Quality Assurance Project Plan

Site 7 – RTC Silk Screen Shop and Site 17 – Pettibone Creek & Boat Basin

Remedial Investigation & Risk Assessment

Volume II of II
Appendix IV - Laboratory Standard Operating Procedures

Naval Training Center Great Lakes
Great Lakes, Illinois

Southern Division
Naval Facilities Engineering Command

Contract Number N62467-94-D-0888

Contract Task Order 0154

July 2001

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QUALITY ASSURANCE PROJECT PLAN
SITE 7 – RTC SILK SCREEN SHOP
AND
SITE 17 – PETTIBONE CREEK & BOAT BASIN
REMEDIAL INVESTIGATION & RISK ASSESSMENT

NAVAL TRAINING CENTER GREAT LAKES
GREAT LAKES, ILLINOIS

COMPREHENSIVE LONG-TERM
ENVIRONMENTAL ACTION NAVY (CLEAN) CONTRACT

Submitted to:
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VOLUME II

APPENDIX IV

LABORATORY STANDARD OPERATING PROCEDURES

SOP Number	Title
LQM	Section 8.0 – Work Processes and Operations, Excerpted from Lab Quality Manual
LQM	Section 9.0 – Quality Assessment and Response, Excerpted from Lab Quality Manual
QAMP	Quality Assurance Management Plan
QA-001	Standard Operating Procedures
QA-003	Quality Control Program
QA-005	Determination of Method Detection Limits for Chemical Tests
QA-008	Data Recording Requirements
QA-009	Reporting Limits
QA-011	Acceptable Manual Integration Practices
QA-014	Determination of IDL
PITT-QA-0003	Glassware Prep
NC-QA-0018	Statistical Evaluation of Data and Development of Control Charts
PITT-QA-0051	Sample Receiving and Chain of Custody
CORP-MT-0006	Preparation and analysis of Mercury in Aqueous Samples by Cold Vapor Atomic Absorption Spectroscopy, Method 245.5 CLP-M, SOW ILMO3.0
CORP-MT-0008	Preparation and analysis of Mercury in Solid Samples by Cold Vapor Atomic Absorption Spectroscopy, Method 245.5 CLP-M, SOW ILMO3.0
CORP-MS-0002-PT	Determination of Volatile Organics by GC/MS Methods 8260B, 624 and 524.2
CORP-MS-0001-PT	GC/MS based on Methods 8270C and 625
CORP-GC-0001PT	Gas Chromatography Analysis based on Method 8000B, 8021A, 8081A, 8082, and 8151A; SW-846 8141A and 8310
CORP-MT-0001	Inductively Coupled Plasma-Atomic Emission Spectroscopy, Spectrometric Method for Trace Element Analyses, SW846 Method 6010B and EPA Method 200.7
CORP-MT-0005PT	Preparation and Analysis of Mercury in Aqueous Samples by Cold Vapor Atomic Absorption Spectroscopy, SW 846 7470A and MCAWW 245.1

CORP-MT-0007	Preparation and Analysis of Mercury in Solid Samples by Cold Vapor Atomic Absorption Spectroscopy, SW 846 7471A and MCAWW 245.5
PITT-WC-0018	Cyanide-Semi-Automated, Pyridine-Barbituric Acid for Total (Method 335.4) and Amenable (SM 4500-6) Cyanide Analyses in Water and Soil (Method 9012A)
CORP-IP-0004	Toxicity Characteristic Leaching Procedure and Synthetic Precipitation Leaching Procedure
NC-WC-0017	Total Organic Carbon (TOC) and Total Inorganic Carbon (TIC) SW 846 Method 9060 and EPA Method 415.1
PITT-WC-0058	Total Organic Carbon Analyses for Solid Matrices by Walkley Black
AVS/SEM	Acid Volatile Sulfide (AVS) and Selected Simultaneous Extractable Metals in Sediment
S3A	Test Method for Particle Size of Soils – Geotechnics
PITT-WC-0026	PH electrometric EPA Method 150.1 Method 9045C (soil) and SW846 9040B
Navy IR CDQM	Navy Installation Restoration Chemical Data Quality Manual (IR CDQM)
DOD QSM	Department of Defense Quality Systems Manual for Environmental Laboratories

Section 8.0 Work Processes and Operations
Excerpted from Laboratory Quality Manual for STL Pittsburgh

SEVERN TRENT SERVICES

Laboratory Quality Manual for

STL Pittsburgh

450 William Pitt Way
Pittsburgh, PA 15238
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Approved by:

4/10/01
Laboratory Director Date

4/10/2001
Technical Director Date

4/10/2001
Quality Assurance Manager Date

Revision 0
September 1, 2000
Controlled Copy Number: _____

8.0 Work Processes and Operations

Many activities related to environmental projects activities are planned and designed externally to the laboratory or field operation, and are presented to the laboratory in the form of a contract, work plan, sampling and analysis plan (SAP) or QA Project Plan (QAPP). Laboratory and field activities are in turn planned, implemented, and assessed by STL to meet client requirements according to approved procedures and methodologies. The LQM provides the systems to document and implement these activities. The execution and assessment of the implemented operational systems are detailed in STL SOPs. The entire process is assessed on a regular basis for conformance to prescribed requirements.

