

7.7 Hydrochloric acid (HCl): reagent grade

7.8 Hydrochloric acid (1.0 N): Transfer about 800 mL of reagent water to a 1-L volumetric flask. Slowly and carefully add 83.3 mL of concentrated HCl to the 1-L volumetric flask. Dilute to volume with reagent water and mix thoroughly by inverting the flask.

NOTE: Solutions that contain HCl must be prepared under a fume hood.

7.9 Nitric acid (HNO_3): reagent grade

7.10 Nitric acid (approx. 1.0 N): Transfer about 800 mL of reagent water to a 1-L volumetric flask. Slowly and carefully add 70 mL of concentrated HNO_3 to the 1-L volumetric flask. Dilute to volume with reagent water and mix thoroughly by inverting the flask. This solution is used for cleaning the glass fiber filters when the waste is evaluated for metals..

NOTE: Solutions that contain HNO_3 must be prepared under a hood.

8.0 STANDARDS

The calibration and spiking standards that are used for the analysis of the leachate produced by the TCLP are given in the appropriate analytical method. (Table 1)

9.0 SAMPLE PREPARATION

9.1 Preliminary Determination of Percent Solids

If the sample contains no obvious free liquids, this step may be omitted. If there is any doubt as to whether the sample contains free liquids, this step must be performed.

9.1.1 Weigh out an approximately 100-g sub-sample of the well-mixed waste into a pre-weighed 600-mL glass beaker. Weigh the beaker/sample and record this weight on the extraction log to the nearest 0.1 g.

9.1.2 Determine and record the weight of the filter pad. Place the tared filter pad on the filtration device.

9.1.2 Transfer the sample in the beaker to the filtration device. The sample should be added directly to the filter pad. Try to avoid getting the sample on the sides of the filtration vessel.

NOTE: If the waste has solid and liquid phases, it is recommended that the 100-g aliquot be allowed to settle to facilitate filtration.

$$W_{sample} = W1 - W2$$

where

9.1.4 Calculate the weight of sample added to the filtration device:

W1 = tare weight of the beaker + sample (g)
W2 = weight of the beaker after the sample has been added to the filter (g)

9.1.5 Place the top on the filtration device and clamp it into place. Place a pre-weighed (tared) receiving container under the filtration device.

9.1.6 Attach a nitrogen line or air line to the filtration vessel and gradually increase the pressure in 10 psi increments. Collect the liquid that is filtered out in the receiving container. Gradually increase the pressure until the pressure in the filtration device is 50 psi. Continue the pressure filtration for 2-5 minutes until no further liquid is filtered out of the sample.

9.1.7 Slowly release the pressure in the filtration vessel. After the pressure has returned to atmospheric pressure (no further pressure released from the vessel), remove the top of the filtration device. The solids portion may be removed for the extraction fluid determination.

9.1.8 Weigh the collection beaker and record the weight of the beaker/liquid phase. Calculate the percent solids:

$$percent\ solids = \frac{W1 - W2}{W1} \otimes 100$$

where

W1 = weight of total sample (solids + liquids) added to the filtration device (g)
W2 = weight of the liquid phase (g)

9.1.9 If the amount of solids on the pad is very small but the percent solids are greater than 0.5%, remove the filter pad from the filtration vessel and place it into an oven maintained at 100 C ± 2 C for 1 hour. This step is preformed to eliminate any water or solvents that may be trapped in the filter pad. The weight of water or solvent trapped on the pad may be significant if the percent solids is low.

Reweigh the filter pad and calculate the percent dry solids as follows:

$$precent\ dry\ solids = \frac{Wp2 - Wp1}{W_{sample}} \otimes 100$$

where

Wp2 = weight of the filter pad and dry solids (g)
Wp1 = weight of the filter pad (g)
W_{sample} = weight of sample added to the filtration device (g)

9.1.9.1 If the percent dry solids of the sample is less than 0.5%, the filtered liquid portion of the sample is the TCLP leachate. Filter additional aliquots of the waste to produce enough leachate to support the required analyses.

9.1.9.2 If the percent dry solids of the sample is greater than 0.5%, notify the supervisor immediately. Do not proceed until given further instructions.

The following steps are used as default guidance:
-discard the filter and solids that were used to evaluate the percent dry solids
-filter a larger aliquot of waste to produce enough solids to 1) determine the extraction fluid to use (9.3) and 2) to perform the TCLP on the solids portion. A minimum of 10g of solids is required to proceed-5g for the extraction fluid determination and 5g for the TCLP. For example, if sample contains 1% solids, a minimum of 1000g of sample would have to filtered to produce 10g of solids(1000g x 0.01 = 10g).

If sufficient sample is not available to produce 10g of solids, stop the procedure and notify the supervisor.

9.1.10 The liquid obtained by filtering the sample must be retained until the TCLP procedure is completed. Transfer the liquid phase to a glass container and store at 4C until the TCLP leachate is completed. A plastic container may be used if only metals are being evaluated and the liquid phase is aqueous. The liquid phase will be combined with the TCLP leachate, if compatible.

9.2 Particle Size Reduction

The solid portion of the sample must be evaluated for particle size. This may be accomplished in one of two ways:

- passing the solid portion through a 9.5mm sieve.
- measuring the particle size of the solid with a ruler.

If the particle size is greater than 9.5mm, the solid portion is prepared for extraction fluid determination and extraction by crushing, cutting, or grinding the waste. The vessels used for homogenizing the sample must be compatible with the type of analysis and should not contribute to contamination. For example, plastic bags may be used to homogenize samples for metals only but must not be used for semivolatiles.

9.3 Extraction Fluid Determination
The determination of which extraction to use is based on the buffering capacity of the solid portion of the waste sample. If the percent solids (9.1) of the sample are less than 0.5%, this step does not have be performed.

9.3.1 Reduce the particle size of the sample to 1mm or less (Section 9.2) and weigh 5.0 g of the solid portion of the sample from the solids determination or 5.0 g of a sample that contains no obvious free liquids into a 500-mL Erlenmeyer flask.

9.3.2 Add 96.5 mL of reagent water to the flask. Add a magnetic stir bar to the flask, cover the beaker with a watch glass, and stir the sample on a magnetic stir plate for 5 minutes.

9.3.3 Measure the pH of the sample with a properly calibrated pH meter (STL SOP BA70).

9.3.3.1 If the pH of the solid sample is less than or equal to 5, extraction fluid #1 is used for the TCLP.

9.3.3.2 If the pH of the solid sample is greater than 5, add 3.5 mL of 1.0 N HCl to the sample and swirl the sample for 30 seconds. Place a watchglass on the flask and place the container in a water bath maintained at 50C . Allow the sample to equilibrate to 50C and remain in the waterbath for 10 minutes.

9.3.3.3 After 10 minutes at 50C, remove the sample from the waterbath and allow the sample to cool to room temperature.

9.3.3.4 Measure the pH of the solid sample with a properly calibrated pH meter. If the pH is less than or equal to 5.0, extraction fluid #1 is used for the TCLP. If the pH is greater than 5.0, extraction fluid #2 is used for the TCLP.

9.4 Leaching Procedure

The solids from the solids determination can be used to prepare the TCLP leachate. If sample contains less than 0.5% solids, the filtered liquid is the TCLP leachate. If the sample contains a very low level of solids and the solids filtered from the sample were heated to determine the percent dry solids, a new aliquot of the waste sample must be used to prepare the TCLP leachate. Sufficient solids should be obtained to provide enough leachate to support the required analyses. The minimum volume of leachate required to meet the TCLP threshold limits are given in the following table:

Parameter	Minimum Volume Required (mL)
Metals (ICP) and Mercury	100mL
SVOC (BNA)	200mL
Pesticides	20mL
Herbicides	10mL

9.4.1 Transfer the solids portion of the waste (including the filter) or 100grams of the waste, if the percent solids is obviously 100%, to a container that will hold the solids portion of the waste sample and the volume of the extraction fluid needed. If the extraction container will not hold 100g of waste (when waste has no obvious liquids) and 2000mL of extraction fluid, the waste may be divided into two or more aliquots and added to separate extraction containers. After the leaching is completed, proportional volumes of leachate are filtered from each vessel and combined.

NOTE: The analyst must start with a minimum of 100g of waste. If less than 100g of waste is available, an anomaly report must be initiated.

If SVOC or SVOC/metals are being evaluated, use a glass container; if only metals are being evaluated, a plastic container may be used.

9.4.2 Add the volume of the appropriate extraction fluid equal to 20 times the weight of the solid portion of the waste sample added to the extraction vessel.

Volume of extraction fluid (mL) = W_{solids} x 20

where

W_{solids} = weight of solids portion of the waste sample added to the extraction vessel(g)

9.4.3 Place the cap on the extraction vessel and seal the cap with Teflon tape. Place the extraction vessel into the rotary extraction device and rotate the sample at 30 rpm for 18 hours ± 2 hours. The temperature is maintained at 23C ± 2C during the extraction. Record the temperature on the TCLP log.

NOTE: Pressure may develop in the extraction vessel as the sample is rotated. Stop the extraction after a short time and vent each sample. Some types of samples, e.g., those with high carbonates, may develop significant pressure after a short period of time, especially if extraction fluid #2 is used.

9.4.4 After the extraction period is over, remove the samples from the rotation device. Place the samples in an upright position and allow the solids to settle. This will facilitate the filtration of the leachate.

9.4.5 Set up the filtration device and filter the leachate through the 0.7-um filter pad. Collect the leachate in a glass container.

9.4.6 Determine if the leachate and the liquid phase (if any) are compatible by placing T mL of each liquid into the same small container. Note if leachate and liquid phase combine or separate.

9.4.6.1 If the leachate and the liquid phase are **not compatible**, the leachate and the liquid phase are analyzed separately. The TCLP results are based on a weighted average of the results of the analysis of the leachate and the result from the analysis of the liquid phase.

9.4.6.2 If the leachate and the liquid phase are compatible, the entire solid phase leachate and the entire liquid phase are combined prior to preparation and analysis. The TCLP results are based on the analysis of the combined sample. See Appendix A for directions on calculating the volume of each fraction to combine if the entire solid phase leachate is not filtered (e.g., for analyses that require only a small volume of combined leachate)

NOTE: If the leachate is difficult to filter, filter only enough of the leachate to support the required analyses. The filter may be changed if clogged to facilitate the filtration. Combine the leachate and liquid portion of the sample, using the same proportion of each fraction. For example, if one half of the volume of the leachate is filtered, it is combined with one half of the volume of the liquid portion of the sample; if one fourth of the volume of the leachate is filtered, it is combined with one fourth of the volume of the liquid portion of the sample, etc...

9.4.7 The leachate, liquid, or leachate/liquid combination is preserved and stored in the same manner as a routine field sample. If metals are being determined on the TCLP sample, transfer a portion to a labeled plastic container and acidify with nitric acid to pH<2.

10.0 PROCEDURE

The procedures for the determination of the target compounds are given in the appropriate analytical SOP.

11.0 DATA ANALYSIS/CALCULATION

The procedures for the qualitative and quantitative evaluation of the analysis of the leachate(s) for the target compounds are given in the appropriate analytical SOP. (Table 1)

$$TCLP, mg/L = \frac{C_1V_1 + C_2V_2}{V_1 + V_2}$$

If the liquid and leachate are analyze separately, the results are combined mathematically:

where

C_1 = concentration of liquid phase(mg/L)
V_1 = volume of liquid phase(L)
C_2 = concentration of leachate from the solid phase(mg/L)
V_2 = volume of leachate from the solid phase(L)

12.0 QUALITY CONTROL/QUALITY ASSURANCE

12.1 An extraction fluid blank must be processed for each batch of 20 or fewer samples that are subjected to the TCLP. If a batch consists of samples requiring both extraction fluid #1 and extraction fluid #2, a fluid blank for both extraction fluids must be taken through the entire TCLP, leachate preparation, and analytical procedures.

12.2 For each batch of 20 or fewer samples, a TCLP fluid blank is spiked according to the sample preparation section given in the various analytical procedures. If both types of extraction fluid are in the extraction batch, that is, both extraction fluids #1 and #2 are used, use extraction fluid #1 for the TCLP fluid spike. Table 1 of this SOP lists the compounds that are included in the TCLP leachate spike and the concentration that the sample leachate is spiked.

12.3 Matrix spikes are analyzed only if requested by a client. Table 1 of this SOP lists the compounds that are included in the TCLP leachate spike and the concentration that the sample leachate is spiked.

13.0 PREVENTIVE MAINTENANCE AND TROUBELSHOOTING

No items included in this revision.

14.0 WASTE MANAGEMENT AND POLLUTION PREVENTION

All excess samples, sample leachates, and reagents must be disposed in accordance with SOP CA70: *Waste Management*.

15.0 REFERENCES

Test Methods for Evaluating Solid Waste, Third Edition; U.S. EPA Office of Solid Waste and Emergency Response: Washington, DC, November, 1992.

TABLE 1-TCLP Levels for Non-Volatile and Semi-Volatile Compounds

	Regulatory Threshold Limit (mg/L)	Matrix Spike Level (mg/L)
METALS	EPA 6010/SOP ME70	
Arsenic	5.0	5.0
Barium	100.0	5.0
Cadmium	1.0	1.0
Chromium	5.0	5.0
Lead	5.0	5.0
Selenium	1.0	1.0
Silver	5.0	0.20
METALS	EPA 7470/ SOP ME28/ME29	
Mercury	0.2	0.020
BASE/NEUTRAL ACID	EPA Method 8270/SOP SM05	
o-Cresol	200.0	0.50
m-Cresol	200.0	0.50
p-Cresol	200.0	0.50
Cresol (Total)	200.0	
1,4-Dichlorobenzene	7.5	0.50
2,4-Dinitrotoluene	0.13	0.50
Hexachlorobenzene	0.13	0.50
Hexachlorobutadiene	0.5	0.50
Hexachloroethane	3.0	0.50
Nitrobenzene	2.0	0.50
Pentachlorophenol	100.0	0.50
Pyridine	5.0	0.50
2,4,5-Trichlorophenol	400.0	0.50
2,4,6-Trichlorophenol	2.0	0.50
CHLORINATED HERBICIDES	EPA Method 8150/SOP SG65	
2,4-D	10.0	0.10
2,4,5-TP (Silvex)	1.0	0.10
CHLORINATED PESTICIDES	EPA Method 8081/SOP SG45	
gamma-BHC (Lindane)	0.4	0.010
Heptachlor	0.008	0.010
Endrin	0.02	0.010
Heptachlor Epoxide	0.008	0.010
Methoxychlor	10.0	0.010
Toxaphene	0.5	
Chlordane	0.03	

The matrix spike level is the concentration of the sample after the spiking solution has been added (the theoretical or true concentration).

Appendix A

The following calculations are used to determine the volume of liquid phase and solid phase leachate that are combined to maintain the proper ratio if the entire liquid phase is not combined with the entire solid phase leachate.

1) Determine the volumes of the liquid phase (V1) and solid phase leachate (V2) in the weight (W, nominally 100g) of waste initially evaluated for percent solids.

$$V1 = W \otimes \left(1 - \frac{percent\ solids}{100}\right)$$

assuming a density of 1g/mL

$$V2 = W \otimes percent\ solids \otimes 20$$

2) Calculate the percentage of the liquid phase (%LP) and the leachate from the solids phase (%LSP) if entire volumes were combined:

$$\%LP = \left(\frac{V1}{V1 + V2}\right) \otimes 100$$

$$\%LSP = \left(\frac{V2}{V1 + V2}\right) \otimes 100$$

3) Calculate the volume of liquid phase and leachate from the solid phase to combine to produce a given volume (FV) of the combined fractions:

$$Volume\ of\ liquid\ phase(mL) = \frac{\%LP}{100} \otimes FV$$

$$Volume\ of\ leachate\ from\ solid\ phase(mL) = \frac{\%LSP}{100} \otimes FV$$

4) Combine the calculated volumes in a labeled container, preserve as required, and store as given in Section 5.

TCLP EXTRACTIONS: VOLATILES

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Approved by:

R. Wayne Robb — 16 Aug 2001
Date

Title: Technical Manager, QA

STL X Savannah __ Tallahassee __ Mobile __ Tampa West

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1.0 SCOPE AND APPLICATION

1.1 The Toxic Compound Leaching Procedure (TCLP) is designed to simulate the leaching a waste will undergo when disposed of in a sanitary landfill. It can be used to determine the mobility of certain volatile compounds in liquid, solids, and multi-phase samples. The leachate produces by this zero-headspace procedure must be properly stored and preserved after the leaching procedure. An improperly stored and /or preserved leachate will cause erroneous results.

1.2 Table 1 lists the target compounds that are amenable to this leaching procedure, the regulatory limit for each target compound, and the matrix spiking level for each target compound. The reporting limit (RL), the method detection limit (MDL), and the accuracy and precision criteria for the target compounds are given in Section 5 of the current revisions of the STL *Comprehensive Quality Assurance Plan* and *Corporate Quality Assurance Plan*..

2.0 SUMMARY OF METHOD

2.1 The waste sample is initially evaluated for percent solids. If a waste contains less than 5% solids, the liquid phase after filtration is defined as the TCLP leachate. If the percent solids is greater than 5%, the solids and liquid phases must be separated. The liquid phase (if present) is properly collected, preserved , and refrigerated until time of analysis. The solid phase is extracted with twenty times the weight of the solid phase in extraction fluid for 18 hours. The leachate is collected and if compatible, is combined with the liquid phase from the solids determination. If the leachate is not compatible, the leachate is collected, properly preserved, and stored at 4C+/-2C until time of analysis.

2.2 The leachate is analyzed by purge and trap/GC/MS. If the liquid phase from the solids determination is not compatible with the leachate, the samples are analyzed individually and a weighted average is used to determine the total concentration of the contaminants. The results from the analysis of the leachate/liquid phase is compared to the regulatory limit to determine if the waste sample exhibits hazardous characteristics.

2.3 This SOP is based on SW-846 Method 1311.

3.0 SAFETY

3.1 Use good common sense when working in the lab. Do not perform any procedures that you do not understand or that will put you or others in potentially dangerous situations.

3.2 The analyst must treat each waste sample as a potential hazardous waste. If possible, the waste should be evaluated in a hood or other well ventilated area until the nature of the waste can be determined. The analyst must not be allowed to work alone in a confined area with waste samples until it is determined that the waste poses no immediate threat. An immediate threat would be the release of a toxic gas when the waste container is opened or when the waste is treated with the buffer or acid solutions.

3.3 The analyst must wear a lab coat or an apron and gloves when handling all waste samples. A face mask should be worn and if the sample contains volatile materials, a properly fitted respirator or mask should be worn.

3.4 The analyst must be aware of the potential hazard posed by the reagents used in this procedure. The analyst will prepare reagents using a strong acid (hydrochloric acid), a weak acid (acetic acid), and a strong base (sodium hydroxide). The MSDS for each reagent is located at each lab division. The MSDS lists the type of hazard that each reagent poses and safe use and handling procedures for the reagent.

4.0 INTERFERENCES

4.1 Interferences encountered in the analysis of the leachate or liquid phase of the sample are discussed in the appropriate analytical method (Table 1).

4.2 The ZHE extraction vessels must not be rinsed with solvents that will interfere with the analysis of the target compounds. The extraction vessels must be stored in an area that is free from contamination and the extraction procedure must take place in an area that is free from contamination.

5.0 SAMPLE COLLECTION, HANDLING, AND PRESERVATION

5.1 Waste samples are collected in glass containers with minimum headspace and refrigerated at 4C +/-2C until the time of the leaching procedure. The waste samples may contain very high levels of VOC and should be segregated from the "normal" samples. The waste sample must undergo the TCLP within fourteen (14) days of collection.

5.2 The liquid phase (from the solids determination) or the leachate are collected and stored with no headspace in a 40mL vial equipped with a Teflon-lined cap. Aqueous liquid phase should be preserved with 0.1mL of concentrated hydrochloric acid (HCl) per 40mL of sample prior to storage with zero headspace at 4C +/- 2C. The pH of the leachate is checked prior to storage. If the pH is greater than 2, 0.1mL of HCl is added per 40mL of leachate and the sample is stored at 4C +/- 2C. The leachate or liquid phase must be analyzed within 14 days of the leaching procedure.

6.0 APPARATUS AND MATERIALS

6.1 Extractor-Capable of holding several zero headspace extraction (ZHE) vessels and rotating the vessels continuously at a rate of 30rpm +/- 2rpm. The extractor must be maintained at 25C +/-2C during the TCLP.

6.2 Zero headspace extraction (ZHE) vessel- 500mL vessel capable maintaining zero headspace during the extraction procedure, available from Analytical Testing and Consulting Services, Inc. The vessel must allow for the initial liquid/solid phase separation and final leachate filtration while maintaining zero headspace conditions.

Two types of ZHE are currently used by STL:

1) The manual ZHE device uses a 48ft-lb torque wrench to turn the threaded piston rod and move the piston inside the vessel body.
2) The gas pressurized ZHE device uses nitrogen to move the piston inside the vessel body.

6.3 Filter media-Whatman GC/F, 90mm diameter, 0.70um pore size

6.4 pH meter

6.5 Laboratory balance-accurate to 0.01g

6.6 Laboratory glassware-beakers

7.0 REAGENTS

7.1 Reagent water-laboratory deionized water or other source of water that does not contain

the target compounds. A volume of water may be purged with nitrogen for at least 4 hours before use. The reagent water should be checked for impurities prior to the use of the reagent water to prepare the extraction fluid or other reagents.

7.2 Sodium hydroxide (NaOH)-reagent grade

7.3 Sodium hydroxide (1.0 N)-Dissolve 40.0g of NaOH in 800mL of reagent water contained in a 1-L volumetric flask. Dilute to volume with reagent water and mix thoroughly. Transfer the 1.0 N NaOH to a glass container equipped with a Teflon-lined cap. Do not store basic solutions in volumetric glassware equipped with ground- glass joints.

7.4 Glacial acetic acid (CH3COOH)-reagent grade

7.5 Extraction fluid #1(this is the only extraction fluid that is used for the TCLP for volatiles)- Combine 5.7mL of glacial acetic acid with 64.3ml of 1.0 N NaOH in a 1.0-L volumetric flask and dilute to volume with reagent water. The pH of this solution should be 4.93+/- 0.05. The extraction fluid should be prepared daily and the pH of each batch of extraction fluid must be verified prior to use. Larger volumes of extraction fluid may be prepared so that there is sufficient extraction fluid for each sample and for an extraction fluid blank for each batch of samples.

8.0 STANDARDS

The standards and spiking solutions that are used for the analysis of the leachate produced by the TCLP are given in STL SOP VM20:*Volatile Compounds by GC/MS (8260)*.

9.0 SAMPLE PREPARATION

The preparation steps should be performed quickly to minimize the loss of VOC from the waste.

9.1 The particle size of the sample must be reduced so that the sample can pass through a 9.5mm sieve. This particle size of the sample may be reduced by crushing, grinding, or cutting the sample. This step must be performed quickly to minimize the loss of VOC.

9.2 Weigh out approximately 100g of the solid waste sample into a pre-weighed 400-mL beaker. Weigh the beaker and record the weight on the extraction log.

9.3 Remove the filter holder of the ZHE vessel. The piston inside the ZHE should be very close the filter holder at this point. The piston may have to be "backed off" from the opening to allow the sample to be added to the vessel.

9.4 Transfer a 25g portion of the waste sample in the beaker to the vessel. Reweigh the beaker and calculate the weight of sample(Wsample) that was transferred to the vessel.

Wsample = weight of beaker after addition(g) - initial weight of the beaker/sample(g)

Since the total volume of the ZHE vessel will accommodate 25g of sample and 500mL of extraction fluid, the maximum weight of sample added to the ZHE vessel is 25g.
NOTE: Some types of samples may have very low densities-e.g., fabric samples, cardboard, or fly ash. The analyst will have to estimate the maximum weight of sample that will allow the use of the maximum amount of extraction fluid without overfilling the ZHE vessel. A rule of thumb is to error on the low side to ensure sufficient room in the extraction vessel for the waste sample and the extraction fluid.

9.5 Replace the filter holder assembly on to the ZHE vessel. Connect a pre-weighed syringe to the ZHE turn the piston handle or increase the pressure to 10psi until the piston slightly compresses the sample.

9.5.1 If the manual ZHE is being used, continue to turn the torque wrench and collect the liquid phase from the sample until the torque wrench slips. The pressure applied to the sample inside the ZHE vessel will be about 50psi when the wrench slips. Close the valve on the ZHE. Label and store the liquid phase in the volatiles refrigerator.

9.5.2 If the nitrogen pressurized ZHE vessel is being used, increase the pressure in 10psi increments to 50psi and collect the liquid phase in the syringe. The pressure should be maintained at each level for two minutes until no more liquid is filtered from the sample. Close the valve on the ZHE. Label and store the liquid phase in the volatiles refrigerator.

$$percent\ solids = \frac{(W_{sample}) - (Ws2 - Ws1)}{W_{sample}} x\ 100$$

9.6 Weigh the syringe containing the liquid phase and calculate the percent solids:

where

W_{sample} = weight of sample added to the ZHE (g)
Ws2 = weight of the syringe and the liquid phase of the sample (g)
Ws1 = weight of the syringe (g)

If the percent solids is less than 5%, the filtered liquid phase is considered the TCLP leachate. The solids portion is discarded and the liquid phase is preserved and refrigerated prior to analysis to determine if the sample demonstrates hazardous characteristics.

9.7 Calculate the volume (Vexf) of extraction fluid #1 that is to be added to the ZHE .

$$Vexf(mL) = (W_{sample} - (Ws2 - Ws1)) \times 20$$

where

W_{sample} = weight of sample added to the ZHE (g)
Ws2 = weight of the syringe and the liquid phase of the sample (g)
Ws1 = weight of the syringe (g)

NOTE: The volume of extraction fluid added to the ZHE is twenty times the weight of the ***solid portion of the sample.***

9.8 Manual ZHE

9.8.1 Add Vexf (mL) of extraction fluid #1 to a separatory funnel. Connect tubing from the separatory funnel to the ZHE. The ZHE positioned so that the valve is pointing up.

9.8.2 Open the valve on the ZHE and slowly turn the piston handle to draw all of the extraction fluid into the vessel. The extraction fluid will flow through the filter and into the ZHE vessel.