Standard practices for STL Pittsburgh operations are detailed in this section. Specific project or program requirements that differ from those described here can be met, but they must be explicitly stated in approved contracts, work plans, QAPPs or other project documents. Special project requirements can generally be accommodated provided that they are properly documented, communicated, and they do not cause the laboratory to violate relevant regulatory requirements.

Table 8.2-3 lists the test methods performed by STL Pittsburgh. Table 8.2-2 lists the SOPs associated with those methods. Table 8.0-1 provides a list of the major equipment in place at the laboratory, and Figure 8.11 (at the end of this Section) shows the laboratory floor plan.

8.1 Traceability of Measurements

STL documents all laboratory activities in sufficient detail to allow their reconstruction. To this end, documentation is generated to trace a sample from its point of origin, through receipt in the laboratory, analysis, reporting and disposal.

The required documentation includes, but is not limited, to:

- Chain of custody documenting movement and possession of samples
- Sample preparation
- Sample analysis
- Calibration and QC data associated with the samples
- Instrument maintenance
- Control of ancillary equipment and materials (e.g., DI water and glassware)
- Sample disposal
- Final reports

These topics are described in this section. Traceability of chemical standards is also discussed in Section 5.2.4.

8.2 Analytical Methods

Whenever possible, STL operations use industry- and regulatory agency-recognized analytical methods from source documents published by agencies such as the Environmental Protection Agency (EPA), Department of Energy (DOE), and the American Society for Testing and Materials (ASTM) as described in STL's SOPs. Analytical methods performed

by STL Laboratories are given in Table 8.2-3 lists the methods routinely performed at the laboratory. The methods pending or approved by a NELAC Accrediting Authority are indicated in the table.

Method performance data, as described in Section 8.2.2 below, are developed by the laboratory operations staff to demonstrate method proficiency. The operations staff and the QA staff evaluate and approve the performance data before a methodology is performed routinely. The method must also be described and documented in an SOP.

8.2.1 Standard Operating Procedures

SOPs are required for all repetitive analytical and administrative activities ranging from the receipt of samples in the laboratory through their analysis, reporting, and subsequent disposal. Training, health and safety procedures, QC, method procedures, and instrument and equipment calibrations are included in SOPs. SOP requirements are discussed in the Policy # QA-001, "Standard Operating Procedures". The specifications in the policy meet NELAC requirements. Table 8.2-2 lists laboratory standard operating procedures.

New SOPs and proposed SOP revisions are reviewed by technically qualified lab personnel. SOPs are controlled documents and are distributed and maintained as described in Policy QA-001. Requirements for SOP approval and frequency of review are listed in Tables 2.4-3 and 2.4-4. All significant modifications to the published method are described in a section of the SOP. All operations must be performed as described in these SOPs.

Planned changes in procedure, which may occur due to expected sample matrix effects or project requirements, are documented in the project files. These planned changes may be documented using nonconformance memos, NCMs (see discussion of NCMs in section 9.1), project-specific case narratives, or as modifications or additions to associated QAPPs.

Unplanned deviations in the SOPs, which may occur due to sample matrix or other events, are documented in NCMs and in the project-specific case narratives.

8.2.2 Method Validation and Verification

Before analyzing samples by a new method or method modification, the method must be verified or validated. After which, analyst capability must be demonstrated (see Section 4.4).

8.2.2.1 Method Verification

Method verification is required for methods developed by authoritative agencies, such as EPA or ASTM. The level of verification can vary

depending on the type of method or level of modification, but generally should include:

- Determination of method sensitivity,
- Determination of working range,
- An initial demonstration of capability (as specified by NELAC), and
- A written SOP or project-specific written protocol.

Each of these are described in the next section.

8.2.2.2 Method Validation

A complete validation is required for methods developed by STL Pittsburgh. While method validation can take a variety of courses, the following are the key concerns:

Determination of Method Selectivity

Method selectivity is the demonstrated ability to discriminate the analyte(s) of interest from other compounds in the specific matrix or matrices. In some cases, to achieve the required selectivity for an analyte, a confirmation analysis is required as part of the method

Determination of Method Sensitivity

Method sensitivity is normally demonstrated using the 40CFR 136B method detection limit protocol (see MDLs, section 8.2.3, below), but can also be based on variance of blank results, and signal-to-noise ratios.

Determination of Interferences

This is demonstrated by analyzing samples of the matrix of interest that is known to be free of the analyte(s) of interest.