9.8.3 Close the valve and the invert the ZHE several times to mix the contents of the ZHE. Open the valve and slowly turn the piston handle until the extraction fluid just flows out of the valve. Close the valve.

9.9 Gas-pressurized ZHE

9.9.1 Add Vexf (mL) of extraction fluid #1 to the extraction fluid reservoir. Connect tubing from the reservoir to the ZHE. The ZHE positioned so that the valve is pointing up.

9.9.2 Open the valve on the ZHE and slowly add the extraction fluid into the vessel. The extraction fluid will flow through the filter and into the ZHE vessel.

9.9.3 Close the valve and the invert the ZHE several times to mix the contents of the ZHE. Open the valve and slowly increase the pressure until the extraction fluid just flows out of the valve. Close the valve.

9.10 Place the ZHE on the rotary extractor and rotate the samples for 18 hours. The temperature of the room must be maintained at 23C +/- 2C during the leaching step.

9.11 After the leaching period has finished, remove the ZHE from the rotary extractor. Open the valve on the ZHE and turn the piston to expel the leachate from the ZHE. The leachate is collected 40-mL VOA vials equipped with Teflon-lined caps. Collect at least four vials and acidify the leachate samples with approximately 0.10ml of concentrated hydrochloric acid. Store the leachate samples at 4C +/- 2C until analysis by GC/MS.

EXAMPLE
A waste sample is submitted to STL for evaluation for TCLP VOC. The waste sample is mixture of solids (primarily soil) and water. The waste sample is thoroughly mixed and an aliquot of the waste sample is weighed into a 400mL beaker.

1) The weight of the aliquot is determined to be 120g.

weight of aliquot = (weight of beaker + aliquot) - (weight of beaker)

The weight of the waste sample added to the ZHE is 24g.

2) The ZHE is pressurized to expel the liquid phase and the liquid phase is collected in a pre-weighed syringe.

weight of liquid phase(g) = (weight of liquid phase + syringe) - (weight of syringe)

The liquid phase has a weight of 10g.

$$percent\ solids = \frac{(weight\ of\ aliquot) - (weight\ of\ liquid\ phase)}{(weight\ of\ aliquot)} x\ 100$$

3) The percent solids is calculated.

4) The ZHE contains 14 g of the solids phase of the waste sample. The volume of extraction fluid #1 that is added to the ZHE is 14 x 20 =280ml. The sample is rotated for 18 hours at 30rpm while maintaining the temperature at 23C +/- 2C.

$$percent\ solids = \frac{24g - 10g}{24g} x\ 100 = 58.3\%$$

5) The entire leachate in the ZHE is filtered and the volume of the of the leachate is determined.

6) 1mL of the leachate and 1mL of the liquid phase are combined to determine if they are compatible. In this case, the leachate and the liquid phase are compatible.

Any combination of volumes (liquid phase and leachate) that maintains the basic ratio of the leachate to the liquid phase may be used for convenience.

10.0 PROCEDURE

The analytical procedure is given in STL SOP VM20:*Volatile Compounds by GC/MS (8260).*

11.0 DATA ANALYSIS/CALCULATIONS

The procedure for the qualitative and quantitative evaluation of the analysis of the leachate for VOC is given in STL SOP VM20:*Volatile Compounds by GC/MS (8260).*

If the liquid and leachate are not compatible and are analyzed separately, combine the

$$Analyte\ concentration(mg/L) = \frac{(V_1)(C_1)+(V_2)(C_2)}{V_1+V_2}$$

results mathematically using the following equation:

where

V_1 = volume of the liquid (L)
C_1 = concentration of the liquid (mg/L)
V_2 = volume of the leachate (L)
C_2 = concentration of the leachate (mg/L)

NOTE: The volume of the liquid and leachate must be expressed as liters (1mL = 0.001L).

12.0 QUALITY CONTROL/QUALITY ASSURANCE

12.1 TCLP Batch

12.1.1 An extraction fluid blank must be processed for each batch of twenty or fewer samples that are subjected to the TCLP.

12.1.2 For each batch of twenty or fewer samples, one sample must be taken through the TCLP in duplicate.

12.1.3 For each batch of twenty or fewer samples, one sample leachate spiked according to the sample preparation section given in the analytical procedures. Table 1 of this SOP lists the compounds that are included in the TCLP leachate spike and the concentration that the sample leachate is spiked.

13.0 TROUBLESHOOTING

No items for this section in this revision.

14.0 PREVENTIVE MAINTENANCE

No items for this section in this revision.

15.0 REFERENCES

15.1 *STL Comprehensive Quality Assurance Plan* and *STL Corporate Quality Assurance Plan*, current revisions.

15.2 *Test Methods for Evaluating Solid Wastes, Third Edition, SW-846*; US EPA Office of Solid Waste and Emergency Response: Washington, DC.

TABLE 1

TCLP Levels for Volatile Compounds - EPA 8260/SOP VM20		
Parameter	**Reg. Limit (mg/L)**	**Matrix Spike Level (mg/L)**
Benzene	0.5	0.50
Carbon tetrachloride	0.5	0.50
Chlorobenzene	100.0	0.50
Chloroform	6.0	0.50
1,2-Dichloroethane	0.5	0.50
1,1-Dichloroethylene	0.7	0.50
Methyl ethyl ketone	200.0	0.50
Tetrachloroethylene	0.7	0.50
Trichloroethylene	0.5	0.50
Vinyl chloride	0.2	0.50

OXIDATION-REDUCTION POTENTIAL (ORP)

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Approved by:

R. Wayne Robbins — 26 Dec 2000
R. Wayne Robbins — Date
Title: STL Technical Manager, QA

Approved by:

01-02-01
Date
Title: Laboratory Director
STL X Savannah __ Tallahassee __ Mobile __ Tampa West

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1.0 SCOPE AND APPLICATION

The purpose of this SOP is to describe the procedures used to determine the oxidation-reduction potential in water and soil matrices in the range of 0 to approximately +1000. This SOP is prepared by and for STL Savannah, STL Tallahassee, STL Mobile, and STL Tampa West.

2.0 SUMMARY OF METHOD AND DEFINTIONS

2.1 Oxidation-reduction potential (ORP) is defined as the electromotive force between a noble metal electrode and a reference electrode when immersed in a solution. The ORP measurement establishes the ratio of oxidants and reductants prevailing within the solution. By this measurement, the ability to oxidize or reduce species in the solution may be determined.

2.2 ORP is measured by immersing a calibrated electrode pair (sensing and reference) into an aqueous solution and reading and recording the millivolt signal (the ORP). A modification of the reference method is performed to determine the ORP in soils and solids. A 5g aliquot of the solid is mixed with 100 ml of reagent water and extracted for two hours. The solids are allowed to settle and the ORP is determined on the aqueous phase.

2.3 This SOP is based on the guidance in ASTM Method D 1498-76 (re-approved 1981) and Standard Methods 2580 (proposed).

NOTE: Both reference methods recommend that ORP be determined at the time of sampling. The measurement of ORP in the laboratory may result in lower or higher values due to the time between sampling and analysis. No hold time criterion is given in either method.

3.0 SAFETY

3.1 The analyst should wear a lab coat, gloves, and eye protection when performing this procedure. Use good common sense when working in the lab. Do not perform any procedures that you do not understand or that will put you or others in potentially hazardous situations.

3.2 The analyst should be familiar with the Material Safety Data Sheets (MSDS) for each reagent used in this procedure.

4.0 INTERFERENCES

The ORP electrodes reliably measured ORP in nearly all aqueous solutions and in general are not subject to solution interference from color, turbidity, colloidal matter and suspended matter.

The ORP of an aqueous solution is sensitive to change in temperature of the solution, but temperature correction is rarely done due to its minimal effect and complex reactions. Temperature corrections are usually applied only when it is desired to relate the ORP to the activity of an ion in the solutions.

The ORP of an aqueous solution is sensitive to pH variations when the oxidation-reduction reaction involves either hydrogen or hydroxyl ions. The ORP generally tends to increase with an increase in hydrogen ions and to decrease with an increase in hydroxyl ions during such reactions.

Reproducible oxidation-reduction potentials cannot be obtained for chemical systems that are not reversible. The measurement of end point potential in oxidation-reduction titration is sometimes of this type.

If the metallic portion of the ORP electrode is sponge-like, materials absorbed from solutions may not be washed away, even by repeated rinsings. In such cases, the electrode may exhibit a memory effect, particularly if it is desired to detect a relatively low concentration of a particular species immediately after a measurement has been made in a relatively concentrated solution. A brightly polished metal electrode surface is required for accurate measurements.

The ORP resulting from interactions among several chemical systems present in mixed solutions may not be attributable to any single chemical.

5.0 SAMPLE COLLECTION, HANDLING, AND PRESERVATION

Aqueous and soil/solid samples are routinely collected in glass or plastic containers. The containers should be filled with minimum headspace. No chemical preservative should be added. The samples are iced at the time of collection and maintained at 4°C (less than 6°C with no frozen samples) in the laboratory until the time of analysis. The samples should be analyzed as soon as possible.

6.0 APPARATUS AND MATERIALS

6.1 pH meter or other meter compatible with the ORP electrodes, capable of measuring to $^{+}$1400mV.

6.2 ORP combination electrode - platinum electrode with silver/silver chloride reference cell

6.3 Disposable cups or other suitable containers

6.4 Teflon stir bars

6.5 Magnetic stirring plate

7.0 REAGENTS

Reagents must be traced in accordance with STL SOP AN44:*Reagent Traceability*

7.1 Reagent water - laboratory deionized water

7.2 Electrode filling solution

8.0 STANDARDS

Standards must be tracked in accordance with STL SOP AN41:*Standard Material Traceability.*

8.1 Ferrous ammonium sulfate (Fe(NH4)2 - (SO4)2•6H20) - reagent grade

8.2 Ferric ammonium sulfate ((FeNH4(SO4)2•6H_2O) - reagent grade

8.3 Sulfuric acid - reagent grade, specific gravity of 1.84

8.4 Redox Standard Solution (ORP=+476)
Dissolve 39.21g of ferrous ammonium sulfate, 48.22g of ferric ammonium sulfate, and 56.2ml of concentrated sulfuric acid in reagent water and dilute to 1.0L with reagent water. Store the solution with minimum headspace in an amber container at 4°C. Prepare a new solution every three months (quarterly) or sooner if ORP measurements fail the acceptance criteria of ± 10mV.

9.0 SAMPLE PREPARATION

9.1 Aqueous samples require no preparation except to equilibrate to room temperature prior to ORP measurement. All samples must be analyzed in duplicate; that is, separate aliquots of the sample must be analyzed.

9.2 Soils and solids

9.2.1 Remove the samples from storage and allow to equilibrate to room temperature.

9.2.2 Homogenize the sample thoroughly and weigh two 20-20.5g potions of the sample a separate containers. Glass or plastic containers may be used. The volume of the container should be sufficient to hold the sample and reagent water.

9.2.3 Add a volume (mL) of reagent water equal to the weight (g) of sample added to the container. For example, if 20g of sample is added to the container, add 20mL of reagent water.

9.2.4 Mix the sample and reagent water thoroughly and allow the sample to sit for 10 minutes with occasional stirring.

9.2.5 Measure and record the ORP of the sample/water slurry using the procedures in Section 10 of this SOP.

9.2.6 Prepare a reagent blank by adding 20mL of reagent water to a container. Process the blank in the same manner as the samples.

10.0 ANALYTICAL PROCEDURE

10.1 Prepare the electrode and meter in accordance with the manufacturer's specifications.

10.2 Check the sensitivity of the ORP electrodes by placing the electrodes in the Redox Standard (8.4). Allow the reading to stabilize. Add a small aliquot of dilute sodium hydroxide solution and note the speed and direction of the reading. If the ORP drops sharply when the sodium hydroxide is added, the electrodes are sensitive and operating properly. If ORP <u>increases</u> sharply, the polarity is reversed and must be corrected in accordance with the manufacturer's manual. If the ORP does not respond when caustic is added, or if the response is sluggish, the electrode should be cleaned in accordance with the manufacturer's instructions.

10.3 Place a new aliquot of the Redox Standard (8.4) into a cup and add a Teflon stir bar. Slowly mix the solution and determine the ORP. The true value is +476 and the reading should be within 10mV (±10mV). If the reading is not within the acceptance range, perform electrode cleaning or maintenance in accordance with the manufacturer's instructions.

10.4 Allow the samples to equilibrate to room temperature.

10.5 For aqueous samples, transfer an aliquot of the sample to a disposable, plastic container. Add a Teflon stir bar and place on the stir plate. For soils, place a Teflon stir bar in the water/sample slurry and place on the stir plate.

10.6 Rinse the electrode three times with reagent water. Immerse the electrode into the sample a slowly mix the sample. Allow the reading to stabilize and record.

Repeat with the second sample aliquot. The readings should agree within 10mV. Report the average of the two readings as the ORP.

ANALITICAL SEQUENCE

Sensitivity Check
Redox Standard (476 ± 10mV)
10 Sample Readings
Redox Standard (476 ± 10mV)
10 Sample Readings
Redox Standard (476 ± 10mV)

11.0 DATA ANALYSIS AND CALCULATIONS

ORP is a direct readout and requires no calculations.

12.0 QUALITY CONTROL / QUALITY ASSURANCE

12.1 The sensitivity and polarity of the electrode must be checked each time ORP is determined.

12.2 The Redox Standard must be analyzed at a minimum frequency of once per every ten (10) samples.

12.3 All samples must be analyzed in duplicate. The duplicate should agree within ± 10mV.

If the readings do not agree within 10mV, repeat the preparation and analysis of the sample. If the results agree within 10mV, report the average of the readings. If the second analysis does not agree, contact the supervisor or technical manager for guidance.

If repeated duplicate analyses of the sample do not agree within 10mV, report both readings and qualify the results.

12.4 Determination of the method detection limit is not required for this procedure since this is an empirical measurement like the determination of pH. The initial demonstration of capability must be performed in accordance with SOP CA92: *Evaluation of IDOCs*.

13.0 PREVENTIVE MAINTENANCE AND TROUBLE SHOOTING

Follow manufacturer's instructions

14.0 WASTE MANAGEMENT AND POLLUTION PREVENTION

Excess samples, reagents, and QC items must be disposed of in accordance with STL SOP CA70:*Waste Management*.

15.0 REFERENCES

American Society for Testing and Materials (ASTM) Method D1498-76 (re-approved in 1981)

Standard Methods for the Examination of Water and Wastewater; 18th Edition (1992)Oxidation-Reduction Potential (2580 - Proposed)

Approval Signature: R. Wayne Robbins
Title : Corporate QA Manager Date : Aug 11, 1998

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DISSOLVED OXYGEN
(Azide Modification)

1.0 SCOPE AND APPLICATION

This method is applicable to the laboratory measurement of dissolved oxygen in natural and wastewater samples which have been collected in the field and "fixed" with the proper Winkler reagents. The reporting limit for dissolved oxygen by this method is 0.1 mg/L.

2.0 SUMMARY OF METHOD

Divalent manganese added to a sample containing dissolved oxygen is oxidized to higher valence states. In the presence of iodide in acidic solution, any oxidized manganese is reduced to the divalent state, with the subsequent stoichiometric liberation of iodine. The liberated iodine is titrated with a standard solution of thiosulfate. This method is based on Standard Method 4500-O-C and EPA Method 360.2.

3.0 SAFETY

3.1 Do not perform any procedures that you do not understand or that will put you or others in potentially hazardous situations.

3.2 Wear a lab coat or apron, gloves, and eye protection when performing the analysis.

3.3 The analyst must be familiar with the Material Safety Data Sheets for each reagent and standard used in this procedure.

4.0 INTERFERENCES

4.1 Ferric iron is an interferant at concentrations greater than 100 mg/L; the potassium fluoride modification described in Standard Methods can be used to eliminate this interference.

4.2 The interference caused by ferrous iron can be eliminated by using the permanganate modification of the Winkler titration described in Standard Methods.

5.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

Samples are collected in 300-mL glass BOD bottles containing the required reagents. Appendix A contains the from that is sent tot he field with all dissolved oxygen sample containers.

6.0 APPARATUS AND MATERIALS

Burette-10mL with 0.1mL increments

7.0 REAGENTS

7.1 Manganous sulfate: Hach powder pillows

7.2 Alkali-iodide-sodium azide solution: Hach powder pillows

7.3 Sulfamic acid: Hach powder pillows

7.4 Starch indicator: Commercially prepared.

7.5 Sodium thiosulfate solution: commercially prepared, 0.025 N standardized solution. Standardized weekly using the procedures found in SL SOP GE 100: *Sulfide by Iodometric Titration* (Section 7.15)

8.0 STANDARDS-none required

9.0 SAMPLE PREPARATION-none required.

10.0 PROCEDURE

Samples are received from the field already prepared with proper reagents.

10.1 Pour 200 mL of prepared sample into an Erlenmeyer flask.

10.2 Titrate with standardized 0.025 N $Na_2S_2O_3$ solution to a pale straw color. It is important to titrate to this color before adding the starch indicator. Add a few drops of starch indicator and continue titration dropwise until the blue color first disappears.

10.3 Calculate the dissolved oxygen concentration. For titration of 200 mL of sample that has been treated with the appropriate reagents:

$$\text{mg/L O2} = V \otimes \frac{1\,\text{mg/L O2}}{\text{mL 0.025N thiosulfate solution}}$$

where V = volume of 0.025N sodium thiosulfate to reach endpoint (mL)

11.0 CALCULATIONS

Calculation of dissolved oxygen given in Section 10.

12.0 QUALITY CONTROL/QUALITY ASSURANCE

Duplicate analyses are performed if samples are available.

13.0 TROUBLE-SHOOTING-none

14.0 PREVENTIVE MAINTENANCE-none

15.0 REFERENCES

1. *Standard Methods for the Examination of Water and Wastewater*, Eighteenth Edition; American Public Health Association: Washington, DC, 1992.

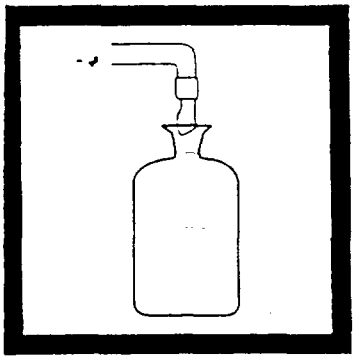
2. *Methods for Chemical Analysis of Water and Wastes,* EPA-600/4-79-020; USEPA EMSL Office of Research and Development, Cincinnati, Ohio. March 1983

Method 8229

OXYGEN, DISSOLVED (DO)

For water, wastewater and seawater

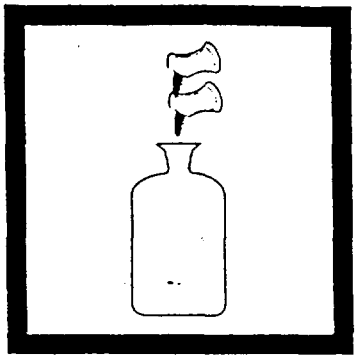
Azide Modification of Winkler Method Buret Titration* ; USEPA Approved



1. Collect a water sample in a clean, 300-mL, glass-stoppered BOD bottle.

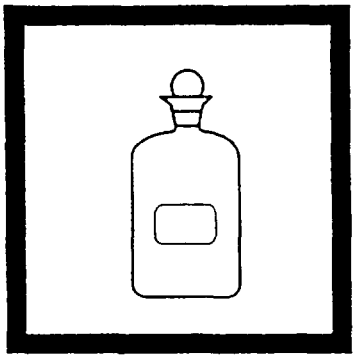
Note: Overflow the bottle two or three minutes to remove any trapped air bubbles.

Note: If samples can not be analyzed immediately, see Sampling and Storage following these steps.



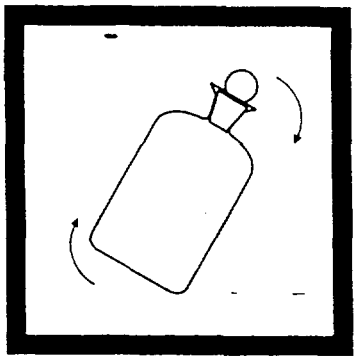
2. Add the contents of one Manganous Sulfate Powder Pillow and one Alkaline Iodide-Azide Reagent Powder Pillow.

Note: One mL of Manganous Sulfate Solution and 1 mL of Alkaline Iodide-Azide Reagent can be substituted for the respective powder pillows.



3. Immediately insert the stopper so that no air is trapped in the bottle. Invert several times to mix.

Note: A flocculent precipitate will form. It will be orange-brown if oxygen is present or white if oxygen is absent. The floc will settle very slowly in salt water and usually will require an additional five minutes before proceeding with Step 5.



4. Wait until the floc in the solution has settled. Again invert the bottle several times and wait until the floc has settled.

Note: Waiting until floc has settled twice assures complete reaction of the sample and reagents. Results will not be affected if the floc does not settle.

* Adapted from *Standard Methods for the Examination of Water and Wastewater.*

DISSOLVED FERROUS IRON: COLORIMETRIC

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Approved by:

R. Wayne Robbins — 21 March 2001
Date

Title: Technical Manager, QA

STL: ✓ Savannah __ Tallahassee __ Mobile __ Tampa West

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1.0 SCOPE AND APPLICATION

1.1 This procedure is used to determine the dissolved ferrous iron in domestic and natural waters and certain industrial wastes. Ferric iron can be calculated by subtracting the ferrous iron concentration from the total iron concentration.

1.2 The reporting limit (RL), the method detection limit (MDL), and the accuracy and precision criteria are listed in the current revision of the *Laboratory Quality Manual* prepared by and for STL Savannah, STL Tallahassee, STL Mobile, and STL Tampa West. The routine RL for ferrous iron is 0.10mg/L.

2.0 SUMMARY OF METHOD AND DEFINITIONS

2.1 Dissolved ferrous iron is determined colorimetrically by its reaction with 1,10-phenanthroline. The reaction produces an orange color which is measured at 510nm.

2.2 Method Clarifications and Modifications
This procedure is for the determination of dissolved ferrous iron. No digestion procedure is performed prior to analysis. The sample must either be filtered in the field and preserved at that time by the addition of 1mL of concentrated hydrochloric acid (HCl). If field filtration is not possible, the sample is sent to the lab un-preserved and unfiltered. The sample is filtered in the lab and preserved at that time if the sample cannot be analyzed within 24 hours of collection.

Standard Methods, 18th Edition, states to "determine the ferrous iron at the sampling site because of the possibility of changes in the ferrous-ferric (iron) ratio with time in acid solution." Acidification of a sample containing particulates may cause the iron present in the solids to become soluble. Therefore, an un-preserved sample is the recommended for laboratory determination of the ferrous iron content.

2.3 Definitions

Dissolved ferrous iron - the ferrous iron in a sample that has been passed through a 0.45um filter

2.4 This method is based on the guidance in Standard Method 3500-Fe-D and in HACH Method Iron, Ferrous, 1,10-Phenanthroline Method .

3.0 SAFETY

3.1 Use good common sense when working in the lab. Do not perform any procedures that you do not understand or that will put you or others in potentially dangerous situations.

3.2 The analyst will use strong acids and bases in the procedure. The analyst must wear a lab coat or apron, eye protection, and latex gloves when performing the method.

3.3 The analyst must be familiar with the Material Safety Data Sheets (MSDS) for each reagent and material used in this procedure.

4.0 INTERFERENCES

The reaction is of ferrous iron with 1,10-phenanthroline is free from common interferences. Long storage times or exposure of samples to light must be avoided. Protect from light and analyze as soon as possible.

5.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

Samples are routinely collected in 250-mL plastic bottles with no preservative. Samples are iced at the time of collection and stored at 4°C (less than 6C but not frozen) until the time of analysis. Protect from light and analyze the samples as soon as possible.

If the sample(s) cannot be analyzed within 24 hours of collection, filter the samples through a 0.45um filter and adjust the pH to <2 with concentrated HCl. Store the samples at 4°C (less than 6C but not frozen) and protect from light. Analyze as soon as possible.

6.0 APPARATUS AND MATERIALS

6.1 Spectrometer for use at 510nm or a filter-photometer equipped with a green filter having maximum transmittance near 510nm. One centimeter cells compatible with the spectrometer are routinely used.

6.2 Volumetric Flasks - 100mL

6.3 Analytical Balance

6.4 Pipettes

6.5 Disposable plastic beakers (25mL)

6.6 Graduated cylinders (25mL or 50mL)

6.7 Filters - 0.45 um

7.0 REAGENTS

Reagents must be tracked in accordance with STL SOP AN44: *Reagent Traceability.*

7.1 Reagent water-lab-generated deionized water

7.2 Sodium Hydroxide, 5N: Dissolve 20 grams of NaOH in reagent water and dilute to 100mL.

7.3 Hydrochloric Acid, reagent grade.

7.3 Hach Ferrous Iron Reagent Powder Pillows.

8.0 STANDARDS

The preparation of standards must be documented in accordance with STL SOP AN41: *Standards Materials Traceability*. Different volumes of standards can be prepared at the discretion of the lab. The vendors and sources of standard materials may be different from those listed.

8.1 Calibration Standards

8.1.1 Ferrous Iron Calibration Stock Solution, 1000 mg/L: prepare by dissolving 0.7022 grams of ferrous ammonium sulfate hexahydrate in reagent water and diluting to 100mL with reagent water.

8.1.2 Ferrous Iron Calibration Intermediate Standard, 100 mg/L: Dilute 10mL of 1000 mg/L ferrous iron calibration stock solution to 100mL with reagent water.

8.1.3 The calibration standards are prepared using the following table for guidance. Add 20-30mL of reagent water into six 100-mL volumetric flasks. Add the appropriate volumes of intermediate standard and dilute to volume with reagent water.

Cal Std	Intermediate Conc (mg/L)	Volume of Int (mL)	Final Volume (mL)	Cal Std Conc (mg/L)
blank	NA	0	100	0.000
1	100	0.050	100	0.050
2	100	0.10	100	0.10
3	100	0.20	100	0.20
4	100	0.50	100	0.50
5	100	1.0	100	1.0

8.2 Calibration Verification Standards

8.2.1 Ferrous Iron Calibration Verification Stock Solution, 1000 mg/L: prepare by dissolving 0.7022 grams of ferrous ammonium sulfate hexahydrate in reagent water and diluting to 100-mL. This ferrous ammonium sulfate hexahydrate must be from a source that is different than that used for the calibration standards.

8.2.2 Ferrous Iron Calibration Verification Standard (ICV/CCV), 0.50 mg/L: Dilute 0.050mL (50uL) of 1000 mg/L ferrous iron calibration verification stock solution to 100mL with reagent water.

9.0 SAMPLE PREPARATION

Filter the sample through a 0.45um filter and adjust to pH 4.8-5.0 before the test using dilute base or acid as necessary. The pH must not exceed 5 or the ferrous iron may be converted to ferric iron, which will not be measured by this test.

10.0 ANALYSIS PROCEDURE

10.1 The spectrometer is turned on and allowed to become thermally stable before beginning to analyze the standards and samples. It will take a minimum of thirty minutes for the spectrometer to warm up. Remove the samples from the refrigerator and allow them to equilibrate to room temperature while the spectrometer is warming up.

10.2 Transfer two 25-mL aliquots of each calibration standard, verification standard, and calibration blank to separate labeled disposable beakers. One aliquot will be treated with the color reagent and the untreated aliquot will be used to zero the spectrometer.

Transfer two 25mL portions of each filtered sample to be tested into separate labeled disposable beakers.

One aliquot will be treated with the color reagent, and the second untreated aliquot will be used to zero the spectrophotometer to correct for color due to the sample.

For the filtered sample chosen as the MS/MSD, transfer four aliquots of sample into labeled separate disposable beakers. One aliquot will be treated with the color reagent, two aliquots will be spiked and treated with the color reagent, and the remaining untreated aliquot will be used to zero the spectrophotometer.

Spike the 25mL aliquots of each filtered sample designated as the MS or MSD with 0.050mL of the Ferrous Iron Intermediate Calibration Standard (100 mg/L). This will yield a 0.20 mg/L matrix spike (see calculation below).

$$Cms = \frac{0.050mL \otimes 100mg/L}{25mL} = 0.20mg/L$$

10.3 Add a powder pillow to one portion of each calibration standard, verification standard, and sample and to each spiked sample aliquot. Let stand for a minimum of 5 minutes for full color development (sample must be analyzed within 30 minutes of the addition of the powder pillow).

10.4 Analysis and Evaluation of the calibration standards

10.4.1 Transfer a portion of a calibration standard without the powder pillow to the absorption cell. Zero the instrument with this portion. Immediately transfer the standard with the powder pillow to the absorption cell and record the reading. Repeat for all standards.

10.4.2 Use a calculator or spreadsheet to evaluate the calibration curve using linear regression. The correlation coefficient must be greater than or equal to 0.995 for the curve to be used to quantify samples.

10.5 Analysis of the Calibration Verification Standards and Blanks

10.5.1 Transfer a portion of the ICV/CCV standard without the powder pillow to the absorption cell. Zero the instrument with this portion. Immediately transfer the standard with the powder pillow to the absorption cell and record the reading. The ICV/CCV standard must be read at the beginning and end of the analysis run and after every 10 samples.

10.5.2 Calculate the concentration of the ICV/CCV using the regression curve.
- the concentration of the ICV must be within 10% of the true concentration.
- the concentration of the CCV must be within 20% of its true concentration.

10.5.3 Transfer a portion of the ICB/CCB standard without the powder pillow to the absorption cell. Zero the instrument with this portion. Immediately transfer the standard with the powder pillow to the absorption cell and record the reading. The ICB/CCB standard must be read at the beginning and end of the analysis run and after every 10 samples (after the ICV/CCV standard).

10.5.4 Determine the concentration of the ICB/CCB using the regression curve. The concentration of the blank must be less than the RL listed in the *Laboratory Quality Manual.*

10.6 Sample Analysis

10.6.1 Transfer the portion of the sample (un-spiked and without the powder pillow) into the absorption cell and re-zero instrument.

10.6.2 Transfer the un-spiked portion of the sample with the powder pillow into the absorption cell. Record the reading. From this corrected absorbance reading determine the mg/L of ferrous iron present using the regression curve.

10.6.4 Transfer the spiked portion (if applicable) of the sample with the powder pillow into the absorption cell. Record the reading. From this corrected absorbance reading determine the mg/L of ferrous iron present using the regression curve.

The analysis should follow the sequence:

ANALYTICAL SEQUENCE

Initial Calibration-5 calibration standards
Initial Calibration Verification (ICV)
Initial Calibration Blank (ICB)
10 absorbance readings
Continuing Calibration Verification (CCV)
Continuing Calibration Blank (CCB)
10 absorbance readings
Continuing Calibration Verification (CCV)
Continuing Calibration Blank (CCB)

The sequence continues until all samples have been analyzed or until the verification standards fail to meet the acceptance criteria. Sample data must bracketed by acceptable verification standards

10.7 Calculate the concentration of each spiked and un-spiked sample aliquot using the regression curve.

If any sample or spiked sample absorbance exceeds the absorbance of the highest calibration standard (1.00 mg/L), the sample and spiked sample (if applicable) must be diluted so that the absorbance falls within the working range of the instrument. The dilution factor, DF, is calculated as follows:

$$DF = \frac{Vf}{Vsample}$$

Vf = final volume of the dilution (mL)
Vsample = volume of sample used to prepare the dilution (mL)

11.0 CALCULATIONS

$$C(sample) = C(curve) \otimes DF$$

where

C(sample) = concentration of sample (mg/L)
C(curve) = concentration of sample from curve (mg/L)
DF = dilution factor

The results are routinely reported to two significant figures as "mg/L". See SOP CA80 for additional guidance for reporting results. Report the recovery of the ICV or CCV as the lab control sample.

12.0 QUALITY CONTROL/QUALITY ASSURANCE

12.1 The analytical batch consists of twenty or fewer samples and the associated QC items. The ICB and CCB are evaluated and reported as the method bank. The ICV/CCV are reported as the lab control samples. Matrix spikes are analyzed for every batch of samples or 5% of sample, whichever is more frequent. Since there is no preparation for this procedure, a new batch number is assigned every 20 field samples analyzed on the same day.

If the matrix spikes fail, indicating the presence of matrix interferences, then all samples associated with the MS/MSD must be spiked and analyzed for interferences. Those samples whose matrix spikes fail should be diluted and re-spiked or analyzed by the method of standard additions (MSA).

Evaluate the quality control samples in each batch of samples in accordance with SOP AN02:*Analytical Batching*. SOP AN02 contains the equations for the calculation of accuracy and precision and guidance for corrective actions. The major QC items and recommended corrective actions are summarized in the SOP Summary in the appendix.

12.2 All analysts who perform this test must complete an initial demonstration of capability in accordance with SOP CA92:*Evaluation of IDOCs*.

12.3 The lowest standard in the calibration curve must be at or below the required project reporting limit. For routine samples, the RL is 0.10mg/L.The MDL must be determined in accordance with SOP CA90:*Procedures for the Determination of the Method Detection Limit (MDL.)*.

13.0 PREVENTATIVE MAINTENANCE AND TROUBLE-SHOOTING-No items for this section in the current revision of SOP.

14.0 WASTE MANAGEMENT AND POLLUTION PREVENTION

Excess samples and reagent s must be disposed in accordance with SOP CA70:*Waste Management.*

15.0 REFERENCES

15.1 *Standard Methods for the Examination of Water and Wastewater*; Eighteenth Edition; American Public Health Association: Washington, DC, 1989.

15.2 *Water Analysis Handbook*; HACH Company, 1985

APPENDIX – SOP SUMMARY

COLLECTION, PRESERVATION, AND STORAGE
Samples are routinely collected in 250-mL plastic bottles with no preservative. Samples are iced at the time of collection and stored at 4°C (less than 6C but not frozen) until the time of analysis. Protect from light and analyze the samples are soon as soon as possible. If the sample(s) cannot be analyzed within 24 hours of collection, filter the samples through a 0.45um filter and adjust the pH to <2 with concentrated HCl. Store the samples at 4°C (less than 6C but not frozen) and protect from light. Analyze as soon as possible.

QC ITEM	FREQUENCY	ACCEPTANCE CRITERIA	CORRECTIVE ACTION
Initial Calibration	Initially and when verification standards fail to meet acceptance criteria	Minimum three point curve with correlation coefficient >=0.995 and acceptable ICV	-reevaluate curve -re-prep and re-analyze one or more standards -prepare new stock, calibration standards, and re-analyze
Initial Calibration Verification(ICV)	After initial calibration	+/-10% of true value	-reevaluate calibration curve -re-prep and re-analyze ICV standard -re-prep ICV stock -re-calibrate
Continuing Calibration Verification (CCV)	After every 10 absorbance readings	+/-20% of true value	-reevaluate calibration curve -re-prep and re-analyze CCV standard -re-prep CCV stock -re-calibrate
Initial/Continuing Calibration Blank (ICB/CCB)	After verification standards	< RL	-reevaluate calibration curve -re-prep and re-analyze ICB/CCB standard -locate source of contamination and re-prep and re-analyze ICB/CCB
Lab control sample (LCS)	The ICV and CCV are prepared from a source independent of the calibration standards and is reported as the LCS.		
Matrix spike/Matrix spike duplicate (MS/MSD)	Per batch of 20 or fewer samples (1 MS and 1 MSD per 20 samples)	Recovery within LQM control limits	-report recoveries and flag results as having matrix interference -spike all samples associated with the MS/MSD and evaluate for matrix interferences -dilute the samples to minimize the matrix interferences, re-spike and reanalyze -analyze samples by MSA
Initial Demonstration of Capability (IDOC)	Per analyst	SOP CA92	SOP CA92
Method Detection Limit (MDL)	Annually	SOP CA90	SOP CA90

NITRITE AND NITRATE PLUS NITRITE
LACHAT QUICKCHEM AE PROCEDURE

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Approved by:

October 26, 1999

Title: STL-SL QA Manager Date

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1.0 SCOPE AND APPLICATION

1.1 This automated method for nitrite and nitrate plus nitrite determination is applicable to ground water, drinking water, surface water, domestic and industrial wastes, sediments, and soils.

1.2 The method detection limit(MDL), the reporting limit, and the accuracy and precision limits are in Table 5 of the STL-SL Laboratory Quality Management.

2.0 SUMMARY OF METHOD

2.1 This procedure utilizes reduction of nitrate to nitrite by copper-doped cadmium granules followed by reaction with sulfanilamide and N- (1-Naphthyl) ethylenediamine dihydrochloride to form a pinkish violet compound. EDTA in the buffer solution prevents precipitation of metal hydroxides. The concentration of nitrite in the sample is determined directly by colorimetric analysis (without cadmium reduction) and the concentration of nitrate is determined by difference:

$$\text{Nitrate} = (\text{Nitrate} + \text{Nitrite}) - \text{Nitrite}$$

2.2 This SOP is based on EPA Method 353.2, Lachat Method 10-107-04-1-C and an EPA/CE method.

3.0 SAFETY

3.1 Exercise good common sense when handling chemicals and samples. Wear rubber gloves, a lab coat and safety glasses.

3.2 The Material Safety Data Sheets (MSDS) for each reagent and standard used in this procedure are located at each lab division. The MSDS list the potential hazard that each reagent poses and specified safe handling procedures. The analyst must be familiar with the potential hazard that each reagent poses.

4.0 INTERFERENCES

4.1 Extreme sample pH may interfere. Proper sample preservation and adjustment just prior to analysis should alleviate this problem. Turbidity and color in samples must be filtered and/or diluted prior to analysis.

4.2 Residual chlorine and other oxidizing agents will oxidize the cadmium column, resulting in lower column efficiency. Add sodium thiosulfate to the samples containing residual chlorine prior to analysis.

5.0 SAMPLE COLLECTION, PRESERVATION AND HANDLING

5.1 Aqueous samples are routinely collected in plastic 250mL bottles. Samples for nitrite are not preserved. Samples for nitrate or nitrite plus nitrate are acidified to pH < 2 with sulfuric acid. The samples are iced at the time of collection and maintained at 4°C (less than 6C with no frozen samples) until the time of analysis.

5.2 Soils and sediments are routinely collected in plastic containers and iced at the time of collection. The samples are maintained in the lab at 4C (less than 6C with no frozen samples) until the time of preparation and analysis.

5.3 Samples are screened upon arrival in the lab for chlorine and proper preservation.

6.0 APPARATUS AND MATERIALS

6.1 QuickChem AE autoanalyzer with appropriate materials for the determination of nitrite and nitrate plus nitrite.

6.2 Filters, 0.45 um

6.3 Volumetric flasks

6.4 Volumetric pipettes

7.0 REAGENTS

Reagents must be tracked in accordance with STL-SL SOP AN44: *Reagent Traceability*. The preparation of the autoanalyzer reagents is described in Lachat QuikChem Method 10-107-04-1-C.

7.1 Reagent water- deionized, Type II.

8.0 STANDARDS

All standard preparations must be documented in accordance with STL-SL SOP AN41: *Standard Material Traceability*.

8.1 Nitrite

8.1.1 Sodium nitrite-reagent grade.

8.1.2 Sodium nitrite stock (100mg-N/L)- Dissolve 0.493g of sodium nitrite in 700-800mL of reagent water in a 1-L volumetric flask. Dilute to volume with reagent water and transfer to a labeled storage container.

8.1.3 Sodium nitrite intermediate standard (10mg-N/L)- Transfer 10mL of the nitrite stock (100mg-N/L) to a 100-mL volumetric flask and dilute to volume with reagent water.

8.1.4 Potassium nitrite-reagent grade. Potassium nitrite is used to prepare the lab control standard for nitrite.

8.1.5 Potassium nitrite stock (100mg-N/L)- Dissolve 0.304g of potassium nitrite into 400mL of reagent water in a 500-mL volumetric flask. Dilute to volume with reagent water and transfer to a labeled storage container.

8.1.6 Nitrite calibration standards

CAL STD	Intermediate(mg/L)	mL intermediate	Final volume (mL)	Conc(mg-NO2-N/L)
Blank	-	-	-	-
1	10	0.50	100	0.050
2	10	1.0	100	0.10
3	10	5.0	100	0.50
4	10	10	100	1.0
5	10	15	100	1.5
6	10	20	100	2.0

8.1.7 Lab control standard (LCS)- Transfer 0.50mL of the potassium nitrite stock standard (100mg-N/L) to a 100mL volumetric flask and dilute to volume with reagent water. The theoretical concentration is 0.50mg –N/L

8.2 Nitrate plus nitrite

8.2.1 Potassium nitrate- reagent grade

8.2.2 Nitrate stock (100mg NO3-N/L)-Dissolve 0.7221g of potassium nitrate into 700-800mL of reagent water in a 1-L volumetric flask. Dilute to volume with reagent water and transfer to a labeled storage container.

8.2.3 Nitrate intermediate standard (10mg NO3-N/L)- Transfer 10mL of the nitrate stock (100mg-N/L) to a 100-mL volumetric flask and dilute to volume with reagent water.

8.2.4 Nitrate Calibration Standards

CAL STD	Intermediate(mg/L)	mL intermediate	Final volume (mL)	Conc(mg-NO3-N/L)
Blank	-	-	-	-
1	10	0.50	100	0.050
2	10	1.0	100	0.10
3	10	5.0	100	0.50
4	10	10	100	1.0
5	10	15	100	1.5
6	10	20	100	2.0

9.0 SAMPLE PREPARARTION

9.1 Analyze aqueous samples directly as given in Section 10. Samples with turbidity should be filtered prior to analysis. Solid samples are extracted as described below. The leachate is filtered and analyzed in the same manner as water samples.

9.2 Nitrite

9.2.1 Homogenize the sample and weigh 5.0 to 5.5g of sample into a 125mL plastic container. Record the weight to the nearest 0.1g. Weigh two additional 5-g aliquots of the sample chosen for the MS and MSD.

9.2.2 Add 100mL of reagent water to each of two 125mL plastic containers. Label one container as the method blank and the other as the lab spike (LCS). Add 0.50mL of the 100mg/L stock to the LCS. The theoretical concentration of the LCS, assuming a sample weight of 5.0g and 100% solids, is :

$$C(mg/kg) = \frac{0.50mL \otimes 100mg/L}{5.0g} = \frac{0.00050L \otimes 100mg/L}{0.0050kg} = 10mg/kg$$

9.2.3 Add 0.50mL of the 100mg/L stock to the MS and to the MSD. The theoretical concentration of the MS and MSD is calculated:

$$C(mg/kg,dw) = \frac{0.50mL \otimes 100mg/L}{W \otimes solids} = \frac{0.00050L \otimes 100mg/L}{W \otimes solids} = \frac{0.050mg}{W \otimes solids}$$

where
W = weight of sample extracted (kg)
solids = (percent solids)/100

9.2.4 Add 100mL of reagent each sample container.

9.2.5 Shake or rotate the closed container for 2 hours.

9.2.6 Allow the sediment to settle and filter 25mL of the leachate through 0.45um filter and collect the leachate in a plastic container. Store at 4C until the time of analysis.

9.3 Nitrate plus nitrite

9.3.1 Homogenize the sample and weigh out 1.0 to 1.2g of sample into a 250-mL Erlenmeyer flask.. Weigh two additional 1-g aliquots of the sample chosen for the MS and MSD.

Add 0.50mL of the 100mg/L stock to the LCS. The theoretical concentration of the LCS, assuming a sample weight of 1.0g and 100% solids, is :

$$C(mg/kg) = \frac{0.50mL \otimes 100mg/L}{1.0g} = \frac{0.00050L \otimes 100mg/L}{0.0010kg} = 50mg/kg$$

9.3.2 Add 0.50mL of the 100mg NO3-N/L stock to the MS and to the MSD. The theoretical concentration of the MS and MSD is calculated:

$$C(mg/kg,dw) = \frac{0.50mL \otimes 100mg/L}{W \otimes solids} = \frac{0.00050L \otimes 100mg/L}{W \otimes solids} = \frac{0.050mg}{W \otimes solids}$$

where
W = weight of sample extracted (kg)
solids = (percent solids)/100

9.3.3 Add 50mL of reagent water to each flask and 3 to 4 drops of concentrated sulfuric. The process may be stopped at this point for 24 hours.

9.3.4 Add 50mL of reagent water to each acidified sample and boil each sample for 15 minutes. All samples and QC must be treated in the same manner.

9.3.5 Allow the samples to cool to room temperature before proceeding to the next step.

9.3.5 Transfer the solids and liquids from the flask to a centrifuge tube and centrifuge the slurry at 2000rpm for 5 to 10 minutes. Decant the liquid phase into a 200mL volumetric flask.

9.3.6 Add 50mL of reagent water to the centrifuge tube and mix. Centrifuge again at 2000rpm for 5 to 10 minutes. Decant the liquids into the volumetric flask.

9.3.7 Add an additional 50-mL aliquot of reagent water to the centrifuge tube and mix. Centrifuge again at 2000rpm for 5 to 10 minutes. Decant the liquids into the volumetric flask and dilute to final volume with reagent water.

9.3.8 Filter the leachate through a 0.45um filter prior to analysis.

10.0 ANALYTICAL PROCEDURE

Set up the autoanalyzer as shown in the Lachat guide document and analyze the standards and samples as described in the analytical sequence. Nitrite is determined without cadmium reduction; nitrate plus nitrite is determined with cadmium reduction.

10.1 Analytical Sequence

Initial Calibration
Initial Calibration Verification (ICV)
Initial Calibration Blank (ICB)
10 samples (including MB and LCS)
Continuing Calibration Verification (CCV)
Continuing Calibration Blank (CCB)
10 samples (including MS/MSD)
CCV
CCB

The sequence continues until all of the samples have been analyzed or until the verification standards fail to meet the acceptance criteria. The criteria are given in the SOP Summary in Appendix A.

10.2 Dilution factor

If the concentration of a sample exceeds the highest level calibration standard, the sample must be diluted to bring the concentration within the working range of the analyzer. The dilution should be chosen to bring the concentration of the diluted sample to the mid range of the calibration curve. The dilution may be done manually or may be performed using the Lachat 8000 "auto dilution".

The dilution factor, DF, is calculated:

$$DF = \frac{\text{Final volume of dilution(mL)}}{\text{Volume of sample (mL)}}$$

The dilution factor should be a reasonable multiple of 2, 5, or 10. The following table lists some common dilution factors.

Volume of sample(mL)	Volume of Diluent(mL)	Final Volume (mL)	Dilution factor
1.0	9.0	10	10
2.0	8.0	10	5
5.0	5.0	10	2
1.0	99	100	100
2.0	98	100	50
5.0	95	100	20

11.0 CALCULATIONS

11..1 Liquid samples

$$C(mg/L) = Ccurve \otimes DF$$

Ccurve = concentration of sample or sample dilution from the calibration curve (mg/L)
DF =dilution factor

The sample result is generated by the data system from the calibration curve and requires that the dilution factor be supplied for proper calculation.

11.2 Soil and Solids Leachates

$$C(mg/k,dw) = Ccurve \otimes \frac{F \otimes DF}{W \otimes solids}$$

Ccurve = concentration of sample or dilution from the calibration curve (mg/L)
F = final volume of leachate/extract (L)
DF =dilution factor
W = weight of sample extracted (kg)
Solids = (percent solids)/100

11.3 Calculation of Nitrate Concentration

$$\text{Nitrate} = (\text{Nitrate} + \text{Nitrite}) - \text{Nitrite}$$

where
Nitrate = concentration of nitrate as nitrogen (mg/L or mg/kg,dw)
(Nitrate + Nitrite) = concentration of nitrate plus nitrite as nitrogen (mg/L or mg/kg,dw) by cadmium reduction
Nitrite = concentration of nitrite as nitrogen (mg/L or mg/kg,dw) without cadmium reduction

NOTE: If the concentration of nitrite or nitrate plus nitrite is less than the reporting limit, let the concentration equal zero when calculating the nitrate concentration.

12.0 QUALITY CONTROL/QUALITY ASSURANCE

Follow the guidance in STL-SL SOP AN02:*Analytical Batching*, to evaluate the QC. The QC requirements are summarized in the SOP Summary in Appendix A.

13.0 PREVENTIVE MAINTENANCE

Replace sample pump tubes monthly.
Replace pump tubes on the board at least bimonthly, more often when run frequency exceeds 2 per week.
Valve flares need to be replaced annually.

14. TROUBLESHOOTING

14.1 Negative peaks for the instrument blank and low standards are usually due to analyte in the carrier. Replace with fresh and protect from contamination with the analyte.

14.2 Whenever efficiency drops below 90%, recopperize the column. Typically, recopperizing will be required only every month or two. Samples high in sulfides may shorten column life.

15.0 REFERENCES

15.1. "Methods for Chemical Analysis of Water and Wastes"; U.S. EPA Office of Research and Development: Cincinnati, OH, March, 1983.

15.2. "QuickChem AE Method 10-107-04-1-C"; Lachat Instruments, Milwaukee WI, January 1996

15.3. EPA/CE-91-1 Technical report, May 1981: Environmental Protection Agency/Corps of Engineers Technical Committee on Criteria for Dredged and Fill Material; "Procedures for Handling and Chemical Analysis of Sediment and Water Samples".

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action
Initial Calibration -minimum 5 points with lowest point @ RL	Before sample analysis, every six months, and when continuing calibration verification fail.	Regression curve with correlation coefficient >=0.995	-Evaluate curve and check calculations -Reanalyze standard(s) -Remake and reanalyze standard(s) -Inspect instrument for proper operation
Initial Calibration Verification (ICV) and Continuing Calibration Verification (CCV)	After initial calibration and after every 10 sample measurements; daily to verify curve.	+/-10% of expected value	-Check calculation -Reanalyze ICV/CCV -Remake and reanalyze ICV/CCV -Recalibrate -Inspect instrument for proper operation
Initial Calibration Blank (ICB) and Continuing Calibration Blank (CCB)	After ICV and CCV	< RL STL-SL CQAP Table 5	-Check calculations -Reanalyze ICB/CCB -Determine source of contamination and reanalyze samples if necessary
Reporting limit (RL) Standard-lowest standard in initial calibration curve -required for FLA DEP QAPP	Daily	Detected	-reanalyze -remake and reanalyze -recalibrate
Cadmium column efficiency check -mid-level nitrite standard	Daily	+/-10% of expected value against the nitrate-N curve	-reanalyze -check calculations -remake and reanalyze -recalibrate -replace cadmium column
Method Blank -for analyses that require no preparation, the ICB/CCB are reported as the method blank	Per batch	< RL STL-SL CQAP Table 5	-Check calculations -Reanalyze method blank -Determine source/cause of contamination and reanalyze associated samples if necessary
LCS-spiked with standard from second source	Per batch	STL-SL CQAP Table 5	-Check calculations -Reanalyze -AN02 Decision Matrix

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action
MS/MSD	5% of samples	STL-SL CQAP Table 5	-Check calculations -Reanalyze -AN02 Decision Matrix
Initial Demonstration of Capability	Per analyst	-linearity criteria -recovery of QCS within 90-110% -determination of MDL	-Reanalyze samples
MDL Study	Annually	-STL-SL SOP CA90	-reanalyze samples

Approval Signature: R. Wayne Robbins	
Title: Corporate QA Manager	Date: 5/12/98

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TURBIDIMETRIC SULFATE (375.4/9038)

1.0 SCOPE AND APPLICATION

This procedure can be used to determine sulfate in groundwater, drinking water, surface water, and domestic and industrial wastewater. The reporting limit and accuracy and precision criteria re listed in Section 5 of the current SL quality assurance plans.

2.0 SUMMARY OF METHOD

2.1 The sample is reacted with barium chloride to form barium sulfate. The turbidity or absorbance of the sample is measured and recorded every thirty seconds for four minutes and the maximum turbidity or absorbance is compared to standards analyzed under the same conditions. The reference methods limit the upper range of the calibration curve to 40mg/L. Concentrations of sulfate above 40mg/L require dilution prior to analysis.

2.2 This method is based on EPA Method 375.4 and SW-846 Method 9038.

2.3 Modifications:

-Section 7.3.4 of SW-846 9038 states: "Check the reliability of the calibration curve by running a standard with every three or four samples." SL analyzes a second source initial calibration standard after the ICAL and a same source calibration verification every 10 samples.

-Section 8.2 of SW-846 9038 states: "Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis." SL analyzes a seven point calibration curve at 5mg/L increments form 5mg/L to 40mg/L. The curve is verified after every 10 samples analyses, which corresponds to about one hour between verifications.