Determination of Range

In most cases, analytical range is determined and demonstrated by comparison of the response of an analyte at different concentrations to targeted criteria. Often the targeted criteria are represented by the goodness of fit or linearity of the experimental data to a continuous mathematical function or curve. The curve is used to establish the range of quantitation, with the lower and upper values representing the upper and lower quantitation limits. Curves are not limited to linear relationships.

Determination of Accuracy and Precision

Accuracy and precision studies are generally performed using replicate analysis of samples of known concentration. The resulting percent recovery and relative standard deviation, or other precision measure, is calculated and compared to a set of target criteria.

Documentation of Method
The method is formally documented in an SOP (see policy QA-001 for details). If a method modification is being performed for a specific short-term project, the modification should be described in a written protocol that is approved by the lab's client, in addition to the in-house approvals required by QA-001.

Continued Demonstration of Method Performance
Continued ability of the lab to perform the method is addressed in the SOP. Generally this is accomplished with the specified calibration and batch QC requirements.

8.2.3 Method Detection Limits

It is STL Pittsburgh's policy to follow the specification in the U.S. EPA 40 CFR Part 136 Appendix B in determining MDLs for chemical tests. The STL requirement for this procedure is further detailed in Policy QA-005 entitled "Determination of Method Detection Limits for Chemical Tests." This policy requires that the MDLs be determined for each analyte of interest representing the aqueous and solid matrices within the capability of the primary analytical methods. The laboratory's current MDLs are given in Table 8.2-4 .

8.2.4 Instrument Detection Limits

Instrument Detection Limits (IDLs) are required to be performed quarterly for metals constituents and cyanide when analyses are performed in support of Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) activities or when the USEPA CLP SOW protocol is required. IDLs are not required by the SW-846 methods, with the exception of method 6020.

When required, IDLs will be performed in accordance with the procedures defined in the applicable USEPA SOW, ILMO3.0 or subsequent versions, and Policy QA-014, "Determination of Instrument Detection Limits".

Prior to acceptance and use for reporting purposes, all data from detection limit studies and reporting limits must undergo technical review and approval by the laboratory management and QA staff.

8.2.5 Reporting Limits

Reporting limits are established and modified within STL according to the STL Policy QA-009, "Reporting Limits." Two reporting limit conventions are discussed in the policy: the standard Reporting Limit (RL) and the Project-Specific Reporting Limit (PSRL). The standard STL Reporting Limit (RL) is the lowest level at which measurements become quantitatively meaningful. The RL is always greater than the statistically determined MDLs. PSRLs are used when project data quality objectives (DQO) require a reporting limit other than the RL. PSRLs

tailor STL's product to meet customer requirements. Higher PSRLs may be established based on maximum contaminant level (MCLs), applicable or relevant and appropriate requirements (ARARs), or project-specific data quality objectives (DQOs). PSRLs below the lab's standard RL may be used, but they must be supported by the MDL and the instrument calibration. A standard at the PSRL taken throughout the entire preparation and extraction procedure may be used to support a PSRL with QA approval. The STL RLs and PSRLs are maintained in the LIMS.

For radiochemistry, whether the net result is negative, zero, or positive, the actual calculated result is reported with its associated propagated uncertainty. The minimum detectable concentration (MDC) is affected by many factors, such as the length of count, chemical yield, half-life, background of the instrument, counting efficiency, and the matrix interference. The MDC for radiochemical analyses is defined as the smallest amount (activity or mass) of an analyte in a sample that will be detected with a probability beta of non-detection (Type II error) while accepting a probability alpha of erroneously deciding that a positive (non-zero) quantity of analytes is present in an appropriate blank sample (Type I error). MDCs are determined according to Policy QA-007, "Determination of Minimum Detectable Concentration for Radiochemical Tests."

8.3 Data Quality Objectives

Data quality objectives (DQOs) are qualitative and quantitative statements used to ensure the generation of the type, quantity, and quality of environmental data that will be appropriate for the intended application (EPA 1994)[1]. Typically, DQOs are identified during project scope and the development of sampling and analysis plans. In this LQM, however, we refer to only the analytical DQOs because laboratories generally do not have any authority over sample collection, shipment, or other field-related activities that may affect the data quality of the environmental sample before the sample is received in the laboratory. The EPA has established six primary analytical DQOs for environmental studies. These DQOs are precision, accuracy, representativeness, completeness, comparability, and detectability.

The components of analytical variability (uncertainty) can be estimated when QA and QC samples of the right types and quantities are incorporated into measurement procedures at the analytical laboratory. STL incorporates numerous QA and QC samples to obtain data for comparison with the analytical DQOs and to ensure that the measurement system is functioning properly. The QA/QC samples and their applications, described in Section 8.4, are selected on the basis of method- or client-specific requirements. Field blanks, field duplicates, and performance evaluation (PE) samples are received from the client as unknown samples. Analytical laboratory QC samples for inorganic, organic, and radionuclide analyses may include calibration or instrument blanks, method blanks, background, duplicates, replicates, laboratory control samples (LCSs), calibration standards, matrix spikes (MSs), matrix spike duplicates (MSDs), surrogate spikes, and yield monitors.