-Section 8.5 of SW-846 Method 9038 states: "Verify calibration with an independently prepared check standard every 15 samples." SL analyzes an independent calibration standard after initial calibration. After the calibration curve is verified, the curve is checked every 10 samples by the analysis of a calibration standard.

3.0 SAFETY

3.1 Use good common sense when working in the lab. Do not perform any procedures that you do not understand or that will put you or others in potentially dangerous situations.

3.2 Each analyst must be familiar with the Material Safety Data Sheets (MSDS) for each standard and reagent used in this procedure.

4.0 INTERFERENCES

4.1 Silica above 500mg/L will interfere.

4.2 Color and turbidity due to the sample matrix can cause positive interferences which must be accounted for by the use sample blanks analyzed with no reagent. The absorbance or turbidity of the blank is subtracted from the absorbance or turbidity of the treated sample and the concentration is determined from the corrected response.

5.0 SAMPLE HANDING AND PRESERVATION

Aqueous samples are routinely collected in 120mL plastic containers with no chemical preservative. The samples are iced at the time of collection and maintained at 4C (less than 6C with no frozen samples) until the time of analysis. Samples should be analyzed as soon as possible with a maximum holding time of 28 days.

6.0 APPARATUS AND MATERIALS

6.1 Spectrometer or turbidimeter with compatible cells. A 1cm spectrometer cell is usually sufficient to detect a 5mg/L sulfate standard.

6.2 Volumetric glassware

6.3 Pipettes

7.0 REAGENTS

7.1 Reagent water

7.2 Hach Sulfaver reagent pillows

8.0 STANDARDS

The preparation of standards must be documented in accordance with SL SOP AN41: *Standard Material Traceability.*

8.1 Potassium sulfate

8.2 1000-ppm SO_4 standard-Dissolve 1.815 g potassium sulfate in 800 mL DI water in a 1-L volumetric flask. Dilute to volume.

8.3 Calibration standards

CAL STD	Stock Conc (mg/L)	Vol of Stock (mL)	Final Vol (mL)	Conc Cal Std (mg/L)
ICV/CCV	NA	0	100	0
A	1000	0.5	100	5.0
B	1000	1.0	100	10
C	1000	1.5	100	15
D	1000	2.0	100	20
E	1000	2.5	100	25
F	1000	3.0	100	30
G	1000	3.5	100	35
H	1000	4.0	100	40

8.4 Calibration Verification

The calibration verification standard must be from a source independent from the calibration standards. The verification can be a certified solution or a check sample from ERA, etc or may be prepared from a separate material containing sulfate. See Section 5.6 of SW-846 Method 9038 for the preparation of a sulfate standard from sulfuric acid..

8.5 Matrix spikes
Matrix spikes are prepared by adding 0.50mL of the 1000mg/L sulfate stock solution to 25mL of sample. The theoretical concentration is

$$MS(mg/L) = \frac{0.50mL \otimes 1000mg/L}{25mL} = \frac{0.00050L \otimes 1000mg/L}{0.025L} = 20mg/L$$

9.0 SAMPLE PREPARATION
No sample preparation is generally required. Samples with very high concentrations of particulates or highly colored samples may require filtration prior to analysis. If filtration is required, the project manager is notified through an anomaly report.

10.0 ANALYTICAL PROCEDURE

10.1 Initial Calibration
A calibration curve must be established initially and when ever the verification standards fail the acceptance criteria.

10.1.1 Prepare the initial calibration standards as described in Section 8.3.

10.1.2 Add one Hach powder pillow to each standard, mix each standard thoroughly, and allow the turbidity to develop for 5-10 minutes.

10.1.3 Zero the instrument with the calibration blank.

10.1.4 Measure the turbidity or the absorbance of each standard at 30 second intervals over a four minute period. Record the maximum reading obtained over the four minute period.

10.1.5 Evaluate the standard data using linear regression and calculate the correlation coefficient of the curve. If the correlation coefficient is greater than r equal to 0.995, the curve may be used for quantitation. If not, new points should be prepared, analyzed, and evaluated.

10.1.6 Analyze the initial verification standard (ICV). The verification standard must be within +/-10% of the true concentration. If not, recalibrate.

10.2 Continuing Calibration Verification

The calibration curve must be verified after every 10 samples. Prepare and analyze the ICV standard and determine the concentration from the calibration curve. If the concentration of the ICV is within 10% of the true concentration, the calibration curve has been verified and may be used for samples.

NOTE: A new calibration curve is not required each day samples are analyzed. The curve may be verified on succeeding days by the analysis of the ICV and calibration blank(CCB). See the tables in Section 10.3 for the analytical sequences with and without the initial calibrations.

10.3 Sample Analysis

Analytical Sequence with ICAL

Initial calibration Standards
Initial Calibration Verification (ICV)
Initial Calibration Blank (ICV)
10 sample analyses
Continuing calibration Verification (CCV)
Continuing calibration Blank(CCB)
10 sample analyses

Analytical Sequence – daily after ICAL

Initial calibration Verification (ICV)
Continuing calibration Blank(CCB)
10 sample analyses
Continuing calibration Verification (CCV)
Continuing calibration Blank(CCB)
10 sample analyses

10.3.1 Remove the samples from the storage refrigerator and allow the samples equilibrate to room temperature. Turn on the spectrophotometer or turbidimeter and allow the instrument to warm up. Set the spectrophotometer to 420nm.

10.3.2 Prepare the standards in accordance with Section 8.3. if performing an initial calibration of the instrument. If the calibration is being verified, prepare the ICV standard and a 20mg/L calibration standard if more than 10 samples are analyzed. The calibration standards have a shelf life of 28 days if properly stored.

10.3.3 Transfer two 25mL aliquots of each sample to separate labeled containers. Disposable plastic cups are recommended. Prepare MS/MSD at a frequency of 5% of samples(see Section 8.5).

10.3.4 Add a Hach powder pillow to one of the sample aliquots and mix well. Allow the turbidity to develop for 5-10 minutes. If the sample turns extremely turbid, discard the sample and perform the analysis on a more dilute aliquot.

10.3.5 Read and record the turbidity of the untreated sample aliquot to correct for sample color or turbidity. A single reading is required for the untreated sample.

10.3.6 Read and record the turbidity or absorbance of the corresponding treated sample aliquot every thirty seconds for a period of four minutes.

10.3.7 Determine the concentration of the sample using the corrected absorbance or turbidity. The corrected reading is calculated:

$$Tc = T2 - T1$$

Tc = corrected turbidity (or absorbance)
T2 = maximum turbidity (or absorbance) of treated sample aliquot
T1 = turbidity (or absorbance) of the untreated sample aliquot

10.3.8 If the concentration of the sample exceeds 40mg/L, a more dilute aliquot must be analyzed. Since the calibration is based on a sample volume of 25mL, calculate the dilution factor (DF):

$$DF = \frac{25mL}{V}$$

where V= volume of sample used to prepare the dilution

11.0 CALCUALTIONS

The concentration of sulfate in the sample is calculated :

$$Concentration(mg/L) = Ccurve \otimes DF$$

where
Ccurve= concentration form the regression curve(mg/L)
DF = dilution factor

12.0 QUALITY CONTROL/QUALITY ASSURANCE

See SL SOP AN02: Analytical Batching for calculations of QC items and guidance on the evaluation of QC data. The ICV standard may be used to verify the calibration and may also be reported as the lab control standard (LCS).

13.0 PREVENTIVE MAINTENANCE-none

14.0 TROUBLE-SHOOTING-none

15.0 REFERENCES

1. *Methods for Chemical Analysis of Water and Waste*; U.S. Office of Research and Development: Cincinnati, OH, March, 1983.

2. *Test Methods for Evaluating Solid Waste, Third Edition*; U.S. EPA Office of Solid Waste and Emergency Response: Washington, DC November, 1986.

Approval Signature: R. Wayne Robbins	
Title: Corporate QA Manager	Date: 12/18/98

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ALKALINITY (AND OTHER CARBONATE SPECIES)

1.0 SCOPE AND APPLICATION

This method is applicable to the determination of alkalinity in drinking, surface and saline waters, and domestic and industrial wastes. The reporting limit (RL) and the accuracy and precision criteria are listed in Section 5 of the current Savannah Laboratories' quality assurance plans.

2.0 SUMMARY OF METHOD

The sample is titrated to an endpoint of pH 4.5 with standardized acid. The phenolphthalein alkalinity may also be determined by titrating to an endpoint of 8.3. This SOP also references a program accessible on the SL LIMS that can be used to calculate the concentrations of various forms of carbonate species from the total alkalinity and the initial pH of the sample: carbonate, bicarbonate, hydroxide alkalinity, total CO_2, and free CO_2.

This method is based on EPA Method 310.1 and Standard Methods 2320B and 4500-CO2-D.

3.0 SAFETY

3.1 Do not perform any procedures that you do not understand or that will put you or others in potentially dangerous situations.

3.2 The analyst should wear eye protection, gloves, and a lab coat or apron when performing this procedure.

3.3 The analyst must be familiar with the Material Safety Data Sheets (MSDS) for each reagent and standard in this procedure.

4.0 INTERFERENCES

Extremely turbid, oily, and soap-containing samples will affect the analysis by coating the pH electrode.

5.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

Samples are routinely collected in 250-mL plastic containers with no preservatives. The samples are iced at the time of collection and are maintained at 4C (less than 6C with no frozen samples) until the time of analysis. Holding time is 14 days.

6.0 APPARATUS AND MATERIALS

6.1 pH meter with electrode

6.2 Magnetic stirrer and stir bars

6.3 Burette, 10mL with 0.02mL increments

6.4 Beakers, flasks, plastic cups (disposable styrene)- appropriate volume to perform titration

6.5 Analytical balance

7.0 REAGENTS

Reagents must be tracked in accordance to SL SOP AN44: *Reagent Traceability.*

7.1 Reagent water-lab generated deionized water

7.2 Sodium carbonate (Na2CO3) –reagent grade

7.3 Sodium carbonate solution, approximately 0.05 N: Transfer approximately 0.25g (250mg) of sodium carbonate to a 100mL volumetric flask. Record the weight added to the flask to the nearest 0.1mg (0.0001g). Dissolve the salt in a small volume of reagent water and dilute to volume with reagent water. Calculate the normality, N, of this solution as follows:

$$N(eq/L) = \frac{W \otimes \frac{eq}{53g}}{100mL} \otimes \frac{1000mL}{L}$$

where

W = weight of sodium carbonate (g)

7.4 Sulfuric acid (H2SO4) – reagent grade

7.5 Sulfuric acid (H2SO4) solution, approximately 0.02 N: Dilute 0.6 mL concentrated H_2SO_4 to 1 L with DI water. This solution may be purchased and standardized prior to use. Standardize against ~0.05N $NaCO_3$ solution as described below.

-Calibrate the pH meter in accordance with SL SOP BA70.
-Fill the 10mL burette with the 0.02N sulfuric acid solution.
-Transfer 15.0mL of the ~0.05N sodium carbonate solution to a 100mL beaker and add a small stir bar.
-Place the beaker on the stir plate. Submerge the pH probe below the liquid. Do not allow the stir bar to hit the probe-this will cause erratic readings.
-Add 5-6 drops of bromocresol green indicator. The color should be blue. (The indicator is added to help gauge the endpoint of the titration.
-Titrate the sodium carbonate solution with the 0.02N sulfuric acid until the pH is 4.5. The indicator will turn pink near the endpoint. Titrate very slowly as the pH approaches 4.5.
-Record the volume of 0.02N sulfuric acid needed to reach the endpoint.
-Repeat the titration two more times with fresh portions of 0.05N sodium carbonate solution.
-Calculate the normality, Na, of the 0.02N sulfuric acid solution as follows for each of the three standardizations:

$$Na = \frac{Nb \otimes Vb}{Va}$$

where

Na = normality of the sulfuric acid solution(meq/mL)
Nb = normality of the sodium carbonate solution (meq/mL) (see Section 7.3)
Va = volume of sulfuric acid required to reach the endpoint(mL)
Vb = volume of sodium carbonate solution titrated (mL)

-Average the three titrations to obtain the normality of the sulfuric acid solution used to calculate the alkalinity of the field samples and QC.

8.0 STANDARDS
All standards must be tracked in accordance with SL SOP AN44: *Standard Material Traceability.*

An external QC sample must be obtained from a reputable vendor and analyzed with each batch of samples.

9.0 SAMPLE PREPARATION
No sample preparation is required.

10.0 PROCEDURE

10.1 Routine Alkalinity

10.1.1 Calibrate the pH meter according to SL SOP BA70.

10.1.2 Fill burette with standardized 0.02 N sulfuric acid.

10.1.3 Pour 50 mL of sample (at room temperature) into a plastic cup on the magnetic stirrer. Add a magnetic stir bar. While slowly stirring sample, determine and record the sample pH. Do not allow the stir bar to hit the probe-this will cause erratic readings.

10.1.4 Place about six drops of bromocresol green indicator into the sample. A blue color should appear. The purpose of the indicator is for ease of endpoint detection.

10.1.5 Titrate the sample to a pH of 4.5. The indicator color near pH 4.5 will change from blue to pink. Record titer.

NOTE: If phenolphthalein alkalinity is required, first titrate the sample to pH 8.3, and record this titer to use in the phenolphthalein alkalinity calculation. If the sample pH is below 8.3, the sample has no phenolphthalein alkalinity.

10.1.6 Calculate the alkalinity, as mg/L calcium carbonate, as follows:

$$Alkalinity(total) = \frac{A \otimes N}{V} \otimes \frac{50mg}{meq} \otimes \frac{1000mL}{L}$$

where

A = volume of standard acid (mL) to bring pH to 4.5
N = normality of standard acid (meq/mL)

The phenolphthalein alkalinity, as mg/L calcium carbonate, is calculated:

$$Alkalinity(phenolphthalein) = \frac{D \otimes N}{V} \otimes \frac{50mg}{meq} \otimes \frac{1000mL}{L}$$

where

D = volume of standard acid (mL) to bring pH to 8.3
N = normality of standard acid (meq/mL)

10.2 Low Level Alkalinity (<20mg/L)

10.2.1 Calibrate the pH meter according to SL SOP BA70.

10.2.2 Fill burette with standardized 0.02 N sulfuric acid.

10.2.3 Pour 100mL to 200mL of sample (at room temperature) into a 250mL beaker and place on the magnetic stirrer. Add a magnetic stir bar. While slowly stirring sample, determine and record the sample pH. Do not allow the stir bar to hit the probe-this will cause erratic readings.

10.2.4 Place about six drops of bromocresol green indicator into the sample. A blue color should appear. The purpose of the indicator is for ease of endpoint detection.

10.2.5 Titrate the sample to a pH range of 4.3 to 4.7. The indicator color near pH 4.5 will change from blue to pink. Record titer and pH reading.

10.2.6 Continue to add titrant until the pH is lowered by 0.3 pH units. Record the volume of titer and final pH. Calculate the low level alkalinity, as mg/L CaCO3, as follows:

$$Alkalinity(low) = \frac{(2B - C) \otimes N}{V} \otimes \frac{50mg}{meq} \otimes \frac{1000mL}{L}$$

where

B = volume of titrant to first endpoint (mL)
C = volume of titrant to lower pH by 0.3 units (mL)
N = normality of the sulfuric acid solution (meq/mL)
V = volume of sample titrated (mL)

11.0 CALCULATIONS

The calculations for alkalinity are given in Section 10.

A computer program accessible on the SL LIMS can be used to calculate the concentrations of various forms of carbonate species from the total alkalinity and the initial pH of the sample. The carbonate species that can be calculated include carbonate, bicarbonate, hydroxide alkalinity, total CO_2, and free CO_2.

To access the program, type "ALK-CO2" at the prompt (>). Follow the program to input the total alkalinity and pH data, and allow the computer to calculate the concentrations of the various carbonate species.

12.0 QUALITY CONTROL/QUALITY ASSURANCE

The analytical batch consists of twenty or fewer samples and the associated QC: a method blank, an LCS, and duplicate samples for every 10 samples.

See SL SOP AN02: *Analytical Batching* for the equations needed to calculate accuracy and precision and for guidance on evaluation of batch QC results.

13.0 PREVENTIVE MAINTENANCE-none

14.0 TROUBLE-SHOOTING-none

15.0 REFERENCES

1. *Methods for Chemical Analysis of Water and Wastes*; U.S. EPA Office of Research and Development, Cincinnati, OH, March, 1983.

2. ***Standard Methods for the Examination of Water and Wastewater, Sixteenth Edition and Eighteenth Edition***; American Public Health Association: Washington, DC, 1985, 1992.

DISSOLVED GASES IN WATER

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Approved by:

R. Wayne Robbins 24 Apr 2001
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1.0 SCOPE AND APPLICATION

This method may be used to determine the concentration of certain gases dissolved in aqueous samples. This method is based on the paper *Dissolved Oxygen and Methane in Water by a GC Headspace Equilibration Technique* (Kampbell and Wilson, USEPA; Vendegrift, NSI; March 1989) and document RSKSOP-175 (8/11/94): *Sample Preparation and Calculations for Dissolved Gas Analysis in Water Samples Using A GC Headspace Equilibration Technique*. Tables 1-3 list the compounds that may be determined by this procedure.

NOTE: Dissolved nitrogen is not measured by this procedure since nitrogen is used for the headspace gas; oxygen is not determined because of the high probability of contamination from the atmosphere and the narrow range of concentrations that may be determined by the TCD. Dissolved oxygen can be readily determined by electrode or by Winkler titration.

2.0 SUMMARY OF METHOD

2.1 A known volume of nitrogen is injected into a filled VOA vial (40-mL with Teflon-lined cap) while the same volume of liquid is withdrawn. The inverted vial is placed in a sonicator for 10 minutes. A volume of the headspace is transferred into a sample injection loop. The headspace sample is injected into a packed column connected to either a flame ionization detector (FID) or thermal conductivity detector (TCD). Standards are prepared and analyzed in the same manner as samples.

2.2 Henry's Law states: The mass of a slightly soluble gas that dissolves in a definite mass of a liquid at a given temperature is very nearly directly proportional to the partial pressure of that gas. This law is applicable to dilute concentrations of gases at pressures of one atmosphere or less. This procedure assumes that Henry's Law applies "equally" to the field samples and to the standards analyzed under the essentially same conditions (temperature, pressure, and headspace volume).

3.0 SAFETY

Use good common sense when working in the lab. Do not perform any procedure that you do not understand or may put you or others in potentially hazardous situations.

4.0 INTERFERENCES

The primary interference will occur from analytes that are "degassed" from the sample into the headspace along with the target analytes. The non-target will usually be gasoline constituents such as alkenes, branched alkanes, or BTEX.

5.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

5.1 If dissolved CO2 and CO are Being Determined

Samples are collected in 40mL VOA vials with zero headspace and no preservative is added. If acid is added, dissolved carbonates will be converted to CO2 and bias the results. The vials are iced at the time of collection and stored in the lab at 4C (less than 6C with no frozen samples) until analysis. The samples should be analyzed as soon as possible with a maximum hold time of 14 days.

5.2 If Dissolved Hydrocarbons Only are Being Determined

Samples are collected in 40mL VOA vials with zero headspace and preserved by the addition of 0.1mL of 1:1 HCl or H2SO4 (HCl is default; H2SO4 on request). The vials are iced at the time of collection and stored in the lab at 4C (less than 6C with no frozen samples) until analysis. The

sample should be analyzed as soon as possible with a maximum hold time of 14 days. Do not use samples that have been acidified for the analysis of CO2 or CO.

6.0 APPARATUS AND MATERIALS

6.1 Gastight syringes: 5.0-mL and 0.5-mL

6.2 THM vials with Teflon-lined caps: 40-mL

6.3 Tedlar bag, 1L

6.4 Ultrasonic bath

6.5 Gas chromatograph: equipped with FID and TCD

6.6 Sample injection valve with various sample "loops" - 1.0-mL, 0.50-mL, 0.25-mL, and 0.10-mL loops

7.0 REAGENTS

7.1 Reagent water - lab deionized or volatile free water

7.2 Nitrogen - zero grade or better

8.0 STANDARDS

The preparation of standards must be tracked in accordance with SOP AN41: *Standard Material Traceability.*

The standards used for dissolved gases are Scotty II cylinders containing mixtures of various analytes in nitrogen. The standards are injected into vials containing reagent water to prepare the calibration and QC samples. The Scotty II cylinders used are:

Catalogue No.	Mix Number	Components
Supelco 3-30300 C1 - C6 Aliphatics	220	Methane, Ethane, n-propane, n-butane, n-pentane, n-hexane @ 100ppm V in N2.
Supelco 3-32300 C2-C6 Olefine	222	Ethene, propene, 1-butene, 1-pentene, 1-hexene @ 100ppmV in N2
Supelco 2-3437	216	Carbon monoxide, carbon dioxide, methane, ethane, ethene, acetylene @ 1% v/v in N2
Supelco 2-3438	217	Carbon dioxide, carbon monoxide, hydrogen, oxygen @ 0.5% v/v in N2
Supelco 2-2562	109	99% Methane

The preparation of dissolved gas standards is based on the following equation:

$$ppmV = ug / L \, x \, \frac{24.47}{MW}$$

where

ppmV = parts per million concentration on a volume per volume basis.
ug/L = micrograms of analyte per unit volume
24.47 = molal gas constant @ STP
MW = molecular weight of analyte

$$ug/L = ppmV \, x \, \frac{MW}{24.47}$$

A rearrangement of the equation gives the following

To determine the mass (ug) of a standard where the ppmV concentration is known, plug in the numbers and solve for ug/L. For example, a standard that has methane at 1% (10000ppmV) on

$$ug/L = 10000ppmV \, x \, \frac{16}{24.47} = 6539ug/L = 6539ng/mL$$

a volume basis is converted to mass of methane per unit volume:

If 5.0mL of this gas is added to 35mL of water (the VOA vial holds 40mL; we remove 5mL adding

$$\frac{6539ng/ml \, x \, 5.0mL}{35mL} = 934ng/mL = 934ug/L$$

the standard), the micrograms of methane per liter of water is:

8.1 FID Analysis of C1 Through C6 Aliphatics and/or Olefinic Hydrocarbons

The procedures in this section are used to analyze samples for dissolved gases in the C1 to C6 carbon range. Any of the analytes or concentration of the analytes in Table 1 may be measured, or a subset of the compounds may be measured.

8.1.1 Add 0.2mL of 1:1 HCl to each of five 40mL VOA vials and fill with reagent water. No headspace must be present in the vial.

8.1.2 To prepare the calibration standards, invert the VOA vial and inject the appropriate volume of standard and/or nitrogen into the vial while simultaneously withdrawing an equal volume of water. The preparation requires two gastight syringes equipped with chromatographic needles. The volume of standard and nitrogen required to prepare the standards are given in the following table:

Standard	mL Alipahtic Std. (Mix 220, 100ppmV)	mL Olefinic Std. (Mix 222, 100ppmV)	Mix 216 1% V/V	mL N2
Method Blank	0	0		5.0
STD1	0.10	0.10		4.8
STD2	0.5	0.50		4.0
STD3	5.0	0		0
STD4	0	5.0		0
STD5	0	0	0.25	4.75

If only aliphatics are to be measured, the olefin standards may be omitted, if only olefins are to be determined, the aliphatics may be omitted. Make sure the total volume of headspace added to each vial is constant at 5.0mL.

NOTE: Standard 5 adds an additional standard for methane, ethane, and ethene to bridge the calibration gap between the TCD and FID analyses.

The concentrations of the analytes in the standards are:

Analyte	Method Blank	Std1	Std2	Std3	Std4	Std5
Methane	0	0.19	0.95	9.3		46.5
Ethane	0	0.35	1.76	17.6		88
n-Propane	0	0.51	2.55	25.5		
n-Butane	0	0.68	3.4	34		
n-Pentane	0	0.84	4.2	42		
n-Hexane	0	1.0	5.0	50		
Ethene	0	0.33	1.64		16.3	82
Propene	0	0.49	2.45		24.5	
1-Butene	0	0.65	3.25		32.5	
1-Pentene	0	0.82	4.1		41	
1-Hexene	0	0.98	4.9		49	

Concentration units for the standards are micrograms of analyte per liter of water (ug/L).

8.1.3 Fill an additional vial for the lab control (LCS). The LCS is prepared from a standard independent of the standard used to prepare the calibration standards. The standard used to prepare the LCS is made from Supelco Mix 216 containing methane, ethane, and ethene (this mix also contains acetylene, carbon dioxide, and carbon monoxide).

- meter 1.0L of nitrogen into a Tedlar bag.

- remove 10mL of nitrogen from the bag with a gastight syringe
- add 10ml of Mix 216 to the bag and knead the bag to mix the gases. This is the spiking mix. The concentration of each component is 100ppmV.

8.1.4 Add 1.0 mL of the spiking mix and 4.0mL of N2 to the vial containing the reagent water. Label the vial the LCS.

The theoretical concentrations are:

Analyte	ug/L LCS
Methane	1.9
Ethane	3.5
Ethene	3.3

If an MS or MSD is requested, add 1.0mL of the spiking mix and 4.0mL of N2 to a separate aliquot of the sample.

8.2 GC/TCD Analysis (Carbon Dioxide, Carbon Monoxide, methane, Ethane, and Ethene)

8.2.1 Fill four VOA vials with reagent water. No headspace should be present in the vial. Do not add acid if

8.2.2 Prepare the calibration standards by inverting the vial and injecting the appropriate volume of standard and/or nitrogen into the vial while simultaneously withdrawing an equal volume of water. This procedure requires two gastight syringes equipped with chromatographic needles. The volume of standard and nitrogen required to prepare the standards are given in the following table:

Standard	mL Mix 216	mL N2
Method Blank	0	5.0
STD1	0.20	4.8
STD2	1.0	4.0
STD3	5.0	0

The concentrations of the analytes in the standard are:

Analyte	Method Blank	STD1	STD2	STD3
Carbon monoxide	0	65	325	1625
Carbon dioxide	0	103	515	2575
Methane	0	37	185	925
Ethane	0	70	350	1750
Ethene	0	103	515	2575

Concentration units for the standards are micrograms of analyte per liter of water (ug/L)

NOTE: The working range of the TCD can be extended by analyzing higher concentrations of standards. This is particularly important for samples with high levels of analytes. The error due to dilutions can be significant-do not dilute the samples if the levels exceed the calibration by more than a factor of ten-extend the working range of the calibration.