[1] "Guidance for the Data Quality Objectives Process", EPA 600/R-96/005, September 1994.

8.3.1 Precision And Accuracy

Precision is an estimate of variability, that is, it is an estimate of agreement among individual measurements of the same physical or chemical property, under prescribed similar conditions. The precision of a measurement system is affected by random errors. Precision is expressed either as relative standard deviation (RSD) for replicate measurements greater than two or as relative percent difference (RPD) for duplicate measurements. Table 8.6-1 illustrates the formulae used to calculate units of precision (i.e., RSD and RPD).

Accuracy is the degree of agreement between a measurement and the true or expected value, or between the average of a number of measurements and the true or expected value. Systematic errors affect accuracy. For chemical properties, accuracy is expressed either as a percent recovery (R) or as a percent bias (R - 100).

The precision and accuracy measures that are to be used in evaluating inorganic, organic, and radionuclide constituents at STL are provided in Tables 8.4-5 through 8.4-7, in method-specific SOPs, and in the documentation for the analytical method of interest.

Precision and accuracy are determined, in part, by analyzing data from matrix spike and matrix spike duplicates, unspiked duplicates, LCSs, and single blind audit samples. For radiochemical determinations, counting statistics can also provide an estimate of uncertainty. A description of these QC samples is provided in Section 8.4.

8.3.2 Completeness

Completeness is a measure of the percentage of measurements that are judged to be valid measurements. At a minimum, the objective for completeness of data is 90% for each constituent analyzed.

8.3.3 Representativeness

Representativeness is the degree to which data accurately and precisely represent a characteristic of a population, a variation in a physical or chemical property at a sampling point, or an environmental condition. Data representativeness is primarily a function of sampling strategy; therefore, the sampling scheme must be designed to maximize representativeness. Representativeness also relates to ensuring that, through sample homogeneity, the sample analysis result (concentration) is representative of the constituent concentration in the sample matrix. At STL, efforts must be made to analyze an aliquot that is representative of the original sample, and to reasonably homogenize the sample before subsampling.

8.3.4 Comparability

Comparability is a measure of the confidence with which one data set can be compared to another. To ensure comparability, all laboratory analysts are required to use uniform procedures (i.e., SOPs) and a uniform set of units and calculations for analyzing and reporting environmental data.

8.4 Quality Control Samples

Two types of Quality Control (QC) samples are field QC samples and laboratory QC samples. Field QC samples are collected during the sampling event and are useful in determining sampling precision and accuracy and monitoring for contamination that may occur during collection, transport or storage of environmental samples. Laboratory QC samples are routinely added at the laboratory to the normal sample stream. Successful analysis of these samples demonstrates that the laboratory is operating within prescribed requirements for accuracy and precision. In addition, utilizing matrix-specific laboratory QC samples, information regarding the effect of the matrix or field conditions on the analytical results can be obtained. The following sections describe common field and laboratory QC samples.

8.4.1 Field QC Samples

When field QC sample collection and analysis are required for a project, it is the responsibility of the project sampling supervisor to ensure that this sampling is performed correctly and at the project-required frequencies. Field QC samples may or may not be identified as such to the laboratory and are considered by the laboratory as field samples for the purpose of QC batching, sample preparation and analysis. Field QC sample results are reported in the same manner as actual field samples, unless a specific deliverable is requested by the client. No correction of the analytical data is done in the laboratory based on the analysis of field QC samples. Field QC sample types, applicability to organic and inorganic analyses, precision and accuracy applications and by whom they are introduced are summarized in Table 8.4-1.

8.4.2 Laboratory QC Samples

Laboratory performance QC is required to ensure the laboratory systems (instrumentation, sample preparation, analysis, data reduction, etc.) are operating within acceptable QC guidelines during data generation as required to meet the client’s objectives. Laboratory QC samples consist of method blanks (MB), instrument blanks, laboratory control samples (LCS) and calibration verification samples. In addition to laboratory performance QC, matrix-specific QC is utilized to determine the effect of the sample matrix on the data being generated. Typically, this includes matrix spikes (MS), matrix spike duplicates (MSD), sample duplicates, and the use of surrogate compounds.

Laboratory and matrix-spike QC sample types are summarized in Tables 8.4-2 through 8.4-4. In addition, Tables 8.4-5 through 8.4-7 list laboratory QC samples, acceptance criteria and corrective actions by reference method for inorganic methods, organic methods, and the USEPA CLP Statements of Work respectively. The following sections provide descriptions of laboratory QC samples and their frequency of use. Policy QA-003, "Quality Control Program", describes in detail the QC data evaluation process.