8.2.3 Fill an additional vial for the lab control. The LCS is prepared from a standard independent of the standard(s) used to make the calibration standards. An intermediate methane standard is prepared from the pure methane cylinder:

- meter 1.0L of nitrogen into a Tedlar bag
- remove 10mL of nitrogen from the bag with a gastight syringe.
- Add 10mL of Mix 109 (99% methane) to the bag and knead the bag to mix the gases. The concentration of this methane spiking mix is 10000ppmV.

8.2.4 Add 1.0mL of the methane spiking mix (10000ppmV), 1.0mL of Mix 217 to the vial, and 3.0 of nitrogen. Label the vial as the LCS. The theoretical concentrations are:

Analyte	ug/L LCS
Methane	187
Carbon dioxide	257
Carbon monoxide	152

If an MS or MSD is requested, add 1.0mL of the 10000ppmV methane spiking mix, 1.0mL of Mix 217, and 3.0mL of nitrogen to a separate vial.

9.0 SAMPLE PREPARATION

9.1 Remove the samples from the storage refrigerator and allow the samples to come to room temperature. Prepare the appropriate calibration standards (Section 8) while the samples are warming up.

9.2 Fill a Tedlar bag with nitrogen. This will be the reservoir of nitrogen to be added to the vials.

9.3 Fill a 5.0mL gastight syringe with nitrogen from the Tedlar bag.

9.4 Invert the VOA vial and puncture the Teflon cap with the syringe and needle. Puncture the cap with a second gastight syringe. Fill the VOA vial with the nitrogen while withdrawing the displaced water with the second syringe. Keep the vial in the inverted position until the time of analysis.

9.5 Place each sample, calibration standard, and QC item into the ultrasonic bath for 10 minutes. Remember to keep the vials inverted until the time of analysis.

9.6 Remove the vials from the bath, leaving the vials inverted until analysis.

9.7 After the analysis of the samples, pour the sample into a graduated cylinder and determine the volume of sample. Record this volume on the analysis log.

10.0 PROCEDURE

The analysis of dissolved gases in water is divided into three analytical procedures requiring different columns, detectors, and GC conditions. These conditions are given for guidance. The actual condition must be documented in the data system or maintenance log.

10.1 C-1 Through C-6 Aliphatics/Olefine by GC/FID

Parameter	Conditions
Column/Flow	1% SP-1000 in Carbopack B; 1/8" x 6' SS/20mL/min (He)
Detector/Temperature	FID @ 300C
Injector Port Temperature	250C
GC Temperature Program	45 - 5 min/20C per min/ 225C - hold
Injection Volume	1.0mL (0.25mL and 0.50ml also may be used)

10.2 Methane, Ethane, Ethene, and Acetylene by GC/FID

Parameter	Conditions
Column/Flow	Carbonex 1000 3' X 1/8" SS/20mL/min (He)
Detector/Temperature	FID @ 300C
Injector Port Temperature	250C
GC Temperature Program	35C - 5 min/ 20C per min/225C - hold
Injection Volume	1.0mL (0.25mL or 0.50ml)

10.3 Carbon monoxide, Carbon dioxide, Methane, Ethane, and Ethene by GC/TCD

Parameter	Conditions
Column/Flow	Carbonex 1000 15' x 1/8" SS/20ml/min (He)
Detector/Temperature	250C (TCD 150-200 uA)
Injector Port Temperature	250C
GC Temperature Program	35C - 5 min/20 per min/225C - hold
Injection Volume	1.0mL (0.25mL and 0.50ml also may be used)

10.4 Standard and Sample Analysis

10.4.1 Set the GC to the conditions appropriate for the target analytes. Make sure the system is stable. The injection of neat gas standards may be helpful in determining the condition of the analytical system.

10.4.2 When ready for analysis, turn the vial to an upright position and quickly withdraw 2.0mL of the headspace with a 5mL gastight syringe. Turn the sample injector loop into the "LOAD" position. Inject the headspace into the sample injection loop to completely flush the sample through the loop. Turn the sample injector to the "INJECT" position and start the GC and data system.

10.4.3 Construct a calibration curve by plotting the concentration along the x-axis and the corresponding response (area) along the y-axis. A linear or higher order fit may be used. The correlation coefficient must be greater than 0.99 to use the curve for quantitation. If the correlation coefficient criteria is not met, prepare new calibration standards and reanalyze.

10.4.4 Evaluate the sample data. Compare the retention times of the peaks in the samples to the standard retention times. Use a retention time window if ± 6 seconds (0.1 minute) to identify the target analytes.

10.4.5 If the concentration of a target analyte exceeds the response of the highest calibration standard, a new sample aliquot is prepared and analyzed. Do not inject more than one aliquot from a single vial unless there is no more sample, and notify the supervisor or project manager that this was necessary.

A dilution may be performed by using a smaller sample loop or by diluting the headspace in nitrogen in a Tedlar bag. Do not dilute samples more than a factor of ten. If a higher dilution is required, extend the calibration range and record in the preparation log.

NOTE: The working range of the TCD may be extended by analyzing higher concentration standards to match the concentration of the samples. The TCD is responsive to the target analytes over an extended working range.

10.4.6 After the headspace has been analyzed, pour the liquid sample into a graduated cylinder and record the volume. The volume should be about 35 mL.

10.5 Continuing Calibration Verification

The initial calibration curve is verified every 24 hours by the analysis of midlevel calibration standard or LCS. The recovery (Section 11.2) of the midlevel standard or LCS must be 75-125% of the true concentration. If the recovery is within this range, the initial calibration curve can be used for quantitation. If the recovery is outside of the range, a new calibration curve must be prepared, analyzed, and evaluated.

11.0 CALCULATIONS

11.1 The concentration of the standard (ug analyte per liter of water) is plotted against the response (area) to prepare a calibration curve for each target analyte. The concentration of the sample is calculated:

$$ug / L(water) = ug / L(curve) \, x \, \frac{1.0mL}{V_i} \, x \, \frac{35mL}{V_s} \, x \, DF$$

where

ug/L(curve) =	concentration from the curve
V_i =	volume of headspace injected (mL)
V_s =	volume of sample analyzed (mL)
DF =	dilution factor

$$\%REC = \frac{C}{C_T} x\ 100$$

11.2 The percent recovery is calculated:

where

C =	concentration determined (ug/L)
C_T =	theoretical concentration (ug/L)

12.0 QUALITY CONTROL/QUALITY ASSURANCE

The QC items for each batch of samples will include a method blank and a lab control standard. Matrix spikes are analyzed only if requested by the client and if samples are specifically supplied for the MS/MSD.:

Method blank: The concentration of the target analyte in the method blank must be less than the reporting limit listed in Tables 1-3.

LCS: The lab control standard is prepared by injecting known volumes of the standard into reagent water. The source should be different from those used for the calibration standards. The recovery of the LCS must be
75-125%.

13.0 PREVENTIVE MAINTENANCE-No items in this revision.

14.0 TROUBLESHOOTING-No items in this revision.

15.0 REFERENCES

15.1 *Dissolved Oxygen and Methane in Water by a GC Headspace Equilibration Technique*; Kampbell and Wilson, USEPA; Vendegrift, NSI; March, 1989.

15.2 RSKSOP-175 (8/11/94): *Sample Preparation and Calculations for Dissolved Gas Analysis in Water Samples Using A GC Headspace Equilibration Technique.*

TABLE 1		
C1 - C6 Aliphatic and Olefinic Hydrocarbons by FID		
Analyte	**Molecular Weight**	**Quantitation Limit (ug analyte per liter of water)**
Methane	16	0.19
Ethane	30	0.35
n-Propane	44	0.51
n-Butane	58	0.68
n-Pentane	72	0.84
n-Hexane	86	1.0
Ethylene (Ethene)	28	0.33
Propylene (Propene)	42	0.49
1-Butene	56	0.65
1-Pentene	70	0.82
1-Hexene	84	0.98

TABLE 2		
Subset of Targets by GC/FID		
Analyte	**Molecular Weight**	**Quantitation Limit (ug/L)**
Methane	16	0.19
Ethane	30	0.35
Ethene	28	0.33
Acetylene	26	0.30

TABLE 3		
Target Analytes by GC/TCD		
Analyte	**Molecular Weight**	**Quantitation Limit (ug/L)**
Carbon Monoxide	28	82
Carbon Dioxide	44	128
Methane	16	47
Ethane	30	88
Ethene	28	82

Approval Signature: R. Wayne Robbins	
Title: Corporate QA Manager	Date: 4/13/99

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pH ELECTROMETRIC MEASUREMENT OF WATER, SOILS, AND WASTES

1.0 SCOPE AND APPLICATION

1.1 This procedure can be used to determine the pH of aqueous samples and soil and waste samples. Aqueous samples include monitoring wells, wastewater, and industrial waste such as influents and effluents. Waste samples include solids, sludges, or non-aqueous waste. The possible range pH is 1 to 14.

This SOP also contains procedures for determining pH with pH paper. pH paper can be used to determine if a sample is properly preserved, if a sample has been adjusted to the proper range for extraction, digestion, or leaching, or to approximate the pH before the pH electrode is employed.

1.2 pH is defined by the following equation:

$$pH = -1 (\log [H^+])$$

This shows that pH is a logarithmic function; that is, an increase or decrease of one pH unit represents a ten-fold change in hydrogen ion concentration. The following table demonstrates the relationship between pH and hydrogen ion concentration:

pH	Hydrogen Ion Concentration
1.0	0.10 (1×10^{-1})
2.0	0.010 (1×10^{-2})
3.0	0.0010 (1×10^{-3})
4.0	0.00010 (1×10^{-4})
5.0	0.000010 (1×10^{-5})
6.0	0.0000010 (1×10^{-6})
7.0	0.00000010 (1×10^{-7})
8.0	1×10^{-8}
9.0	1×10^{-9}
10.0	1×10^{-10}
11.0	1×10^{-11}
12.0	1×10^{-12}
13.0	1×10^{-13}
14.0	1×10^{-14}

2.0 SUMMARY OF METHOD

2.1 The pH of an aqueous sample is determined potentiometrically using a combination electrode with temperature compensation. A soil or waste sample is mixed with reagent water. The pH of the solution is measured with the electrode. This procedure may not be used to determine whether a non-aqueous material exhibits the hazardous characteristic of corrosivity (see Chapter 7 of SW-846 Section 7.2).

2.2 The pH meter/electrode is calibrated using a series of certified buffer solutions that bracket the pH of the sample. This procedure for an aqueous sample is based on EPA Method 150.1, SW-846 Method 9040, and SM4500-H+. This procedure for a soil or waste sample is based on SW-846 Method 9045C.

3.0 SAFETY

3.1 Use good common sense when working in the lab. Do not perform any procedure that you do not understand or will put you or others in a potentially hazardous situation.

3.2 The analyst should wear a lab coat or apron, gloves, and eye protection when handling the pH buffers and samples.

3.3 MSDS (Material Safety Data Sheets) are available for each reagent and standard used in the lab. The analyst should be familiar with the information supplied in the MSDS.

4.0 INTERFERENCES

4.1 Coatings of oily material or particulate matter can impair electrode response. These coatings can usually be removed by gentle wiping with a Kimwipe moistened with hexane followed by rinsing with reagent water. Additional cleaning with hydrochloric acid may be required if the response is sluggish after cleaning with hexane. See Standard Methods 4500-H^+ Section 5b.

4.2 Temperature effects are minimized by the use of a meter/electrode confirmation that automatically compensates for temperature. The temperature of the samples should be at or near the same temperature as the buffer solutions.

5.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

Aqueous samples for pH measurement should be collected in 100-mL plastic containers. Waste or soil samples for pH measurement are routinely collected in a 100ml glass or plastic container. All containers should be stored at 4°C ± 2°C until analysis. The pH must be determined as soon as possible after collection.

6.0 APPARATUS AND MATERIALS

6.1 pH Meter: Orion Model 501 or equivalent instrument with combination electrode (Orion 91-55 or equivalent) with temperature compensation.

6.2 50ml beakers or other suitable container

6.3 Magnetic stirrer and Teflon-coated stir bars

6.4 Analytical Balance

6.5 pH Paper - wide and narrow range

7.0 REAGENTS

Reagent Water - Lab generated deionized water

8.0 STANDARDS

8.1 Certified pH buffers to bracket pH range of samples. Suggested buffers are 2.0, 4.0, 7.0, 10.0, and 13.0.

8.2 Check Standard: certified solution from ERA or other vendor.

9.0 SAMPLE PREPARATION

9.1 Sample Preparation of Aqueous Samples

There are no preparation steps for the determination of pH in aqueous samples.

9.2 Sample Preparation of Soil Samples

If there is insufficient soil to use 20g, a smaller aliquot can be used if the 1:1 ratio of sample to water is maintained.

9.2.1 To 20g of soil in a 50ml beaker, add 20ml of reagent water. Add a magnetic stir bar to the beaker and place the beaker on the magnetic stir plate. Stir the suspension for 5 minutes. Additional dilutions are allowed if working with hygroscopic soils and salts or other problematic matrices. If the ratio of water to sample is greater than 1:1, include this information on the reported results.

9.2.2 Let the soil suspension stand for about 1 hour to allow most of the suspended material to settle out from the suspension or filter or centrifuge to obtain the aqueous phase for pH measurement.

9.3 Sample Preparation of Waste Materials

9.3.1 To 20g of waste sample in a 50-mL beaker, add 20mL of reagent water, cover, and continuously stir in the suspension for 5 minutes. Additional dilutions are allowed if working with hygroscopic wastes and salts or other problematic matrices. If the ratio of water to sample is greater than 1:1, include this information in the reported results.

9.3.2 Let the waste suspension stand for about 15 minutes to allow most of the suspended waste to settle out from the suspension or filter or centrifuge to obtain aqueous phase for pH measurement.

NOTE: If the waste is hygroscopic and absorbs all the reagent water, begin the analysis again using 20g of waste and 40mL of reagent water. Include this water to sample ratio with the results.

NOTE: If the supernatant is multiphasic, decant the oily phase and measure the pH of the aqueous phase. The electrode may need to be cleaned (Step 3.3) if it becomes coated with an oily material. (See Standard Methods 4500-H^+, Section 5b. or SW-846 Method 9045C, Section 3.3).

10.0 PROCEDURE

SEQUENCE
Calibrate with 2 buffers
Check pH with third buffer
Analyze check solution
10 sample determinations
Check Solution
10 sample determinations
Check Solution

10.1 Routine Calibration

This procedure describes the calibration for the range of pH 4 to pH 10 since most pH measurements will fall into that range. Make sure that the pH meter has warmed up and that pH is the selected mode of operation. The lot numbers of the pH buffers must be recorded on the pH data sheet.

10.1.1 Place the pH 7.0 buffer in a beaker on the magnetic stir plate and place the pH electrode in the buffer solution. The electrode should be immersed in the buffer but should not come in contact with the Teflon-coated stir bar.

10.1.2 Allow the solution to stir slowly while the measurement is being made. Adjust the "standardize" or "calibrate" knob on the meter until the pH reads 7.0 ± 0.1.

10.1.3 Rinse the pH electrode with reagent water and place the electrode in the pH 4.0 buffer. Allow the solution to slowly stir while the measurement is being made. Adjust the "slope" or "temperature" knob to bring the meter reading to 4.0.

10.1.4 Rinse the electrode with reagent water and place the electrode in the pH 10.0 buffer. Allow the solution to stir slowly while the measurement is being made. The reading should be 10.0 ± 0.1 pH units. If the buffer does not read within the range, repeat the calibration procedure.

NOTE: It is Savannah Labs policy to consider pH measurements in the 4 to 10 range to be bracketed by two calibration buffers when the meter is calibrated by Section 10.1.

10.2 Non-routine Samples

Samples with pH below 4 and above 10 must be measured with the pH meter/electrode calibrated with buffers that bracket the pH. The pH may be estimated using wide range pH paper and the buffers chosen accordingly. The general procedure is the same described in Section 10.1.

10.3 Sample Analysis

10.3.1 Remove the samples from the refrigerator and allow the samples to come to room temperature. The samples and pH buffers used to calibrate the pH meter/electrode must be at or near the same temperature.

10.3.2 Calibrate and verify the pH meter/electrode. The lot numbers of the pH buffers and check standards must be recorded on the data sheet as described in Section 10.1.

10.3.3 Aqueous Samples

Place an aliquot of the well mixed sample into a beaker on the magnetic stir plate. Make sure that the electrode is immersed in the sample but does not contact the Teflon-coated stir bar.

10.3.3.1 Allow the sample to slowly stir while the pH measurement is being made. Record the pH to the nearest 0.1 pH unit and temperature of the sample after the reading has stabilized.

10.3.4 Soil and Waste Samples

Adjust the electrodes in the clamps of the electrode holder so that, upon lowering the electrodes into the beaker, the glass electrode will be immersed just deep enough into the clear supernatant to establish good electrical contact through the ground-glass joint or the fiber-capillary hole. Insert the electrode into the sample solution in this manner. For combination electrodes, immerse just below the suspension.

10.3.5 Rinse the electrode with reagent water. Analyze all of the samples in the analytical batch according to the sequence listed earlier in this section. Record the pH ot the nearest 0.1 pH units and record the sample temperature at the time of the analysis.

10.3.6 After all measurements have been made, return the electrode to the 7 buffer or electrode storage solution and set the meter to "standby." The meter should be left "on" when not in use.

10.4 Use of pH Paper

pH paper provides a quick and easy way to approximate the pH of a sample. pH paper can be used to determine if a sample has been properly preserved or if the pH of a sample is in the proper range for a preparation step.

10.4.1 pH paper should be checked upon receipt and quarterly to make sure that it is functioning properly.

-Examine the pH paper. If the paper is discolored or looks worn, it may be defective.
-Place a piece of pH paper on a watch glass or other suitable surface and add a few drops of a certified buffer solution onto the paper
-Compare the color of the pH paper to the reference colors. If the colors match, the paper can be used. If not, acquire new paper.

10.4.2 Determination of pH with pH Paper

Dip a glass rod or disposable Pasteur pipet into the sample and touch the rod or pipet to the pH paper. Compare the color to the reference.

NOTE: Do not dip the pH paper into a sample. The pH paper dye can bleed into the sample and affect sample results.

11.0 CALCULATIONS

The measurement of pH requires no calculation since the reading is taken from the meter. The calculation of percent recovery of the check standard and precision of pH is more complex than it first appears because the pH scale is a logarithmic function. The pH must be converted back to a concentration prior to the calculation of accuracy and/or precision since slight differences in the pH represent large differences in concentration.

11.1 Calculation of hydrogen ion concentration from a pH measurement.

$$pH = -1(\log[H^+])$$

$$\frac{pH}{-1} = \log[H^+]$$

$$anitlog\left(\frac{pH}{-1}\right) = [H^+]$$

A calculator that can perform log functions is very handy to make this calculation:

1) enter the pH and change the value to a negative.
2) Take the antilog of the number. (For most calculators that will mean using the 10^x key).

$$\%Rec = \frac{H}{H_T} x\ 100$$

11.2 The percent recovery is calculated:
where

H = hydrogen ion from pH measurement
H_T = theoretical hydrogen ion concentration

EXAMPLE
A check standard is analyzed and the pH is determined to be 8.90. The certified concentration is 9.05. The

$$H_{8.90} = antilog(-8.90) = 1.26\ x\ 10^{-9}$$

$$H_{9.05} = antilog(-9.05) = 8.91\ x\ 10^{-10}$$

$$\%Rec = \left(\frac{1.26\ x\ 10^{-9}}{8.91\ x\ 10^{-10}}\right) x\ 100 = 141\%$$

percent recovery is calculated:

This result makes sense because pH 8.90 represents a higher hydrogen concentration than pH 9.05.

11.3 The precision as %RPD is calculated in the routine way as the relative percent difference between two

$$\%RPD = \left|\frac{H_1 - H_2}{(H_1 + H_2)/2}\right| x\ 100$$

check standards. When sample duplicates are analyzed, the pH must first be converted to hydrogen ion concentration before the %RPD can be calculated:
where

H_1 = hydrogen ion concentration of replicate 1
H_2 = hydrogen ion concentration of replicate 2

EXAMPLE
Two aliquots of the same sample are analyzed and the pH measurements are 8.90 and 9.00. The %RPD is calculated:

$$H_{8.90} = antilog[-8.90] = 1.26 \times 10^{-9}$$

$$H_{9.00} = antilog[9.00] = 1.0 \times 10^{-9}$$

$$\%RPD = \left|\frac{(1.26 \times 10^{-9}) - (1.00 \times 10^{-9})}{(1.26 \times 10^{-9} + 1.0 \times 10^{-9})/2}\right| \times 100 = \left|\frac{0.26 \times 10^{-9}}{1.13 \times 10^{-9}}\right| \times 100 = 23\%$$

12.0 QUALITY CONTROL/QUALITY ASSURANCE

12.1 The pH meter/electrode will be calibrated using two pH buffers that bracket the expected range of pH.

12.2 Duplicate sample measurements will be performed on 10% of the samples.

12.3 A check solution from a separate source will be analyzed after the calibration as an initial calibration verification. A control limit of the theoretical pH ± 0.2 pH units will be used. This is equivalent to the pH recovery range of 63-158% over the pH range of 2 - 13. After every ten samples a check solution buffer will be analyzed as a continuing calibration verification. The pH reading should be ±0.2 pH units of the true value. An RPD control limit of 40% will be used to gauge the acceptability of sample replicates.

13.0 PREVENTIVE MAINTENANCE

No additions to this revision.

14.0 TROUBLESHOOTING

No additions to this revision.

15.0 REFERENCES

1. *Savannah Laboratories' Comprehensive Quality Assurance Plan* and *Savannah Laboratories' Corporate Quality Assurance Plan*, current revisions.

2. EPA Method 150.1; *Methods for Chemical Analysis of Water and Wastes*, EPA 600/4-79-020.

3. SW-846 Methods 9040 and 9045C; *Test Methods for Evaluating Solid Waste, SW-846 Third Edition*.

4. Standard Method 4500-H^+; *Standard Method for the Examination of Water and Wastewater*, 18th Edition.

BA09:05.01.98:1

Approval Signature: R. Wayne Robbins	
Title: Corporate QA Manager	Date: 5/1/98

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TOTAL ORGANIC CARBON-SHIMADZU TOC ANALYZER

1.SCOPE AND APPLICATION

1.1 This method is applicable to the determination of total organic carbon (TOC) in ground water, surface water, drinking water, domestic and industrial wastewater, soils, sediments, and other solids.

1.2 The linear range for TOC aqueous samples is from 1mg/L to 500mg/L for a 250uL injection volume. Samples with TOC concentrations greater than 500mg/L require dilution before analysis. The linear range for soils and solids samples is from 500mg/kg to 235000mg/kg for a 100mg sample.

1.3 The reporting limit(RL), the method detection limit(MDL), and the accuracy and precision criteria are given in Table 5 of the Savannah Labs Comprehensive Quality Assurance Plan (1) or client-specified QAPP.

2.SUMMARY OF METHOD

2.1 Total organic carbon (TOC) is measured by treating a sample with hydrochloric acid (HCl) and purging the sample to eliminate the inorganic carbon present in the sample. The HCl converts any carbonates present in the sample to CO2, which is then purged out of the sample. Purging the sample also eliminates any volatile organic compounds from the sample matrix; therefore, any direct measurement of TOC is actually non-purgeable TOC. The acid treated sample is then combusted at 680C for liquids and 900C for soils. The carbon is converted to carbon dioxide and the carbon dioxide is measured by an infrared (IR) detector. The amount of carbon dioxide, expressed as carbon, is directly proportional to the carbon content of the sample.

2.2 It is important that the analyst know the type of carbon analysis to be determined so that the proper sample can be used for the analysis. The following "equation" shows the relationship between the various forms of carbon that can be measured with this procedure:

$$TC = TOC + TIC$$

where

TC = total carbon
TOC = total organic carbon
TIC = total inorganic carbon

Since TOC has two components, purgeable and non-purgeable, the "equation"can be expanded:

$$TC = npTOC + pTOC + TIC$$

where npTOC = non-purgeable TOC
pTOC = purgeable TOC

Three of these forms of carbon can be measured directly- TC, npTOC, and TIC. The pTOC has to be determined by difference.

In most cases, the pTOC is very small compared to the npTOC and the npTOC is reported as the "total organic carbon".

2.3 This procedure is based on EPA Method 415.1(2), SW-846 Method 9060(3), and the SL COMPQAP(1).

3.SAFETY

3.1 The analyst must protect herself/himself from exposure to the sample matrix. Many of the samples analyzed for carbon content are potentially hazardous. The analyst must wear protective clothing (lab coat or apron), eye protection (eyeglasses or face shield), and disposable gloves when handling the samples.

3.2 The furnace on the carbon analyzer and on the soil analyzer must be cooled to room temperature before maintainence can be performed. The temperature of the analyzer furnace can reach 680C and the soil furnace can reach 900C. The analyst must be very careful to avoid touching these very hot surfaces.

3.3 Care must be taken when handling hydrochloric acid(HCl) and solutions of hydrochloric acid. The inorganic carbon reagent is 2N HCl and must be handled with caution. This acid will cause chemical burns and destroy unprotected clothing. The analyst must also use extreme caution when adding acid to soil samples. The acid should be added slowly to minimize potentially violent reactions that will splatter acid.

3.4 The carrier gas MUST remain on while the instrument is in operation. The analyst must ensure that there is sufficient carrier gas available in the tank to complete the run. Failure to have carrier gas running through the instrument while the combustion furnace is at the operating temperature may result in melting of the combustion tubes.

3.5 The Material Safety Data Sheets(MSDS) for each regent and standard used in this procedure are available for inspection and review by each analyst at each lab division. The MSDS contain information on the potential hazard that each reagent poses and the guidelines for safely handling the reagent. The MSDS also contains some first aid information and should be taken to the first aid center or hospital with any person that requires a higher level of medical attention after exposer to the reagent.

4.INTERFERENCES

4.1 Sample particulates that are larger than the syringe will not be included in the carbon determination. This condition may result in low results if the particulates contain measurable levels of carbon. The analyst should be alert to samples that may clog the sample syringe.

4.2 Liquid samples containing oil or are oily in nature will deactivate the catalyst. The catalyst will have to be regenerated or replaced prior to running other samples. It is highly recommended that oily

samples be analyzed using the soil module or that the CCV and CCB be analyzed immediately after these samples to evaluate the condition of the catalyst.

4.3 It is very important that the inorganic carbon be removed from the sample prior to the direct determination of the TOC (non-purgeable TOC). Failure to remove the inorganic component of the sample may result in artificially high TOC results.

5.SAMPLE COLLECTION, PRESERVATION, AND HANDLING

5.1 Aqueous samples for total organic carbon are collected in 125-mL amber glass containers with zero headspace and preserved with HCl to pH < 2. A light blue dot is placed on the container to indicate that the sample has been preserved with HCl. The sample is iced at the time of collection and is stored at 4C +/- 2C until the time of analysis.

The pH of each aqueous sample for TOC must be determined and recorded when the sample arrives in the lab to ensure proper preservation.

5.1.1 Pour a small aliquot of the well-mixed sample into a small plastic cup.

5.1.2 Dip a piece of wide range pH paper into the sample in the cup. NEVER dip the pH paper into the sample container.

5.1.3 If the pH is less than 2 (<2), the preservative is correct and the sample can be stored in the cooler.

5.1.4 If the pH of the sample is greater than 2 (>2), adjust the pH to less than 2 (<2) with small aliquots of 1:1 HCl solution. Thoroughly mix the acid and sample and re-test another aliquot of the sample. Continue adding small aliquots of acid to the sample until the pH is less than 2. Record the pH of the sample along with any adjustments and/or comments on the TOC sample pH log.

5.2 Soil and sediment samples are collected in 125-ml amber glass containers with minimum headspace. The samples are iced at the time of collection and are maintained at 4C +/- 2C until the time of analysis.

5.3 The hold time for an aqueous sample preserved with HCL is 28 days from the date of collection. The maximum hold time for soil and sediment samples is 28 days from the date of collection.

6.APPARATUS AND MATERIALS

6.1 Shimadzu 5050A Carbon Analyzer

6.2 Volumetric pipets

6.3 Filters (0.45um) and disposable filters

6.4 Volumetric flasks

6.5 Disposable transfer pipets

6.6 Ceramic boats for soil analyses

6.7 Aluminium pans

6.8 Ultra pure compressed air, regulator and appropriate fittings. The compressed air must contain less than 1ppm of carbon dioxide. This gas is used as the carrier and sparge gas for the analysis of aqueous samples.

6.9 Oxygen, regulator, and appropriate fittings. The oxygen is used as the carrier gas in the analysis of soil samples.

7. REAGENTS

7.1 Reagent water- lab-generated deionized water

7.2 Hydrochloric acid (HCl)-concentrated, reagent grade or better. Record the acid lot number in the reagent prep log.

7.3 1:1 Hydrochloric acid solution (50% HCl)- Add approximately 400mL of reagent water to a 2.0-L beaker. Place the beaker on a magnetic stir plate located under a hood. Add a Teflon stir bar to the reagent water and turn the stir plate on. SLOWLY and CAREFULLY add 500mL of concentrated HCl to the beaker in small aliquots. Hydrochloric acid is extremely toxic and has a suffocating odor. After the entire 500-mL of HCl has been added, continue mixing and allow the solution to cool. After the solution has cooled, transfer it to a 1.0-L volumetric flask and dilute to volume with reagent water. This solution should be stored in a glass container. Prepare this solution every six months or as needed. Record the preparation in the reagent prep log.

7.4 2 N HCl Solution-Slowly add 42mL of concentrated HCl to about 150mL of reagent water contained in a 250-mL volumetric flask. Dilute to volume with reagent water. Transfer the reagent to a glass container. This reagent must be prepared under a hood. HCl has a suffocating odor and can cause severe chemical burns.

7.5 Vanadium pentoxide-reagent grade

7.6 Tungsten oxide-reagent grade

8.STANDARDS

8.1 Stock standards

8.1.1 Potassium hydrogen phthalate (KHP)-reagent grade or better.

8.1.2 Potassium hydrogen phthalate, 2000mg Carbon / liter
Dissolve 0.4256g of reagent grade KHP in approximately 800mL of reagent water contained in a 1.0-L volumetric flask. Dilute to volume with reagent water and transfer the stock standard to an amber glass container. Label the container with the standard identification, concentration, analyst's initials, date prepared, and the expiration date. Record the preparation in the standards prep log. Store the standard in the refrigerator

at 4C +/-2C. Prepare this standard monthly or as needed.

8.2 Calibration Standards-TOC

The KHP stock standard is used to prepare the calibration standards for the determination of TOC. The pH of each calibration standard is adjusted to less than 2 with 1:1 HCl. The following table gives the volumes of stock standard needed to prepare the given volume of the calibration standard:

Calibration Standard (mg/L)	mL of 2000mg/L Stock Standard	mL of Reagent Water	Final Volume
500	250	750	1000
200	100	900	1000
100	50	950	1000
50	25	975	1000
10	5.0	995	1000
5.0	2.5	997.5	1000
1.0	0.50	999.5	1000

The concentration of the calibration standard can be determined using the following equation:

$$(Cs)\,(Vs) = (Ccal)\,(Vcal)$$

$$Ccal = \frac{(Cs)\,(Vs)}{(Vcal)}$$

where

Cs = concentration of the stock standard (mg/L)
Vs = volume of stock standard needed to prepare the calibration standard(L)
Ccal = concentration of the calibration standard to be prepared (mg/L)
Vcal = volume of the calibration standard to prepare (L)

9. SAMPLE PREPARATION

9.1 There is essentially no sample preparation for aqueous samples. The samples are loaded on to the autosampler and the sampling sequence is initiated. The analyst should be alert for samples with high solids and particulates that may clog the syringe or may produce results that are lower than might expected.

NOTE: It may be difficult to establish correlation between the TOC, BOD, and COD for samples with high particulates. The syringe system used by the Shimadzu instrument may effectively filter out particulates that may be included in the determination of BOD and COD.

9.2 Soil samples for TOC analysis are dried to produce a free flowing, homogeneous sample. The dried sample is treated with concentrated HCl to convert the carbonates and bicarbonates to carbon dioxide, which evolves from the sample.

9.2.1 Weigh approximately 5g to 10g of the soil or sediment sample into an aluminum pan.

9.2.2 Place the pan in the oven and allow the moisture to evaporate over night at 105C.

NOTE: Heating the soil will drive off the volatile organics. The TOC measured from the soil is the non-purgeable or non-volatile component of the total organic carbon. Since the volatiles are usually very low compared to the non-volatile, the non-volatile component is reported as the TOC.

9.2.3 Remove the samples from the oven. Crush any lumps that may be present with a spatula or spoon and mix the sample to obtain a homogeneous sample.

9.2.4 Weigh out five (5) 100mg portions of the sample into the ceramic "boats". Record the weight of each sample to the nearest 0.1mg on the analysis log.

9.2.5 Add approximately 0.10mL of concentrated HCL to each ceramic "boat". Additional HCl can be added if the soil has a high carbonate content. This step should be performed in a hood.

9.2.6 Place the sample "boats" into the oven to allow the excess HCL to evolve. The sample is now ready for analysis.

10.PROCEDURE

10.1 Aqueous Samples-TOC

10.1.1 Turn the Shimadzu 5050A on and set the following parameters:

Analyzer Furnace: 680 C
Carrier Gas: 150mL/min (ultrapure compressed air)
Purge Gas: 50mL/min (ultrapure compressed air)
Injection Volume: 250uL (0.250mL)
Minimum Number of Replicates: 3
Maximum Number of Replicates: 5

Allow the instrument to equilibrate and the furnace to reach the set point before processing samples.

10.1.2 Set up the calibration standards on the autosampler. The lowest standards should be analyzed first. The analytical sequence is :

Range 1 Calibration Standards:
1.0mg/L
5.0mg/L
10mg/L

Range 2 Calibration Standards
1.0mg/L
10mg/L
50mg/L
100mg/L

Range 3 calibration Standards
1.0mg/L
100mg/L

200mg/L
500mg/L

Initial Calibration Verification(ICV/LCS)
Initial Calibration Blank (ICB)
10 client samples (in replicate)
Continuing Calibration Verification(CCV/LCSD)
Continuing Calibration Blank (CCB)
10 client samples (in replicate, including an MS/MSD per batch of twenty samples)
CCV/LCS
CCB

This sequence continues until there are no more samples to fill the slots. The CCV and CCB must "cap" the end of the analysis sequence. Note that the ICV and the CCV are from a separate source (ERA) and are evaluated for calibration verification and overall analytical control(accuracy and precision)

The initial calibration is performed each time samples are analyzed.

10.1.3 Record the sample identifications on the analysis log sheet to correspond to the position occupied by the samples on the autosampler tray.

10.1.4 Start the analyzer. The samples will be processed automatically.

10.1.5 After the sequence has ended, evaluate the QC and the sample results.

10.1.5.1 If the ICV or a CCV or the ICB or a CCB has failed, the samples analyzed between the failed CCV or CCB must be re-analyzed. The result for the ICV/CCV must be 80-120% of the true value. The results for the ICB/CCB must be less than the quantitation limit of 1mg/L.

10.1.5.2 If a sample contains a concentration of TOC greater than the linear range of the calibration curve, the sample must be diluted and re-analyzed.

10.2 Soil Samples-TOC The TOC analyzer is initially calibrated using a 1-point calibration curve on each analysis range. The curve is plotted from zero through the area corresponding to the standard for the specified range. The calibration levels are:

RANGE	mg KHP	mg Carbon
X1	2.1	1.0
X5	8.0	3.8
X30	50	23.5

These standards define the linear range of the instrument.

10.2.1 Turn the Shimadzu 5050A and soil analyzer module on and set the following parameters:

Soil Analyzer Furnace:	900 C	
Carrier Gas:		50mL/min (oxygen)

Allow the instrument to equilibrate and the furnace to reach the set point before processing samples.

10.2.2 Before samples are processed, a 1.0-mL aliquot of 2N HCl is combusted in the furnace to clean and regenerate the catalyst.

10.2.2.1 Add 0.10mL of 2N HCl to the ceramic "boat"

10.2.2.2 Add sufficient ceramic "wool" to cover the acid.

10.2.2.3 Place the "boat" into the furnace and allow the sample to cycle through the combustion and cooling steps.

10.2.3 A method blank, consisting of the ceramic "boat", ceramic "wool" and metal catalyst (vanadium pentoxide or tungsten oxide), is then processed through the combustion and cooling cycle to evaluate the contribution of the "boat", ceramic "wool", and the metal catalyst to the overall TOC analysis. If the weight of a "blank sample" is assumed to be 100mg, the method blank should be less than 500mg/kg,dw.

10.2.4 After the method blank has been analyzed, the following QC Check Standards are analyzed: four 20-mg portions of dextrose and one 15-mg to 18-mg portion of the EPA Municipal Digested Sludge. The recovery of each of these check standards must be within the SL COMPQAP Table 5 criteria for recovery. The duplicate analyses of the dextrose standards ar e used to evaluate precision, which must be less than the Table 5 limit for %RPD

10.2.5 The client samples are prepared as described in Section 9.2. It is important that all of the inorganic carbon be converted to CO2 prior to the analysis of the soil for TOC.

10.2.6 One of the five prepared portions of soil is analyzed on the X5 range to determine the proper range for that particular sample.

10.2.6.1 If the result for the sample is within the X5 range, that is , if the result is quantifiable but less than the high standard (within the linear range), the X5 range is used and three of the other portions are analyzed on the X5 range. Each sample must be analyzed in quadruplicate.

10.2.6.2 If a peak is not quantified, a second 100mg portion of the sample is analyzed on the X1 range. The three remaining portions of sample are analyzed on the X1 range. Each sample must be analyzed in quadruplicate.

10.2.6.3 If the concentration of the initial analysis exceeds the linear range on the X5 range, a second portion of the sample is analyzed on the X30 range. If the result on the X30 range is within the linear range, the remaining portions are analyzed on the X30 scale. Each sample must be analyzed in quadruplicate.

If result is above the linear range on the X30 range, a smaller aliquot of sample should be weighed and analyzed.

10.2.7 Each soils sample must be analyzed in quadruplicate on the same range setting. The average result of the four replicates is reported unless a request is made for the result of each individual replicate.

11. DATA ANALYSIS/CALCULATIONS

11.1 The concentrations of TOC in client and QC samples are taken from the linear regression curve.

11.1.1 The results for liquid samples are calculated as follows:

mg/L (in sample) = mg/L (from printout) x DF

where

DF = dilution factor

11.1.2 The Reporting Limit (RL) is calculated:

$RL(mg/L) = RL_{qap} \times DF$

where RL_{qap} = reporting limit from Table 5, SL COMPQAP
DF = dilution factor

The SL Quality Assurance Plan Reporting Limit assumes that DF=1.

11.1.3 The results for soil sample is calculated as follows:

mg/kg,dw = mg/kg(from curve)

Since the sample is dried prior to analysis, the result from the printout is given on a "dry weight basis". The weight of the soil is entered into the data system and the result is calculated as mg/kg, dw since the sample is dried prior to analysis.

11.1.4 The Reporting Limit (RL) is calculated:

$$mg/kg,dw = RL_{qap} \times \frac{100mg}{W}$$

where

RL_{qap} = reporting limit from Table 5, SL COMPQAP
W = weight of sample analyzed (mg)

The SL Quality Assurance Plan Reporting Limit and assumes that 100mg(0.100g) of sample is analyzed.

11.2 The concentration of TOC in the lab control and matrix spike samples is determined as in Section 11.1. The concentration is compared to the theoretical spike concentration and the percent recovery is calculated.

11.2.1 0.0mL of the 50mg/L matrix spiking solution is added to a 250mL aliquot of a liquid sample or to 10.0g of a soil sample(the soil sample is mixed with 250mL of reagent water)

11.2.1.1 The theoretical concentration of an aqueous sample that has been spiked with the matrix spiking solution is

$$mg/L = \frac{0.5mL \times 2000mg/L}{100mL} = \frac{0.0005L \times 2000mg/L}{0.100\ L} = 10mg/L$$

11.2.1.2 The theoretical concentration of a soil sample that has been spiked with a 20mg portions of dextrose is:

$$mg/kg,dw = \frac{20mg \times 0.40mg\ C/mg}{100mg} = \frac{8mg\ C}{100mg} = 80000\ mg/kg$$

11.2.1.3 The percent recovery of the matrix spike in the matrix spike sample is calculated:

$$\%recovery\ (\%REC) = \frac{(Cms - Cs)}{Ts} \times 100$$

where

Cms = concentration of the spiked sample (MS or MSD)
Cs = concentration of the unspiked sample
Ts = theoretical concentration of the spike

11.2.1.4 The matrix spike samples are analyzed in duplicate. The relative percent recovery(%RPD), a measure of precision, is calculated for the MS/MSD pair as follows

$$\%RPD = \left| \frac{\%REC(MS) - \%REC(MSD)}{(\%REC(MS) + \%REC(MSD))\ /\ 2} \right| \times 100$$

11.2.2 The lab control standard is purchased from ERA (Environmental Resource Associates). The standard comes in a vial that is diluted to a specified volume with reagent water. The results are compared to the values contained on the certificate of analysis. The lab control sample for soil samples is dextrose. Twenty milligrams of dextrose is weoghed into a ceramic boat and analyzed as a sample. An EPA sample, municipal digested sludge, is also analyzed as a control standard.

11.2.2.1 The recovery of the lab control standard is calculated as follows:

$$\%REC = \frac{Clcs}{Ct} \times 100$$

Where

Clcs = concentration of the LCS or LCSD
Ct = theoretical concentration of the LCS or LCSD

11.2.2.2 The lab control standards samples are analyzed in duplicate. The relative percent recovery(%RPD), a measure of precision, is calculated for the LCS/LCSD pair as follows

$$\%RPD = \left| \frac{\%REC(LCS) - \%REC(LSCD)}{(\%REC(LCS) + \%REC(LCSD))/2} \right| \times 100$$

12. QUALITY ASSURANCE /QUALITY CONTROL

12.1 The analytical batch consists of up to twenty client samples and the associated QC items. The QC items for an analytical batch consist of a method blank, a lab control standard(LCS), a lab control standard duplicate(LCSD), a matrix spike(MS), and a matrix spike duplicate(if there is sufficient volume to perform the MS/MSD)

12.2 Evaluation of QC Data

12.2.1 The **method blank** is reagent water that is taken through all of the analytical procedures. The concentration of TOC in the method blank is a measure of the contamination due to the entire analytical process.

12.2.1.1 The concentration of TOC in the method blank must be less than 1.0mg/L for liquids and 500mg/kg for soils(Assuming a "soil" weight of 100mg(0.1000g).

12.2.1.2 If the concentration of TOC in the method blank is greater than 1.0mg/L for liquids and 500mg/kg for soils, contact the immediate supervisor to determine the cause of the contamination. If the cause of the contamination cannot be determined and corrected, the batch of samples processed with the method blank must be reanalyzed.

12.2.2 The **lab control standard (LCS or LCSD)** is a standard obtained or prepared from a separate source (a source different from the source of the calibration standards) and taken through all of the analytical procedures. The LCS for TOC is purchased from ERA. A certificate of analysis must accompany the lab control standard and the certificate must be kept as a record of the true (theoretical) concentration of the LCS.

12.2.2.1 The recoveries(%REC) of the LCS and LCSD must be between 80% and 120%. The relative percent difference(%RPD) between the LCS and LCSD must be less than 20%

12.2.2.2 If the recovery of TOC in the LCS or LCSD is outside of the 80-120% range, contact the immediate supervisor to determine the cause. If the %RPD of the LCS/LCSD is greater than 20%, contact the immediate supervisor to determine the cause. If the cause of the failure of either the %REC or %RPD cannot be determined and corrected, the batch of samples processed with the LCS/LCSD must be reanalyzed.

12.2.3 The **matrix spike and matrix spike duplicate (MS/MSD)** is prepared by adding a known concentration of a TOC standard to a known volume or weight of a client sample. The spiked samples are processed through the entire analytical procedure. The accuracy and precision results from the MS/MSD are a measure of the effect that the sample matrix has on the determination of TOC.

12.2.3.1 The recoveries(%REC) of the MS and MSD should be between 60% and 140%. The relative percent difference(%RPD) between the MS and MSD should be less than 40%.

12.2.2.2 If the recovery of TOC in the MS or MSD is outside of the 60-140% range, contact the immediate supervisor to determine the cause. If the %RPD of the LCS/LCSD is greater than 40%, contact the immediate supervisor to determine the cause. If the cause of the failure of either the %REC or %RPD cannot be determined and corrected and the LCS/LCSD are within the specified control limits, the cause can be attributed to matrix interference(s).

NOTE : FOR PROJECTS WHICH REQUIRE FLORIDA DEP QAS CRITERIA, MATRIX SPIKE RESULTS WILL BE UTILIZED FOR LABORATORY CONTROL. IF THE MATRIX SPIKES ARE OUT OF CONTROL, LABORATORY CONTROL STANDARD (LCS) AND METHOD CONTROL CRITERIA WILL BE UTILIZED FOR ULTIMATE CONTROL OF THE ANALYTICAL BATCH.

12.3 The **method detection limit (MDL)** is defined as the concentration of the an analyte that can be measured with a 99% confidence that the result is greater than zero. The MDL is determined by spiking 10 aliquots of reagent water or 10 aliquots of blank soil (a soil that has been analyzed previously and found to contain no TOC above the RL) with a known concentration of TOC. The spiked samples are taken through the analytical process. The results of the analysis of the spiked samples is used to calculate the MDL.

12.3.1 Prepare the spiked samples for the determination of the Method Detection Limit.

12.3.1.1 Spike ten(10) 100-mL aliquots of reagent water with 0.10mL of the TOC matrix spiking solution (2000mg/L) to determine the MDL for liquid samples. The concentration of TOC in the water sample is 1.0 mg/L.

12.3.1.2 Spike ten(10) aliquots of a blank soil (a soil that has been analyzed previously and found to contain no TOC above the RL) with 0.025mL of the TOC matrix spiking solution (2000mg/L) to determine the MDL for soil/solid samples. The concentration of the TOC in the soil sample is 1000 mg/kg.

12.3.2 Analyze (Section 10.) the MDL samples. Calculate the concentration of the samples (Section 11.). Enter the data on the LIMS sheets. A LIMS-based program will calculate the MDL. A report will also be generated and returned to each section as a record of the MDL

13. REFERENCES

(1) Savannah Laboratories *Comprehensive Quality Assurance Plan*, 1998

(2) *Method for Chemical Analysis of Water and Wastes;* U.S. EPA Office of Research and Development: Cincinnati, OHIO, March, 1983

(3) *Test Methods for the Evaluating Solids Wastes, Third Edition, SW-846;* US EPA Office of Solid Waste and Emergency Response: Washington, DC.

Approval Signature: R. Wayne Robbins	
Title: Corporate QA Manager	Date: 8/29/97

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TOTAL ORGANIC CARBON IN SOIL: WALKLEY-BLACK METHOD

1.0 SCOPE AND APPLICATION

1.1 This method is used to estimate the concentration of organic carbon in soils, sludges, and oils. The carbon in carbonized materials such as charcoal is not amenable to this procedure.

1.2 The reporting limit (RL), the method detection limit (MDL), and the accuracy and precision limits are given in Section 5 of the Savannah Laboratories Quality Assurance Plans.

2.0 SUMMARY OF METHOD

2.1 Organic carbon in soils is determined by adding 10 mL of standard potassium dichromate and sulfuric acid to a weighed soil sample. After allowing sufficient time for oxidation of the organic carbon, the remaining dichromate is back-titrated with standardized ferrous sulfate and the organic carbon is estimated.

2.2 This method is based on Method 29-3.5.2 from *Methods of Soil Analysis*(1).

3.0 SAFETY

3.1 Use good common sense when working in the lab. Do not perform any procedure that you do not understand or that will put you or others in potentially dangerous situations.

3.2 This procedure calls for the use of a strong oxidizer (potassium dichromate) and a strong acid (sulfuric acid). The analyst must wear a lab coat or apron, protective eye glasses or face shield, and gloves when performing this procedure.

3.3 Material Safety Data Sheets (MSDS) are available for each reagent and standard used in the lab. The analyst should be thoroughly familiar with the MSDS which list safe handling and storage parameters for the materials.

4.0 INTERFERENCES

4.1 The organic matter in soils is, in general, not quantitatively oxidized by the dichromate in this procedure. The TOC result obtained is therefore multiplied by a correction factor to account for the generally low recoveries obtained by the method.

4.2 Certain oxidizable or oxidizing inorganic elements or compounds may interfere. High concentrations of chloride can be a significant positive interference. If the presence of a high level of chloride is suspected, the following correction equation can be used:

TOC, mg/L = Apparent TOC, mg/L - (mg/L Cl^-/12).

When Fe^{2+} is present in soil, its oxidation by dichromate will result in a positive interference. Iron is generally in the oxidized state (Fe^{3+}) in aerated soils, and thus, this generally is not a problem. Highly reduced soil types, such as deeply buried, fine-grained sediments, may contain appreciable quantities of Fe^{2+}. These samples should be dried in a drying oven at 105°C prior to analysis. This will allow for the Fe^{2+} to be oxidized to Fe^{3+}. MnO_2 present can be a negative interference, but only freshly precipitated MnO_2 takes part in this redox reaction; thus MnO_2 interference is thought not to be a serious error in most soils (1).

5.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

Sampling and storage of samples in glass bottles is preferable. Use of conventional polyethylene containers is permissible if it is established that the containers do not contribute contaminating organics to the sample. The sample should be stored at 4C ± 2C until analysis. The analysis should be performed as soon as possible but should be completed within 28 days of collection.

6.0 APPARATUS AND MATERIALS

6.1 Analytical balance

6.2 Drying oven

6.3 Buret, 25-mL

6.4 Erlenmeyer flasks, 250-mL

7.0 REAGENTS

The preparation and standardization of all reagent must be documented in the appropriate log.

7.1 Reagent water - lab generated deionized water

7.2 Potassium dichromate, 1 N: Dissolve 49.04 g of reagent grade $K_2Cr_2O_7$ (dried at 105°C) in DI water in a 1-L volumetric flask, and dilute to volume.

7.3 Ferrous sulfate heptahydrate, 0.5 N: Dissolve 140 g of reagent grade $FeSO_4 \cdot 7H_2O$ in DI water, add 15 mL concentrated sulfuric acid, and dilute to 1000 mL. This titrant should be standardized with each set of samples.

Calculate the normality of the ferrous sulfate as shown below:

$$[FeSO_4], N = \frac{10\ mL \times 1\ N}{mL\ FeSO_4\ used\ for\ titration}$$

Standardize ferrous sulfate daily by titrating 10 mL of potassium dichromate solution.

7.4 Sulfuric acid, concentrated

7.5 Ferroin indicator: Commercially available 0.025M o-phenanthroline-ferrous complex

8.0 STANDARDS

No calibration standards are associated with this procedure. A check standard may be obtained from a reputable vendor such as ERA, APG, or ASI. Municipal digest sludge may be used as a check standard if a certified value is supplied. Ten milliliters (1mL) of the 2000mg/L TOC standard may be also used as a check standard (assume the sample weight is 10g).

8.1 Potassium hydrogen phthalate (KHP)-reagent grade or better.

8.2 Potassium hydrogen phthalate, 2000mg Carbon / liter
Dissolve 0.4256g of reagent grade KHP in approximately 800mL of reagent water contained in a 1.0-L volumetric flask. Dilute to volume with reagent water and transfer the stock standard to an amber glass container. Label the container with the standard identification, concentration, analyst's initials, date prepared, and the expiration date. Record the preparation in the standards prep log. Store the standard in the refrigerator at 4C +/-2C. Prepare this standard monthly or as needed.

9.0 SAMPLE PREPARATION

The sample preparation steps are included as part of the Procedure (Section 10).

10.0 PROCEDURE

10.1 Remove the sample from the refrigerator and allow the samples to come to room temperature. Thoroughly mis the material, removing sticks, rocks, and leaves.