8.4.2.1 Quality Control (QC) Batch

The QC batch consists of a set of up to 20 field samples that behave similarly (i.e., same matrix) and are processed using the same procedures, reagents, and standards within the same time period. This definition of a QC batch is utilized by STL unless there is clear regulatory guidance, contract specifications, or differing client requirements that are explicitly documented. Further details and requirements for the application of the definition of QC batch are described in Policy QA-003.

8.4.2.2 Method Blank

The method blank (MB) is a QC sample that consists of all reagents specific to the method and is carried through every aspect of the procedure, including preparation, cleanup, and analysis. The method blank is used to identify any interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. Potential sources of contamination include solvent, reagents, glassware, other sample processing hardware, or the laboratory environment. In general, the method blank is a volume of deionized laboratory water for water samples, or a purified solid matrix for soil/sediment samples, that is processed as a sample. In the event that no appropriate solid matrix exists, deionized water may be used. The volume or weight of the method blank must be approximately equal to the sample volume or sample weight processed. A method blank shall be prepared with each group of samples processed.

8.4.2.3 Instrument/ Calibration Blank

The instrument blank is an unprocessed aliquot of reagent used to monitor the contamination of the analytical system at the instrument. System contamination may lead to the reporting of elevated analyte concentrations or false positive data. The instrument blank does not undergo the entire analytical process and generally consists of an aliquot of the same reagent(s) used for a sample dilution. Instrument blanks are also referred to as continuing calibration blanks (CCBs).

8.4.2.4 Laboratory Control Sample

A laboratory control sample (LCS) is a laboratory-prepared suitable clean matrix sample that is fortified with target analytes or a solid reference material purchased from an approved vendor. The LCS contains all target analytes specified in the method, and must contain the same analytes as the matrix spike and matrix spike duplicate. For certain regulatory or client programs, an LCS may contain a full list of analytes. However, in these cases, a subset of analytes, as defined by the program, is used to determine the acceptability of a batch of sample data. The LCS recovery data are used to monitor the analytical method performance in terms of analytical accuracy. On-going evaluation of the LCS recoveries demonstrates that the laboratory is performing the method within statistical control (i.e., accuracy and precision) in the absence of matrix interference. The LCS results, coupled with MS data, help determine whether the laboratory performed the method correctly or the sample matrix affected the analytical results. When a laboratory control sample duplicate (LCSD) is required, a percent recovery for each target analyte is calculated, as well as a relative percent difference (RPD) between the LCS and the LCSD.

8.4.2.5 Matrix Spike

A matrix spike (MS) is an environmental sample to which known concentrations of target analytes have been added. MS samples are analyzed to evaluate the effect of the sample matrix on the analytical methodology. MS samples are generated by taking a separate aliquot of an actual field sample and spiking it with the selected target analyte(s) prior to sample extraction. The MS sample then undergoes the same extraction and analytical procedures as the unfortified client sample. Due to the potential variability of the matrix of each sample, these results may have immediate bearing only on the specific sample spiked and not on samples collected at other locations that are included in the QC batch.

8.4.2.6 Matrix Spike Duplicate

A matrix spike duplicate (MSD) is a second aliquot of a sample that is spiked with the selected target analyte(s) and analyzed with the associated sample and MS sample. The results of the MS and MSD are used together to determine the effect of a matrix on the accuracy and precision of the analytical process. Due to the potential variability of the matrix of each sample, the MS/MSD results may have immediate bearing only on the specific sample spiked and not all samples in the QC batch.

8.4.2.7 Sample Duplicate

A sample duplicate is a second aliquot of an environmental sample taken from the same sample container that is processed identically with the first aliquot of that sample. That is, sample duplicates are processed as independent samples within the same QC batch. The results are compared to determine the sample homogeneity and the precision of the analytical process.

8.4.2.8 Surrogates

Surrogates are organic compounds that are similar in chemical composition and behavior to the target analytes but that are not normally found in environmental samples. Surrogates are added to all appropriate samples and QC samples being tested for organic analytes to monitor the effect of the sample matrix and the procedure on the accuracy of the process.

8.4.2.9 Analytical Spike

An analytical spike is created by spiking target analytes into a prepared portion (i.e., post digestion) of a sample just prior to analysis. It provides information on matrix effects encountered during analysis such as suppression or enhancement of instrument signal levels. It is most often used in elemental analysis involving various forms of atomic emission or atomic absorption spectroscopy. A single analytical spike serves as a single point application of the “method of standard additions” or MSA.

8.4.2.10 Interference Check Sample

An interference check sample (ICS) is a solution containing known concentrations of both interfering and analyte elements. Analysis of this sample can be used to verify background and interelement correction factors.

8.4.2.11 Internal Standards

An internal standard (IS) is a compound or element with similar chemical characteristics and behavior in the analysis process to the target analytes, but is not normally found in environmental samples. The internal standard is usually added after sample preparation. The primary function of the internal standard is quantitation, however, it also provides a short-term indication of instrument performance. For isotope dilution methods, internal standards are added during sample preparation and are used for quantitation.