10.2 Weigh out soil sample to contain roughly 10 to 25 mg organic C into a 250-mL Erlenmeyer flask.

- Dark soils and sludges generally contain high concentrations of organic carbon and 0.05 - 0.1 g is weighed out for these samples.
- For medium-colored soils, 0.1 - 2.5 g of sample is used.
- For light-colored soils and sands, 1-5 g of sample is weighed out.

10.3 Place Erlenmeyer flasks containing saturated sediments or other possibly anaerobic soils into a drying oven at 105°C for 1 h, or until they are thoroughly dry.

10.4 Add 10 mL potassium dichromate solution by pipet and swirl to mix. Rapidly add 20 mL of concentrated H_2SO_4 (under a ventilating hood) and swirl to mix. Allow to cool and add 150 mL DI water.

10.5 Filter mixture through a glass fiber filter if it is too turbid to see color changes.

10.6 Add 8-10 drops ferroin indicator. Titrate with ferrous sulfate until color changes from blue-green to maroon. If the titration requires less than 5 mL of $FeSO_4$ titrant, repeat the analysis with a smaller quantity of soil.

11.0 CALCULATIONS

Calculate sample results with the following formula:

$$Organic\ C, mg/kg = \frac{[(mL\ K_2Cr_2O_7 \times 1\ N) - (mL\ FeSO_4 \times FeSO_4)] \times 3000 \times f}{(W)(solids)}$$

where

W = weight of soil (g)
solids = (percent solids)/100
f = 1.3

The factor f is empirically determined, but is taken to have a value of 1.3.

12.0 QUALITY CONTROL/QUALITY ASSURANCE

12.1 Ferrous sulfate is standardized daily by titrating it against 10 mL of 1 N $K_2Cr_2O_7$.

12.2 A QC check standard, municipal digested sludge, or 2000mg/L TOC standard is analyzed in duplicate for every twenty samples.

13.0 TROUBLESHOOTING

No items are included in this revision.

14.0 PREVENTIVE MAINTENANCE

No items are included in this revision.

15.0 REFERENCES

15.1 *Methods of Soil Analysis*; Page, A.L., *et.al.*, ed. American Society of Agronomy: Madison, WI, 1982.

15.2 *Savannah Laboratories' Comprehensive Quality Assurance Plan* and *Savannah Laboratories' Corporate Quality Assurance Plan*, current revisions.

TOTAL ORGANIC CARBON
WALKLEY-BLACK METHOD

Date Received	Analyst's Initials	Sample Log	Sample I.D.	Sample Weight	Titer mL	TOC (mg/kg)	Dry Weight	TOC dwb

SEMIVOLATILE ORGANIC COMPOUNDS IN AMBIENT AIRBNA AND PESTICIDES COLLECTED ON PUF AND PUF/RESIN CARTRIDGES (TO4/TO10/TO13)

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Approved by: R Wayne Potter 24 April 2001
Date
Title: Technical Manager, QA
STL X Savannah __ Tallahassee __ Mobile __ Tampa West

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1.0 SCOPE AND APPLICATION

1.1 This method describes sampling media cleaning and certification procedures, the extraction procedures, and references the analytical methods for the determination of semivolatile organic compounds (SVOC) in ambient air.

1.2 The reporting limit, the method detection limit, and the accuracy and precision limits are listed in Section 5 of the STL Corporate Quality Assurance Plan. Note that the target compounds for the BNA parameters do not correspond exactly to the routine TCL list reported by STL. Several of the target compounds cannot be quantitatively extracted from the media.

2.0 SUMMARY OF METHOD

2.1 Air samples may be collected using a high volume sampler (>1000 L/min) or using a low volume sampler (1-5 L/min.). The types of media used are described in Section 6. A sampling cartridge containing only polyurethane foam may be used to collect samples for pesticides and high molecular weight compounds. If low molecular weight compounds are to be determined, a dual media cartridge containing PUF and XAD-2 resin should be used.

2.2 After sampling, the sampling media cartridges are returned to the laboratory. The glass fiber filter and the XAD-2 resin/PUF are extracted for 16 h in a Soxhlet apparatus. The extract is filtered, concentrated, and analyzed. The extract may be split and/or exchanged to another solvent depending on the analysis required.

2.3 This SOP based on the guidance given in EPA Method TO-4, TO-10, and TO13.

3.0 SAFETY

3.1 Use good common sense when working in the lab. Do not perform any procedures that you do not understand or that will put you or others in potentially dangerous situations.

3.2 The analyst should wear protection for the eyes (lab glasses or face shield), the hands (latex gloves), and the clothes (lab coat or apron).

3.3 The analyst should be familiar with the Material Safety Data Sheets (MSDS) for the standards and reagents used in this procedure.

4.0 INTERFERENCES

4.1 Inadequately cleaned and monitored sampling media can contribute contamination that makes identification and quantitation of the target compounds difficult.

4.2 High levels of non-target compounds can cause problems with the chromatography and can affect the sensitivity and specificity of the detector.

5.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

Air samples for SVOC should be wrapped securely and iced after collection. The sample media should be stored at 4C (0-6C) in the lab. The media should be extracted within 7 days of collection and the extract analyzed within 40 days of extraction.

6.0 APPARATUS AND MATERIALS

6.1 Media for High Volume Sampler

If the client supplies a cartridge compatible with the General Metal Works PS-1 High Volume Sampler, the following media are required:

XAD-2 resin - Supelco 1-0357 (500 g) 20-60 mesh

Polyurethane foam (PUF) plugs: 1" General Metals Works (GPSI-18)

Polyurethane foam (PUF) plugs: 3" General Metals Works (GPSI-18)

Glass fiber filters: 4" Circle General Metal Works GQMA4

One compatible cartridge is: General Metal Works GPSI-4

The high volume cartridges can also be obtained from SKC as a pre-cleaned unit:

SKC Cat #	Application	Description	Sorbent/ Amount
226-129	Fits GMW PS1 TO13	Glass, open 65mmOD x 125mm L	PUF/XAD-2/PUF 50mm/10g/50mm
226-131	Fits GMW PS1 TO4	Glass, open 65mmOD x 125mm L	PUF 75mm

6.2 Low Volume Sampler

The low volume media are purchased as pre-cleaned cartridges from SKC:

SKC Cat #	Application	Description	Sorbent/ Amount
226-143	TO10, TO13	Glass, open 22mm x 100mm L	PUF/XAD-2/PUF 30mm/1.5g/30mm
226-126	TO10	Glass, open 22mm x 100mm L	Glass fiber filter/ PUF 75mm

6.3 Glass pipettes

6.4 Aluminum foil

6.5 Cotton gloves

6.6 Glass or metal rod

6.7 Volumetric glassware

6.8 Microsyringes

6.9 Soxhlet extraction apparatus (glassware and heaters)

6.10 Glass wool

7.0 REAGENTS

7.1 Methylene chloride, pesticide residue grade

7.2 Hexane, pesticide residue grade

7.3 Diethyl ether

7.4 Five- percent diethyl ether in hexane: Add 50mL of diethyl ether to a 1-L volumetric flask and dilute to volume with hexane

7.5 Acetone-pesticide residue grade or equivalent

8.0 STANDARDS

The spiking solutions are given in SOP EX70: *Preparation of Semivolatile Surrogate and Matrix Spiking Solutions*

Compounds	Method	Surrogate Spiking Solution	Matrix Spiking Solution
BNA	8270	1mL BNA surrogate	1mL 8270 or 1mL 625
Pesticides/PCBs	8080	1mL PEST	1mL 608
PAH	8310	1mL 8310-PAH	1mL 8310-MS

9.0 SAMPLE PREPARATION

The General Method Works dual sampling module consists of a filter holder and glass cartridge. Each component of the sampling module must be cleaned and checked prior to the sampling.

9.1 Media

The media may be purchased pre-cleaned or cleaned in the lab. If purchased pre-cleaned, a certificate must be received with the media. If the media is cleaned in the lab, one set of media from each batch of prepared media is extracted and analyzed as a sample to demonstrate that the media has been properly cleaned.

9.1.1 Polyurethane Foam (PUF) Plugs

The PUF plugs are cleaned by extracting in a Soxhlet extraction apparatus for 12 or more hours with hexane.

9.1.1.1 Place up to five PUF plugs in the Soxhlet body. The PUFs should fit snugly but should not be
"crammed " into the Soxhlet extractor. The cleaning solvent must be allowed to penetrate each PUF.

9.1.1.2 Charge the receiving flask with 300-400 mL of methylene chloride.

9.1.1.3 Set up the Soxhlet apparatus and set the heater to cycle every 15-min for 12 hours.

9.1.1.4 After 12 hours, turn off the heater and allow the apparatus to cool.

9.1.1.5 Remove the PUF plugs using stainless steel tweezers and place the PUFs on a sheet of aluminum foil.

9.1.1.6 Allow the PUFs to completely dry at ambient temperature under a fume hood.

9.1.1.7 Store the PUF plugs in a glass jar in the dark.

9.1.2 XAD-2 Resin

9.1.2.1 Place a small wad of glass wool in the bottom of the Soxhlet body.

9.1.2.2 Using a spatula or spoon, transfer the resin to the Soxhlet body. Approximately 100 g of resin can be
cleaned in each Soxhlet body.

9.1.2.3 Place a wad of glass wool on top of the resin to keep it in place during the extraction.

9.1.2.4 Charge the receiving flask with 300-400 mL of methylene chloride.

9.1.2.5 Set up the apparatus and set the heater to cycle every 15-min for 12 hours.

9.1.2.6 Turn off the heater and allow the apparatus to cool.

9.1.2.7 Tilt the apparatus to cause the solvent to drain from the Soxhlet body into the receiving flask.

9.1.2.8 Carefully remove the resin using a metal spatula and place it on aluminum foil under a fume hood.
Allow the resin to completely dry and store in sealed glass jars.

9.1.3 Glass Fiber Filters

The glass fiber filters may be cleaned by Soxhlet extraction with methylene chloride (recommended) or by placing the filters in the muffle furnace at 600°C. The filters should be cooled and stored in glass jars or between sheets of aluminum foil until ready for sampling.

9.2 Assembly of the Glass Cartridge

The glass cartridge contains two one-inch PUF plugs sandwiching ~ 25 g of XAD-2 resin or one three-inch PUF (if no resin is required).

9.2.1 Wear cotton gloves while assembling the glass cartridge component of the sampling media. The gloves used when cleaning the HP mass spectrometers are acceptable.

9.2.2 Rinse the **inside** of the glass cartridge with acetone and hexane in succession to remove any organic contaminants that may adhere to the surface of the glass.

9.2.3 Using stainless steel tweezers or tongs, place a clean 1-inch PUF plug in the glass cartridge. A glass rod may be used to help position the plug securely against the retaining screen. Make sure that there are no gaps or channels present along the interface of the

PUF and the glass wall.

NOTE: If a PUF-only cartridge is to be used, place a single 3-inch PUF securely into the sampling cartridge.

9.2.4 Using a metal spatula, carefully transfer the XAD-2 resin to the glass cartridge. The resin should be
added to form a 1.5 - 2.0" layer. The layer should be uniform with no gaps or channels. Gently tap the side of the glass cartridge to settle the resin.

9.2.5 Place the second 1 inch PUF plug in the glass cartridge to form a PUF/resin/PUF "sandwich." The second (top) plug should rest securely on the resin bed to keep the resin in place during the sampling event.

9.2.6 Wrap the glass cartridge in aluminum foil and store it in a glass jar. The glass jar should have a label that identifies the cartridge, the preparation batch, date of preparation, and the initials of the analyst.

9.3 Extraction

Prior to extracting, the target analytes and analytical procedures must be selected. The ambient air sample can be used to determine the following:

Compounds	Method	Extraction Solvent	Final Volume	Final Solvent
BNA	8270	MeCl2	1.0 mL	$MeCl_2$
Pesticides/PCBs	8080	5% ether in hexane	10 mL	Hexane
PAH	8310	MeCl2 or 5% ether in hexane	1.0 mL	Acetonitrile

The method blank and lab control spike are prepared using the same type of cartridge that was utilized for sampling. The spiking solution is added to the PUF or PUF/resin after it has been placed in the Soxhlet extractor.

9.3.1 Carefully inspect the glass cartridge and glass fiber filter for cracks or holes. Notify the project manager if there are problems with the sampling media.

9.3.2 Wearing cotton gloves, fold the filter twice. The exposed sides should be pointed towards each other.

9.3.3 Place a small plug of glass wool in the bottom of the Soxhlet body.

9.3.4 Using stainless steel tweezers, carefully remove the top foam plug from the glass cartridge and place it into the Soxhlet body.

9.3.5 Using a stainless steel spatula, carefully transfer the XAD-2 resin to the Soxhlet body.

9.3.6 Place the folded filter on top of the resin and carefully remove the second PUF plug. Place it in the
Soxhlet body. This second PUF plug should fit snugly enough to keep the filter and resin from floating on top of the solvent during the extraction. If the low volume sampler is

extracted, place a second plug of glass wool over the media to keep the resin in place.

NOTE: In some cases, the second PUF may be used to check for breakthrough and is extracted separately from the filter and front PUF.

9.3.7 Add the surrogate solution to the media in the Soxhlet body.

9.3.8 Rinse the **inside** of the glass cartridge with several milliliters of extraction solvent and allow the rinsings to flow into the Soxhlet body.

9.3.9 Charge the receiving flask with 300-400 mL of the extraction solvent and extract at approximately 4 cycles per hour for 16 hours.

9.3.10 Allow the unit to cool. Tilt the Soxhlet unit to drain any solvent left in the body into the receiving flask. Dispose of the extracted media in accordance with SOP CA70:*Waste Management.*

9.3.11 Concentrate the extract to the appropriate final volume.

9.3.12 Analyze the sample extract by the appropriate analytical method.

10.0 ANALYTICAL PROCEDURE

Compounds	Method	SOP
BNA	8270	SM05
Pesticides/PCBs	8080	SG45
PAH	8310	LC50

11.0 CALCULATIONS

11.1 Air samples for SVOC are routinely reported as mg/m3 (milligrams of target compound per cubic meter of air sampled). This unit is equivalent to ug/L (micrograms of target compounds per liter of air sampled).

$$\frac{mg}{m3} = \frac{ug}{L} = \frac{C \otimes FV \otimes DF}{V}$$

where

C = concentration of the target compound in the extract(ug/mL)
FV = final volume of the extract in milliliters(mL)
DF = dilution factor
V = volume of air sampled

NOTE: If the volume of sample is not supplied by the sampler, the results are reported as "micrograms per sample", assuming V=1 in the equation.

11.2 The percent recovery of the surrogates or matrix spiking compounds is determined by dividing the micrograms of compound detected by the micrograms of compound spiked:

$$\%REC = \frac{C \otimes FV \otimes DF}{Cs \otimes Vs} \otimes 100$$

where

C = concentration of the target compound in the extract(ug/mL)
FV = final volume of the extract in milliliters(mL)
DF = dilution factor
Cs = concentration of the surrogate or matrix spiking solution (ug/mL)
Vs = volume of surrogate or matrix spiking solution added to the sample(mL)

11.3 Precision is expressed as the relative percent difference between two duplicate samples or two spiked samples:

$$\%RPD = \left| \frac{C1 - C2}{\frac{C1 + C2}{2}} \right| \otimes 100$$

where

C1 = concentration of sample
C2 = concentration of sample duplicate

$$\%RPD = \left| \frac{\%REC1 - \%REC2}{\frac{\%REC1 + \%REC2}{2}} \right| \otimes 100$$

where

%REC1 = percent recovery of the LCS or MS
%REC2 = percent recovery of the LCSD or MSD

12.0 QUALITY CONTROL/QUALITY ASSURANCE

12.1 For every batch of twenty or fewer samples, a method blank/reagent blank, a laboratory control standard (LCS), and laboratory control standard duplicate(LCSD) will be extracted and analyzed. If duplicate samples are supplied, only an LCS will be extracted and analyzed.

12.2 The QC items will be evaluated against the control limits in Section 5 of the Corporate Quality Assurance Plan.

12.3 The method detection limit will be determined in accordance with SOP CA95:*Procedure for the Determination Of Method Detection Limit(MDL)* by spiking cleaned cartridges with the target compounds and analyzing the spiked cartridges in accordance with this SOP.

13.0 PREVENTIVE MAINTENANCE

No items in this revision.

14.0 TROUBLE-SHOOTING

No items in this revision.

15.0 REFERENCES

15.1. STL *Corporate Quality Assurance Plan*, current revision

15.2. TO-4, *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air* (Rev 6/88).

15.3. TO-10, *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air* (Rev 6/88).

15.4. TO-13, *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air* (Rev 6/88).

MODIFIED: TO-15
STANDARD OPERATING PROCEDURES FOR THE DETERMINATION OF VOLATILE ORGANIC COMPOUNDS IN AMBIENT AIR BY GAS CHROMATOGRAPHY/MASS SPECTROSCOPY

Applicable matrix or matrices: ambient air
Standard Compound List and Reporting Limits: see Table 1

Approvals and Signatures

Laboratory Director:	Christopher A. Ouellette	Date:	5/24/01
QA Manager:	Kim B. Watson	Date:	6/1/01
Organics Lab Manager:	Bryce E. Stearns	Date:	5/24/01

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1.0 SCOPE AND APPLICATION

1.1 This document describes a procedure for analysis of 60 polar and non-polar volatile organic compounds (VOCs) in ambient air. The VOCs are separated by gas chromatography and measured by a mass spectrometer. This method presents procedures for sampling into canisters to final pressures both above and below atmospheric pressure (respectively referred to as pressurized and subatmospheric pressure sampling).

MODIFIED: TO-15
STANDARD OPERATING PROCEDURES FOR THE DETERMINATION OF VOLATILE ORGANIC COMPOUNDS IN AMBIENT AIR BY GAS CHROMATOGRAPHY/MASS SPECTROSCOPY

Applicable matrix or matrices: ambient air
Standard Compound List and Reporting Limits: see Table 1

Approvals and Signatures

Laboratory Director:	_____ Christopher A. Ouellette	Date: _____
QA Manager:	_____ Kim B. Watson	Date: _____
Organics Lab Manager:	_____ Bryce E. Stearns	Date: _____

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1.0 SCOPE AND APPLICATION

1.1 This document describes a procedure for analysis of 60 polar and non-polar volatile organic compounds (VOCs) in ambient air. The VOCs are separated by gas chromatography and measured by a mass spectrometer. This method presents procedures for sampling into canisters to final pressures both above and below atmospheric pressure (respectively referred to as pressurized and subatmospheric pressure sampling).

1.2 This method is applicable to specific VOCs that have been tested and determined to be stable when stored in pressurized and sub-atmospheric pressure canisters. Numerous compounds, many of which are chlorinated VOCs, have been successfully tested for storage stability in pressurized canisters. However, minimal documentation is currently available demonstrating stability of VOCs in subatmospheric pressure canisters.

1.3 The target list is shown in Table 1. These compounds can be recovered from canisters near their original concentrations after storage times of up to thirty days (18.2).

Table 1. Analytes, Chemical Abstract Services Numbers and Reporting Limits (RL)

Analyte	CAS No.	RL (ppbv)	Quant Mass Signal	Qualifier Mass
Dichlorodifluoromethane	75-71-8	0.5	85	87
Chloromethane	74-87-3	0.5	50	52
Dichlorotetrafluoroethane	76-14-2	0.5	85	135
Vinyl Chloride	75-01-4	0.5	62	64
1,3-Butadiene	106-99-0	0.5	39	54
Bromomethane	74-83-9	0.5	94	96
Chloroethane	75-00-3	0.5	64	66
Bromoethene	593-60-2	0.5	106	108
Acetone	67-64-1	0.5	43	58
Trichlorofluoromethane	75-69-4	0.5	101	103
Isopropyl Alcohol (2-Propanol)	67-63-0	0.5	45	43
1,1-Dichloroethene	75-35-4	0.5	96	61
Methylene Chloride	75-09-2	0.5	49	84
3-Chloropropene (Allyl Chloride)	107-05-1	0.5	41	46
Carbon Disulfide	75-15-0	0.5	76	
Trichlorotrifluoroethane	76-13-1	0.5	101	151

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Analyte	CAS No.	RL (ppbv)	Quant Mass Signal	Qualifier Mass
trans-1,2-Dichloroethene	156-60-5	0.5	61	96
1,1-Dichloroethane	75-34-3	0.5	63	65
Methyl tertiary-butyl ether	1634-04-4	0.5	73	43
Methyl Ethyl Ketone (2-Butanone)	78-93-3	0.5	43	72
cis-1,2-Dichloroethene	156-59-2	0.5	61	96
Hexane	110-54-3	0.5	57	86
Chloroform	67-66-3	0.5	83	85
Tetrahydrofuran	109-99-9	0.5	42	72
1,2-Dichloroethane	107-06-2	0.5	62	98
1,1,1-Trichloroethane	71-55-6	0.5	97	99
Benzene	71-43-2	0.5	78	77
Carbon Tetrachloride	56-23-5	0.5	117	119
Cyclohexane	110-82-7	0.5	56	84
1,2-Dichloropropane	78-87-5	0.5	63	41
Bromodichloromethane	75-27-4	0.5	83	85
Trichloroethene	79-01-6	0.5	95	130
1,4-Dioxane	123-91-1	0.5	88	58
2,2,4-Trimethylpentane (Isooctane)	540-84-1	0.5	57	41
n-Heptane	142-82-5	0.5	43	71
cis-1,3-Dichloropropene	10061-01-5	0.5	75	110
trans-1,3-Dichloropropene	10061-02-6	0.5	75	110
Methyl Isobutyl Ketone (4-Methyl-2-Pentanone)	108-10-1	0.5	43	58
1,1,2-Trichloroethane	79-00-5	0.5	83	97
Toluene	108-88-3	0.5	92	91
Methyl Butyl Ketone (2-Hexanone)	591-78-6	0.5	43	58

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Analyte	CAS No.	RL (ppbv)	Quant Mass Signal	Qualifier Mass
Dibromochloromethane	124-48-1	0.5	129	127
1,2-Dibromoethane	106-93-4	0.5	107	109
Tetrachloroethene	127-18-4	0.5	166	168
Chlorobenzene	108-90-7	0.5	112	77
Ethylbenzene	100-41-4	0.5	91	106
m,p-Xylene	108-38-3	0.5	106	91
Bromoform	75-25-2	0.5	173	175
Styrene	100-42-5	0.5	104	78
1,1,2,2-Tetrachloroethane	79-34-5	0.5	83	131
o-Xylene	95-47-6	0.5	106	91
2-Chlorotoluene	95-49-8	0.5	91	63
4-Ethyltoluene	622-96-8	0.5	105	120
1,3,5-Trimethylbenzene	108-67-8	0.5	105	120
1,2,4-Trimethylbenzene	95-63-6	0.5	105	120
1,3-Dichlorobenzene	541-73-1	0.5	146	111
1,4-Dichlorobenzene	106-46-7	0.5	146	111
1,2-Dichlorobenzene	95-50-1	0.5	146	111
1,2,4-Trichlorobenzene	120-82-1	0.5	180	182
Hexachlorobutadiene	87-68-3	0.5	225	223

2.0 SUMMARY OF METHOD

2.1 Both subatmospheric pressure and pressurized sampling modes typically use an initially evacuated canister and pump-ventilated sample line during sample collection. Pressurized sampling requires an additional pump to provide positive pressure to the sample canister. A sample of ambient air is drawn through a sampling train comprised of components that regulate the rate and duration of sampling into a pre-evacuated specially prepared passivated canister.

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2.2 After the air sample is collected, the canister valve is closed, an identification tag annotated and attached to the canister, a chain-of-custody (COC) form completed, and the canister is transported to the laboratory for analysis.

2.3 Upon receipt at the laboratory, the canister pressure and tag data is recorded on the analysis sheet, the COC completed, and the canister is attached to the analytical system. During analysis, VOCs are concentrated by collection in a cryogenically cooled trap. The cryogen is then removed and the temperature of the trap is raised. The VOCs originally collected in the trap are revolatilized, separated on a GC column, then detected by one or more detectors for identification and quantitation.

2.4 General Method - The mass spectrometer is calibrated to recognize m/z values in the range of 35-260 amu. Reference spectra and retention times for analytes are obtained by the measurement of calibration standards under the same conditions used for samples. The performance of the mass spectrometer is verified by the injection of 4-Bromofluorobenzene (BFB). Next, the instrument must demonstrate acceptable chemical calibration and linearity by the analysis of five concentrations of a standard mix containing the analytes of interest, as well as the internal standards. Before any samples are analyzed, a method blank must be analyzed to demonstrate that the instrument is free from contamination. All analyses must occur within 24 hours of the injection of the passing BFB. Another analytical sequence may be started by the analysis of a passing BFB MS tune followed by a continuing calibration standard, a laboratory control sample, and a method blank.

3.0 DEFINITIONS

Absolute Pressure-pressure measured with reference to absolute zero pressure (as opposed to atmospheric pressure), usually expressed as kPa, mm Hg, or psi.

Cryogen-a refrigerant used to obtain very low temperatures in the cryogenic trap of the analytical system. A typical cryogen is liquid nitrogen (bp –195.8°C) or liquid argon (bp –185.7°C).

Dynamic Calibration-calibration of an analytical system using calibration gas standard concentrations in a form identical or very similar to the samples to be analyzed and by introducing such standards into the inlet of the sampling or analytical system in a manner very similar to the normal sampling or analytical process.

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Gauge Pressure-pressure measured above ambient atmospheric pressure (as opposed to absolute pressure). Zero gauge pressure is equal to ambient atmospheric (barometric) pressure.

MS/SCAN-the GC is coupled to a MS programmed in the SCAN mode to scan all ions repeatedly during the GC run.

MS/SIM-the GC is coupled to a MS programmed to acquire data for only specified ions and to disregard all others. This is performed using SIM coupled to retention time discriminators. The GC/SIM analysis provides quantitative results for selected constituents of the sample gas as programmed by the user.

Pressurized Sampling-collection of an air sample in a canister with a (final) canister pressure above atmospheric pressure, using a sample pump.

Qualitative Accuracy-the ability of an analytical system to correctly identify compounds.

Quantitative Accuracy-the ability of an analytical system to correctly measure the concentration of an identified compound.

Static Calibration-calibration of an analytical system using standards in a form different from the samples to be analyzed. An example of a static calibration would be injecting a small volume of a high concentration standard directly onto a GC column, bypassing the sample extraction and preconcentration portion of the analytical system.