8.5 Data Collection Operations

Laboratory analyses are designed to produce data that are representative of existing conditions present at the time the sample was obtained. The data collection design includes field sampling events, sample handling and custody, analytical operations, data recording procedures, data assessments, data verification, and data reporting requirements and techniques to assess limitations of data use. These operations are discussed in this section through section 8.10.

8.5.1 Field Collection and Shipment

In order to provide a sample that most accurately represents the test matrix, field sample collection personnel must abide by the sample collection guidelines and procedures established by involved regulatory agencies. A significant part of the efforts of regulatory agencies include the use of "approved" sample containers, chemical and physical preservation techniques, and observance of specified holding times. It is imperative that all samples be collected and preserved according to the appropriate analytical method specified in the QAPP (if one exists). Although the sampling may be performed by non-STL personnel, the importance of sampling and transportation of the sample to the laboratory is understood and must be considered during data validation.

Sampling requirements must be communicated to the sampling team prior to field collection.

Field personnel are responsible for labeling each individual sample collected with the following information:

- Project name
- Unique client sample number
- Sample location (including as appropriate: borehole and depth or grid coordinates)
- Sampling date and time
- Sample preservation
- Analysis required.

An overriding consideration for the resulting analytical data is the ability to demonstrate that the samples have been obtained from the locations stated and that they have reached the laboratory without alteration. Evidence of collection, shipment, laboratory receipt, laboratory custody, and disposal must be documented to accomplish this. Figure 8.5-1 shows an example Chain-of-Custody (COC) form that is used by the STL laboratory to document this evidence. Field personnel are responsible for initiating the COC form.

The prompt shipment of samples to the laboratory is necessary to ensure that required holding times are met. Samples should be shipped by an overnight carrier,

be hand-delivered, or transported in a manner that assures prompt delivery to the laboratory. Some sites require an extensive radioactive screening process before a sample may be shipped. In these cases, it is imperative for the Project Manager to maintain good communications with the client to assure proper staffing of the laboratory in response to a decreased holding time.

FIGURE 8.5-1
Example STL Chain-of-Custody Form

[redacted]

Chain of Custody Record

SEVERN TRENT SERVICES

Severn Trent Laboratories, Inc.

STL-4124 (0700)

Client	Project Manager	Date	Chain of Custody Number 023165
Address	Telephone Number (Area Code)/Fax Number	Lab Number	Page _____ of _____
City / State / Zip Code	Site Contact	Lab Contact	
Project Name and Location (State)	Carrier/Waybill Number		
Contract/Purchase Order/Quote No.			

Analysis (Attach list if more space is needed)

Special Instructions/ Conditions of Receipt

Sample I.D. No. and Description (Containers for each sample may be combined on one line)	Date	Time	Matrix: Air	Aqueous	Sludge	Soil	Other	Containers & Preservatives: Unpres.	H_2SO_4	HNO_3	HCl	NaOH	Zn/Ac/NaOH	Other

Possible Hazard Identification
☐ Non-Hazard ☐ Flammable ☐ Skin Irritant ☐ Poison B ☐ Unknown

Sample Disposal
☐ Return To Client ☐ Disposal By Lab ☐ Archive For _____ Months (A fee may be assessed if samples are retained longer than 3 months)

Turn Around Time Required
☐ 24 Hours ☐ 48 Hours ☐ 7 Days ☐ 14 Days ☐ 21 Days ☐ Other_____

QC Requirements (Specify)

Relinquished By	Date	Time	Received By	Date	Time
1.			1.		
2.			2.		
3.			3.		

8.5.2 Sample Containers, Shipping Containers, Preservatives, and Holding Times

8.5.2.1 Sample Containers

A sample container is defined as the sealed enclosure, usually made of plastic or borosilicate glass that the sample is collected in and stored in until analysis. All sample containers provided by STL operations for environmental sampling are new, with the exception of some air sampling canisters, which must be recertified before reuse, and demonstrated to be clean for their appropriate use. All documentation certifying sample container cleanliness must be maintained by the laboratory or the vendor and can be provided to the client upon request. The sample containers to be supplied are listed in Tables 8.5-1 through 8.5-5. Container volumes listed in these tables may be decreased with the approval of the laboratory QA Manager or Technical Director to accommodate reduced sample volumes required by the facility SOP.

8.5.2.2 Shipping Containers

Shipping containers are defined as the sealed enclosure in which the sample containers are stored during shipment from the sample collection site to the analytical laboratory. Shipping containers must be of sufficient number and size to accommodate the samples in an upright condition. Shipping containers
must also meet all requirements for the shipment of environmental and/or radioactive samples.

Packaged samples must be shipped to the analytical laboratory in a safe manner that preserves the integrity of the samples. The most common method of sample shipment employs coolers or ice chests that are sealed with custody tape and shipping tape. These coolers must be durable and resistant to crushing during shipment. All coolers must be well maintained and cleaned to prevent cross-contamination of the samples. It is the ultimate responsibility of the person collecting and packaging the sample for shipment to ensure that the shipping containers are clean and functional.

To help prevent sample breakage during shipment, additional consideration must be given to providing shock absorbency to all samples packaged inside the shipping container. Use of bubble-wrap around each sample container is the best way to provide this protection. Foam packing materials and vermiculite are also successfully used.

8.5.2.3 Sample Preservatives

Most analytes have a finite holding time in a given sample matrix. Sample preservation is the chemical or physical means by which samples are treated during and/or following sample collection to aid in the stability of the analytes of interest in that matrix. Sample holding times are also adversely affected when samples are improperly preserved, or shipped unpreserved. The preservation of samples at the time of sample collection will follow the requirements of the analytical methods used. This preservation includes the addition of reagents to deter chemical and biochemical degradation and the maintenance of refrigeration during transit and ultimate storage in the laboratory. The required preservatives for the analysis to be performed on each matrix are included in Tables 8.5-1 through 8.5-5.

8.5.2.4 Sample Holding Times

Holding time is defined as the maximum allowable time a sample can be stored after sample collection and preservation (or laboratory receipt for CLP) until appropriate processing occurs (preparation or analysis). The holding time may vary according to method or client requirements. Tests designated with holding times as “analyze immediately or ASAP” are considered parameters that should be tested by field personnel or on-site. Each operation has a system in place to ensure that holding times are monitored by each group within the operating unit. It is the responsibility of each STL associate processing the sample to assure that holding times are met. STL is responsible for meeting all holding times for properly preserved samples received within 48 hours of collection or if less than half the holding time has passed. If these conditions are not met, STL will attempt to expedite sample analysis as soon as possible.

Sample holding times are listed in Tables 8.5-1 through 8.5-5.

8.5.3 Sample Handling

STL Pittsburgh’s SOP PITT-QA-0051 describes the sample receipt and log-in process in detail. The following sections describe the general policies followed by STL.

8.5.3.1 Sample Receipt

Samples shall be received and logged in at STL by a designated sample custodian or other properly trained associate. Upon sample receipt, the sample custodian shall, as appropriate:

- Wear appropriate personal protective equipment. At a minimum, this

consists of gloves, a lab coat, safety glasses, and in some cases a respirator

- Examine the shipping containers to verify that the custody tape is intact
- Examine all sample containers for damage
- Open shipping containers in adequately ventilated areas to assure worker safety
- Determine if the temperature required by the requested testing program has been maintained during shipment. Document the shipping container temperature on the COC
- Compare samples received against those listed on the COC
- Verify that sample holding times have not been exceeded
- Examine all shipping records for accuracy and completeness
- Determine sample pH (if required for the scheduled analysis) (except VOA samples) and record on the COC
- Sign and date the COC immediately (only after shipment is accepted) and attach the waybill
- Note any problems associated with the coolers and samples on the COC, immediately initiate a Condition Upon Receipt Report (CUR) or equivalent format, and notify the PM who in turn notifies the client
- Attach durable (water-resistant) laboratory sample container labels with unique laboratory identification number and test
- Place the samples in proper laboratory storage.

A CUR or an equivalent form/system is generated by sample control during the sample log-in process to document anomalies identified upon the receipt of samples in the laboratory. These anomalies are outside of laboratory control and do not require corrective actions to be taken within the laboratory. The affected client shall be notified by the PM or designee of all CURs generated for their samples. The PM is responsible for resolving with the client how to proceed with the samples and documenting the decision to proceed with the analysis of compromised samples. CURs must be resolved prior to sample preparation and analysis. The completed CUR form shall be stored in the project file. An example CUR is shown in Figure 8.5-2. The report narrative will include an explanation of sample receiving related anomalies. Further details are given in SOP # PITT-QA-0051.

8.5.3.2 Exceptions or Discrepancies

STL reserves the right to reject samples for any of the following reasons:

- No custody seals as required by project
- No chain of custody documentation provided
- Preservation inappropriate for analysis requested
- Sample container inappropriate for analysis requested
- Sample received out of holding time for analysis requested

- Incomplete sample information provided
- Discrepancies between COC and sample labels
- Samples have high levels of polychlorinated dibenzo-p-dioxins/ dibenzo furans (PCDD/PCDFs)
- Samples have a high level gross alpha or beta radiation
- Samples are from a site known to contain chemical warfare agents (CWAs) and the samples have not been screened for them.

These or any other project exceptions or discrepancies are discussed with the client and agreed upon action taken.