Sub-atmospheric Sampling-collection of an air sample in an evacuated canister at a (final) canister pressure below atmospheric pressure, without the assistance of a sampling pump. The canister is filled as the internal canister pressure increases to ambient or near ambient pressure. An auxiliary vacuum pump may be used as part of the sampling system to flush the inlet tubing prior to or during sample collection context, this procedure serves as a qualitative identification and characterization of the sample.

Internal Standards (IS)-Non-target analyte compounds that are similar to the target analytes but are not expected to be found in environmental media (generally, isotopically labeled target analytes are used for this purpose) and are added to every standard, quality control sample, and field sample at a known concentration prior to analysis. IS responses are used as the basis for quantitation of target analytes.

Stock solutions-A concentrated solution containing one or more method analytes prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source.

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Primary Dilution Standard Solution-A solution of several analytes prepared in the laboratory from stock standard solutions and diluted as needed to prepare calibration solutions and other needed analyte solutions.

Calibration Standard (CAL)-A solution prepared from the primary dilution standard solution or stock standard solutions and the internal standards and surrogate analytes. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

Continuing Calibration Verification (CCV)-An analytical standard solution containing all target analytes and internal standard compounds that is used to evaluate the performance of the instrument system with respect to a defined set of method criteria.

Method Blank (ABLK, similarly known as the LABORATORY REAGENT BLANK)-A canister of ambient air or other blank matrix that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, and internal standards that are used with other samples. The ABLK is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

Trip Blank-A canister of ambient air or other blank matrix that is placed in a sample container in the laboratory and treated as a sample in all respects, including shipment to the sampling site, exposure to sampling site conditions, storage, preservation, and all analytical procedures. The purpose of the trip blank is to determine if method analytes or other interferences are present in the field environment (originating from the proximity of sample containers to one another during shipment and storage).

Laboratory Control Sample (LCS)-The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. Its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements. When the results of the matrix spike analysis indicates a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix.

Initial Calibration Verification (ICV)-An analytical standard solution containing all target analytes and internal standard compounds that are prepared from a source external to the laboratory and independent from the source of the initial calibration standards. The purpose of the ICV is to verify that the initial calibration is in control.

4.0 Interferences

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4.1 Contamination may occur in the sampling system if canisters are not properly cleaned before use. Additionally, all other sampling equipment (e.g., pump and flow controllers) should be thoroughly cleaned to ensure that the filling apparatus would not contaminate samples.

5.0 SAFETY

5.1 The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable. Cautions are included for known extremely hazardous materials or procedures.

5.2 STL maintains a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in these methods. Material Safety Data Sheets (MSDS) are made available to all personnel involved in the chemical analysis. STL also has a written environmental health and safety plan.

5.3 The following method analytes have been tentatively classified as known or suspected human or mammalian carcinogens: benzene, carbon tetrachloride, 1,4-dichlorobenzene, 1,2-dichlorethane, hexachlorobutadiene, 1,1,2,2-tetrachloroethane, 1,1,2-trichloroethane, chloroform, 1,2-dibromoethane, tetrachloroethene, trichloroethene, and vinyl chloride. Pure standard materials and stock standard solutions of these compounds should be handled in a hood.

6.0 EQUIPMENT AND SUPPLIES

6.1 Sample Containers

- SUMMA® passivated stainless steel canisters are available from a number of commercial suppliers. STL's major suppliers are Restek and Scientific Instrumentation Specialists.

- Tedlar bags

6.2 Instrumentation:

- VOC Autosampler: Nutech model 3600 automated sytem. This system is capable of introducing samples from up to sixteen canisters in an automated sequence.

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- Cryogenic Concentrator: Nutech model 3550A cryogenic concentrator. The concentrator incorporatesTO-15 cryotrapping techniques.

- CDT Multibed Cryotrap: Effectively removes water and CO_2 while trapping polar and non-polar compounds.

- Electronic Mass Flow Controllers: The Nutech cryogenic concentrator is equipped with an electronic mass flow controller to maintain a constant flow for carrier gas and sample over a range of 0-200 cc/min.

- Cryofocussing Accessory: The Nutech 354A Cryofocussing accessory cryogenically refocuses the sample onto the column head.

- Gas Chromatograph: Hewlett-Packard 5890 Series II

- Mass Spectrometer: Hewlett-Packard 5971 MSD

- Primary Column: Fused silica capillary column, J&W DB-1 60m x 0.35 mm x 1.0 μm or equivalent

- Vacuum Pumps: General purpose vacuum pumps of the type specified in EPA Method TO-15.

6.3 Syringes-1.0mL - 1.0-L gas tight syringes with Luer-Lok tip

6.4 Data System: DOS based PC software for Nutech instrumentation. Hewlett-Packard ChemStation software is used for data acquisition and Hewlett-Packard ChemServer, Target 3.5 software is used for data processing.

6.5 Canister Cleaning System: Entech auto-canister cleaning system (Model 3000)

- Vacuum Pump: Capable of evacuating sample canisters to an absolute pressure of -29.9" Hg.

- Manifold: Equipped with stainless steel and Teflon transfer lines and connections for cleaning up to eight canisters simultaneously.

- Vacuum Gauge: Capable of measuring vacuum in the manifold to an absolute pressure of 0.05-mm Hg or less.

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- Heating Manifolds: Individually thermal-stated heating manifolds used to heat canisters during the cleaning cycle.

7.0 Reagents and Standards

7.1 Gas cylinders of ultrahigh purity helium and zero air.

7.2 Low pressure liquid nitrogen for the cryogenic concentrator and cryofocuser.

7.3 4-Bromofluorobenzene (BFB) for monitoring mass spectral tuning.

7.4 Calibration Standards: The primary standard is purchased through Spectra Gases. The 1 ppmv standard has 60 TO-15 target compounds and is traceable to a NIST standard. The calibration standards are prepared by adding a known amount of the primary standard into a humidified SUMMA canister and pressurizing with zero air to achieve the concentration wanted. The calibration levels (0.5, 5, 10, 20, 40 ppbv) are then achieved by injecting different volumes or further diluting.

7.5 Internal standards (Bromochloromethane, 1,4-Difluorobenzene, and Chlorobenzene-d5) are purchased through Spectra Gases at the 1 ppmv level. They are introduced automatically through the concentrator to achieve a final concentration of 10 ppbv.

7.6 Laboratory Control Samples: The 62 component standard is purchased through Spectra Gases at the 1 ppmv level. The concentration of the LCS is achieved by adding a known amount of the 1 ppmv standard to a humidified canister and then pressurized to achieve the target concentration, which is the midpoint of the calibration curve.

8.0 SAMPLE COLLECTION AND STORAGE

8.1 All canisters must be clean and free of any contaminants before sample collection.

8.2 All canisters are leak tested by evacuating them to approximately –29.5"Hg. The initial vacuum is measured, the canister valve is closed, and the final vacuum is

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checked after at least 8 hours. If acceptable, the vacuum should not vary more than 2"Hg over the time period.

8.3 The canister(s) are connected to the manifold. The vent shut-off valve and the canister valve(s) are opened to release any remaining pressure in the canister(s). The heating band(s) are then attached to the canister(s) and turned on allowing them to heat to 100°C. The number of cycles (≥3) are chosen on the Entech 3000 cleaning system and the "Auto" button is depressed. The canister(s) are first evacuated for 5 minutes by an oiless pump and then they are pressurized with humid zero air to ~10 psig.

8.4 At the end of the evacuation/pressurization cycles, the canister is pressurized to 10 psig with humid zero air. The canister is then analyzed by a GC/MS analytical system. Any canister that has not tested clean (compared to direct analysis of humidified zero air of less than 0.5 ppbv of targeted VOCs) should not be used. 100% of the canisters will be analyzed by GC/MS until they are proven to be clean. From this point on, the canister with the highest TIC in the batch of 8 canisters being cleaned at one time will be analyzed. If this canister is proven to be clean, then the rest of the batch will be certified clean as well.

8.5 The canister is reattached to the cleaning manifold and is then reevacuated to <-29.5" Hg. The canister valve is closed. The canister is removed from the cleaning system and the canister connection is capped with a stainless steel fitting. The canister is now ready for collection of an air sample. An identification tag is initialed, dated, and attached to the inlet of each canister for field notes and chain-of-custody purposes.

8.6 The analytical system is comprised of a GC equipped with a mass-selective detector set in the SCAN mode. All ions are scanned by the MS repeatedly during the GC run over a mass range of 35-265 amu. The system includes a computer and appropriate software for data acquisition, data reduction, and data reporting. A 200-mL air sample is collected from the canister into the analytical system. The sample air is first passed through a mass flow controller, then routed into a cryogenic trap.

8.6.1 The trap temperature is ramped from –40°C to 0°C within 2 minutes and then is dry purged to remove water and CO_2. The trap is then ramped to 150°C and the sample is transferred and trapped again onto the cryofocus assembly. The sample is then injected onto the DB-1 capillary column (0.32-mm x 60-m). *Note: Rapid heating of the trap provides efficient transfer of the sample components onto the gas chromatographic column.]*

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8.6.2 Upon sample injection unto the column, the MS computer is signaled by the GC computer to begin detection of compounds, which elute from the column. The gas stream from the GC is scanned within a preselected range of atomic mass units (amu). For detection of compounds in Table 1, the range should be 35 to 265 amu.

8.7 Sample collection is described in method TO-15.

8.8 Samples collected in SUMMA® canisters are analyzed within twenty days of collection. Other holding times may be selected by the client to conform with local regulatory requirements. Samples collected in Tedlar bags are analyzed within three days of collection.

8.9 The overall condition of each sample container is observed upon receipt and any signs of damage is reported immediately to the client. The pressure of each sample canister is checked by attaching a pressure gauge to the canister inlet and briefly opening the canister valve to obtain the pressure reading. The measurement is recorded on the laboratory analysis sheet. Samples received at a vacuum less than -4.0" Hg must be pressurized to ensure that there is enough sample for analysis. The canisters are pressurized with zero grade air and the dilution factor is calculated and applied to the final results of analysis.

8.10 Samples received in Tedlar bags are inspected for condensation. If it is present, the bag is gently warmed by holding it between your hands in hope that the sample will return to its gaseous state. However, resampling may be necessary if this procedure does not work.

9.0 QUALITY CONTROL

9.1 4-Bromofluorbenzene - Prior to the acquisition of a calibration curve or the analysis of samples, an aliquot of BFB (1 ppmv) is automatically introduced into the GC by way of the Nutech automated sytem. If the spectrum does not meet all criteria in Table 2, another BFB tune is injected into the instrument. If the second BFB tune fails the criteria in Table 2, the MS should be retuned and adjusted to meet all criteria before proceeding with the calibration or the analysis.

9.2 Method Detection Limits - Method detection limits (MDLs) are determined annually in accordance with the method described in 40 CFR, Part 136, Appendix B. The results of these studies are kept on file by the QA Manager.

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9.3 Initial Calibration Verification - An ICV must be run following the acquisition of the five-point initial calibration. The ICV is prepared from a source external to the laboratory and independent from the source of the initial calibration standards. The compounds should be at a concentration of 10 ppbv. The ICV recovery limits are shown in Table 3.

9.4 Internal Standards - The internal response shall be +/- 40% of the mean internal standard response recorded during the analysis of the continuing calibration standard. The retention time shift should not be more than +/-20 seconds from the latest daily calibration check.

9.5 Laboratory Control Sample - A laboratory control sample should be included with each analytical batch. The compounds should be at a concentration of 10 ppbv. The LCS recovery limits are shown in Table 3.

9.6 Method Blank - One blank must be run with every batch of samples after the LCS. A 200-mL sample of laboratory zero air must be analyzed prior to any samples. An acceptable blank must not contain any volatile target analytes at concentrations greater than their reporting limits with the exception of acetone and methylene chloride which must be less than or equal to five times (5X) its reporting limit. If the method blank exceeds these criteria, the analytical system may be out of control. The source of the contamination must be investigated and appropriate corrective measures must be taken and documented before further sample analysis proceeds.

10.0 CALIBRATION AND STANDARDIZATION

10.1 BFB - The ion abundances shown in Table 2 must be met before analysis of calibration standards may proceed.

10.2 Initial Calibration (IC) - The five concentrations for the initial calibration are 0.5, 5, 10, 20, and 40 ppbv. A response factor (RF) is calculated for each analyte and/or isomer pair for each calibration solution using the appropriate internal standard. The calculation is performed as follows:

$$RF = \frac{(A_x)(Q_{is})}{(A_{is})(Q_x)}$$

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where:

A_x = area of the quantitation ion of the analyte
A_{is} = area of the quantitation ion of the internal standard
Q_x = quantity of analyte purged in nanograms or concentration units
Q_{is} = quantity of internal standard purged in ng or concentration units

10.2.1 For each analyte calculate the mean response factor from analyses of the calibration solutions. Calculate the standard deviation (SD) and relative standard deviation (RSD) from each mean (M).

$$RSD = 100\frac{SD}{M}$$

10.2.2 The %RSD average of all analytes must be ≤ 30% (2 compounds are allowed to be ≤40%). The RRT for each target compound at each calibration level must be within 0.06 RRT units of the mean RRT for the compound. The retention time shift for each of the internal standards at each calibration level must be within 20 s of the mean retention time over the initial calibration range for each internal standard.

10.3 Independent Calibration Verification (ICV)- An ICV must be run following the initial calibration. The ICV is purchased from an independent source and is run at a concentration of 10 ppbv. The percent recovery for each compound should be 70-130% for 90% of the compounds. In addition, the internal standard retention time should not change by more than 20 s. from the mid-point standard level of the most recent curve sequence. The integrated areas of the internal standards in the calibration verification standard should not change by more +/-40% from that in the mid-point standard level of the most recent calibration.

10.4 Continuing Calibration Verification (CCV) - Verify the BFB MS tune and perform a continuing calibration verification at the beginning of each 24-hr work shift. The concentration of the CCV is 10 ppbv. The RF is calculated for each analyte compound from the data measured in the continuing calibration check. The percent difference is calculated using the following equation:

$$\%Difference = \frac{RF - RF_v}{RF}(100)$$

RF = mean Response Factor from the initial calibration
RF_v = Response Factor from the analyses of the verification standard

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The percent difference for each CCV should be ≤ 30% for 90% of the compounds. In addition, the internal standard retention time should not change by more than 20 s. from the mid-point standard level of the most recent initial curve sequence. The integrated areas of the internal standards in the calibration verification standard should not change by more than +/-40% from that in the mid-point standard level of the most recent calibration sequence. If the above criterion is not met maintenance is performed on the instrument and/or a new calibration curve is acquired. Alternatively, in keeping with the approach described for the IC, if the average of the responses for all analytes is within 30% for 90% of the compounds, then the calibration has been verified. If the calibration still does not meet the 30% for 90% of the compounds limit, check the instrument operating conditions, and if necessary inject another aliquot of the calibration verification standard. If the response for the analyte is still not within +/-30% for 90% of the compounds, then a new IC must be prepared.

10.5 Laboratory Control Sample (LCS) - One LCS must be run in each 24-hour window following the CCV. The LCS is run at the concentration of 10 ppbv. The percent recovery for each compound should be 70-130% for 90% of the compounds. In addition, the internal standard retention time should not change by more than 20 s. from the mid-point standard level of the most recent curve sequence. The integrated areas of the internal standards in the calibration verification standard should not change by more +/-40% from that in the mid-point standard level of the most recent calibration.

10.6 Method Blank - A method blank is run following the passing of the BFB tune, CCV, and LCS. A 200-mL aliquot of zero grade air is run to verify that the analytical system is clean. An acceptable method blank verifies that there are no volatile organic compounds present above their reporting limits. In addition, the internal standard retention time should not change by more than 20 s. from the mid-point standard level of the most recent calibration. The integrated areas of the internal standards in the method blank should not change by more +/-40% from that in the mid-point standard level of the most recent calibration sequence.

11.0 PROCEDURE

11.1 The analytical system is comprised of a GC equipped with a mass-selective detector set in the SCAN mode. All ions are scanned by the MS repeatedly during the GC run. The system includes a computer and appropriate software for data

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acquisition, data reduction, and data reporting. A 200-mL air sample is collected from the canister or Tedlar bag into the analytical system. The sample air is first passed through the mass flow controller then routed onto a cryogenic trap. The internal standards are then loaded onto the trap. The trap is heated, dry purged, then desorbed onto the cryofocus. The sample is next injected onto the DB-1 capillary column (0.32-mm x 60-m).

[Note: Rapid heating of the trap provides efficient transfer of the sample components onto the gas chromatographic column.]

Upon sample injection unto the column, the MS computer is signaled by the GC computer to begin detection of compounds, which elute from the column. The gas stream from the GC is scanned within a preselected range of atomic mass units (amu). Data is acquired and stored over the nominal mass range 35-260 with a total cycle time (including scan overhead time) of two seconds or less. The cycle time is adjusted to measure five or more spectra during the elution of each GC peak. A multi-stage temperature ramp is used to separate the components of interest for this analysis. A typical GC temperature program is described below.

- Initial temperature: 30° C, initial time 4 min.
- Ramp1: 9° C/min. to 175° C.
- Ramp2: 40° C/min. to 260° C, hold for 1.60 min.

11.2 Identification of Analytes - A sample is identified by comparison of its mass spectrum (after background subtraction) to a reference spectrum in the user-created database. The GC retention time for each analyte should be within +/- 0.5 minutes of the midpoint standard's retention time in the initial calibration curve.

11.2.1 In general, all ions that are present above 10% relative abundance in the mass spectrum of the standard should be present in the mass spectrum of the sample component and should agree within absolute 20%. For example, if an ion has a relative abundance of 30% in the standard spectrum, its abundance in the sample spectrum should be in the range of 10-50%. Some ions, particularly the molecular ion, are of special importance, and should be evaluated even if they are below 10% relative abundance.

11.2.2 Identification requires expert judgment when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When GC peaks obviously represent more than one sample component (i.e., broadened peak with

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shoulder(s) or valley between two or more maxima), appropriate analyte spectra and background spectra can be selected by examining plots of characteristic ions for tentatively identified components. When analytes coelute (i.e., only one GC peak is apparent), the identification criteria can be met but each analyte spectrum will contain extraneous ions contributed by the coeluting compound.

11.2.3 Structural isomers that produce very similar mass spectra can be explicitly identified only if they have sufficiently different GC retention times. Acceptable resolution is achieved if the height of the valley between two peaks is less than 25% of the average height of the two peaks. Otherwise, structural isomers are identified as isomeric pairs. Two of the three isomeric xylenes are examples of structural isomers that are not resolved on the capillary column. These groups of isomers will be reported as isomeric pairs.

12.0 CALCULATIONS

12.1 Dilution factor:

$$DF = \frac{P_1}{P_2}$$

P_1 = Canister pressure before dilution (psig)
P_2 = Canister pressure after dilution (psig)

12.2 Concentrations of Calibrated Compounds:

$$C_x = \frac{(A_x)(C_{IS})}{(A_{IS})(\overline{RRF})}(DF)$$

$\overline{RRF}$ = Average Relative Response Factor from five-point initial calibration.
C_x = Concentration of compound (ppbv)
C_{IS} = Concentration of associated internal standard (ppbv).
DF = Dilution Factor.
A_{IS} = Area of quantitation ion for associated internal standard.
A_x = Area of quantitation ion for compound.

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12.3 Calculation of Recovery - Calculate the recovery of each spiked analyte in the LCS and ICV by the following equation:

$$\text{Recovery} = \%R = \frac{C_s - C_u}{C_n}(100)$$

C_s = Measured concentration of the spiked sample aliquot
C_u = Measured concentration of the unspiked sample aliquot (use 0 for LCS and ICV)
C_n = Nominal (theoretical) concentration increase that results from spiking the sample, or the nominal concentration of the spike aliquot (for LCS and ICV)

12.4 Calculation of Precision - Precision is estimated from the relative percent difference (RPD) of the concentrations (not the recoveries) measured for matrix spike/ matrix spike duplicate pairs, or for duplicate analyses of unspiked samples. The RPD is calculated according to the following equation below.

$$RPD = \frac{(C_1 - C_2)}{\left(\frac{C_1 + C_2}{2}\right)}(100)$$

C_1 = Measured concentration of the first sample aliquot
C_2 = Measured concentration of the second sample aliquot

12.5 Data Reporting - Based on the mass spectra, it is appropriate to report values between the MDL and the RL. In this region, an analyte can be qualitatively detected, but not accurately quantified. Any data point reported in this region is flagged with a "J". STL reports sample specific RL's. Sample specific RL's are derived by taking into account various sample specific data, which can include the amount of the sample subject to testing, % moisture, dilution factor, interferences and the base RL's for the analysis.

12.5.1 Reporting Qualifiers

B = Analyte is found in the associated method blank as well as the sample
D = Compound is identified in an analysis at a secondary dilution factor

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E = Compound quantitation is above the instrument's calibration range for this analysis
J = Indicates an estimated quantitation value
U = Compound was analyzed for but not detected
X = The reported compound is a suspected laboratory contaminant
Y = An additional qualifier which will be defined at the time of use by the data reviewer
Z = The reported result is based on the combined responses from coeluting compounds

12.5.2 Data Package Definitions - Three levels of reporting are available. The difference between these levels has nothing to do with the quality of the work being performed, only how it is presented.

Level 2: A level 2 data package consists of sample results only, and may be available as either an Analytical Report or in a format similar to the OLM Form 1A's.
Level 3: A level 3 data package consists of sample, CLP-like forms with Quality Control results.
Level 4: A level 4 data package consists of a full set of RAS forms, and all supporting documentation.

Electronic-Diskettes are available upon request

13.0 METHOD PERFORMANCE

Method detection limits are calculated using the formula:

$$MDL = S\ t_{(n-1,\ 1\text{-alpha} = 0.99)}$$

Where:
$t_{(n-1,\ 1\text{-alpha} = 0.99)}$ = Student's t value for the 99% confidence level with n-1 degrees of freedom
n = number of replicates
S = the standard deviation of the replicate analyses

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities

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for pollution prevention exist in laboratory operation. The USEPA has established a prevention hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the agency recommends recycling as the next best option.

14.2 The quantity of chemical purchased should be based on expected usage during its shelf life and disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

14.3 For information about pollution prevention that may be applicable to laboratories and research institutions, consult "Less is Better: Laboratory Chemical Management for Waste Reduction", available from the American Chemical Society's Department of Government Regulations and Science Policy, 1155 16th Street N.W. Washington D.C. 20036, (202) 872-4477.

15.0 DATA ASSESSMENT AND ACCEPTANCE CRITERIA AND CORRECTIVE ACTIONS FOR OUT-OF-CONTROL DATA

15.1 Data assessment, acceptance criteria and corrective action for out of control data is summarized in Table 4.

15.2 Corrective actions for out of control data is summarized in Table 4.

16.0 CONTINGENCIES FOR HANDELING OUT OF CONTROL OR UNACCEPTABLE DATA

Summarized in Table 4.

17.0 WASTE MANAGEMENT

The samples that are not utilized in the analysis are vented in the Volatiles Prep Lab hood and further disposed of during the canister cleaning process. The U.S. Environmental Protection Agency requires that laboratory waste management practices conducted be consistent with all applicable rules and regulations. Excess reagents, samples, and method process wastes should be characterized and disposed of in a an acceptable manner. The Agency urges laboratories to protect the air, water and land by minimizing and controlling

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all release from hoods, and bench operations, complying with the letter and spirit of any waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management consult the "Waste Management Manual for Laboratory Personnel", available from the American Chemical Society at the address listed in Section 14.3.

18.0 REFERENCES

18.1 Compendium Method TO-15, "Determination of Volatile Organic Compounds in Ambient Air using Specially Prepared Canisters and Analyzed by Gas Chromatography/Mass Spectrometry", US EPA, January, 1997.

18.2 Kelly T. J. and Holdren, M.W., "Applicability of Canisters for Sample Storage in the Determination of Hazardous Air Pollutants," *Atmos. Environ.*, Vol. 29, 2595-2608, May 1994.

19.0 TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

Table 2. BFB Criteria

BFB Key Ions and Ion Abundance Criteria	
Mass	Ion Abundance Criteria
50	8.0-40.0 percent of mass 95
75	30.0-66.0 percent of mass 95
95	base peak, 100 percent relative abundance
96	5.0-9.0 percent of mass 95

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173	less than 2.0 percent of mass 174
174	50.0-120.0 percent of mass 95
175	4.0-9.0 percent of mass 174
176	93.0-101.0 percent of mass 174
177	5.0-9.0 percent of mass 176

Table 3. Internal Standards

Internal Standard	CAS No.	Quant Mass	Qualifier
Bromochloromethane	74-97-5	128	49
1,4-Difluorobenzene	540-36-3	114	
Chlorobenzene-d5	3114-55-4	117	

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Table 4. TO-15 Quality Control Criteria

Quality Control Criteria	Frequency	Acceptance	Corrective Action
BFB	24 hours	Per Method	Reshoot, Retune
ICAL: 0.5, 5, 10, 20, 40 ppbv	As Required	Average %RSD must be ≤ 30% (2 compounds allowed to ≤40%)	System check, Mix new standards, Recalibrate, Reanalyze
ICV (10 ppbv)	Following Initial Calibration Curve	Average %RSD must be ≤ 30% for 90% of the compounds	System check, Mix new standards, Recalibrate, Reanalyze
CCV (10 ppbv)	Beginning of each 24 hour window	%Difference each CCC ≤30% for 90% of the compounds	System Check, Recalibrate
LCS (10 ppbv)	Following the CCV	%Difference each CCC ≤30% for 90% of the compounds	System Check, Recalibrate
Method Blank	Following each LCS/ICV	Targets < Reporting Limits (Methylene Chloride 5xs RL)	Check for contamination, Reanalyze, correct as required
Internal Standards	In every sample, blank, and QC samples	+/-40%RF from last acceptable calibration; +/-.33 min	System Check, Recalibrate
Samples	Per Request	ISTD must meet their criteria and the concentration must fall within the calibrated range	A dilution is applied to the sample when needed; the target concentration will be the midpoint of the high end of the calibration curve. If the ISTD criterion is failing, the sample is ran again. If the ISTD fail again, the sample is reported out as is.

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