FIGURE 8.5-2

Example STL Condition Upon Receipt Anomaly Report (CUR)
Page 1 of 2

CUR No.: _____
Lot: _____

Date Received: _____
Client: _____ Initiated By: _____
Project Name: _____ RFA/COC Nos.: _____

Condition/Anomaly/Variance (select from legend on back):

Client Sample ID	Analysis Requested	Condition (see legend)	Comments/Actions

Corrective Action:

- [ ] Client informed verbally on: _____ By: _____ In writing on: _____ By: _____
- [ ] Sample(s) processed "as is"
- [ ] Sample(s) ON HOLD until further notice
- [ ] Other action required (see above comments)
- [ ] No action required.

Sample Control Reviewer: _____ Project Manager: _____

SIGNED ORIGINAL MUST BE RETAINED IN THE PROJECT FILE

** Sheet shown is example only. Actual sheets used contain all data shown in different format.*

FIGURE 8.5-2

Example STL Condition Upon Receipt Anomaly Report (CUR)
Page 2 of 2

Legend:

Cooler:
1a Not received, COC available
1b Leaking
1c Other: _____

Temperature:
2a Temp. Blank: _____
2b Cooler Temp: _____
(cooler temp should only be used if there is no Temp. Blank)

Containers:
3a Leaking
3b Broken
3c Extra
3d No labels
3e Headspace (VOA only)
3f Other: _____

Samples:
4a Samples received but not on COC
4b Samples not received but on COC
4c Holding Time Expired
4d Sample Preservative: _____
4e Other: _____

Custody Seals:
5a None
5b Not intact
5c Other: _____

Chain of Custody (COC):
6a Not relinquished by client
6b Incomplete information
6c Other: _____

Container Labels:
7a Doesn't match COC
7b Incomplete information
7c Marking smeared
7d Label torn
7e Other: _____

Other (8): _____
_____
_____

SIGNED ORIGINAL MUST BE RETAINED IN THE PROJECT FILE

** Sheet shown is example only. Actual sheets used contain all data shown in different format.*

8.5.3.3 Sample Log-in

Sample log-in activities at STL are fully documented in SOP PITT-QA-0051. The following is a general description of the log-in process:

- Enter the samples in the laboratory sample log-in book, and/or the LIMS which contains the following information at a minimum:
- Project name or identification number
- Unique sample numbers (both client and internal laboratory)
- Type of samples
- Required tests
- Date and time of laboratory receipt of samples
- Field ID supplied by field personnel
- Notify the PM and appropriate Group/Team Leader(s) of sample arrival
- Place the completed COCs, waybills, and any additional documentation in the project file.

8.5.3.4 Sample Storage

The primary considerations for sample storage are:

- Maintenance at the method prescribed temperature, if required
- Maintenance of sample integrity through adequate protection from contamination from outside sources or from cross-contamination of samples. Low-level and high-level samples, when known, must be stored separately. Samples and standards must be stored in separate refrigerators or freezers. Storage areas for volatile organic test requests should be monitored twice per month by the analysis of a holding (refrigerator) blank (an aliquot of contaminant-free water stored in a VOA vial)
- Security of samples within the laboratory.

The requirements listed in Tables 8.5-1 through 8.5-5 for temperatures and holding times shall be used. Placing of samples in the proper storage environment is the responsibility of sample control personnel. STL will assign individuals the responsibility of notifying the Group/Team Leaders or their designees if there are any samples which must be analyzed immediately because of holding time requirements.

8.5.3.5 Internal Sample Chain-of-Custody and Interlaboratory Transfers

Sample custody within STL laboratories is described in SOP # PITT-QA-0051. Internal COC may be required for programs defined by state or

federal agency. The sample custody documentation shall include the following minimum requirements:

- Name of associate taking custody of the sample from the sample storage area for preparation or analysis
- Dates sample removed from and returned to the sample storage area
- Identification of tests to be performed on the sample aliquot(s) selected by the associate
- Sample matrix
- Laboratory sample numbers
- Sample storage location.

Additional custody records can be provided by the laboratory; at the specific request of the client. Access to STL is restricted to prevent any unauthorized contact with samples, extracts, or documentation.

Samples transferred to a different laboratory than the original receiving facility are transferred under chain-of-custody (COC). The COC is maintained whether the laboratory is another STL facility or a subcontracted laboratory. If the entire sample volume is transmitted, the original copy of the client's COC form will be used to document the relinquishing of the sample and will accompany the sample to its destination. A copy of the completed COC form shall be retained in the laboratory project file. In the case where an aliquot of a sample is shipped from the laboratory, a new COC will be generated by the laboratory and shipped with the sample aliquot. The original COC will be retained in the project file at the site holding the original sample container.

Samples are not transferred to other STL facilities or to subcontractor laboratories without prior approval of the client.

8.5.3.6 Subsampling

Sample preparation procedures are referenced in the method SOPs. Sample subsampling will be performed in accordance with the associated sample prep SOPs.

8.5.3.7 Sample Disposal and Return Chain-of-Custody

After the requested analyses on the samples have been completed, any remaining portions of the samples will be maintained by the sample custodian until the samples are disposed of or returned to the client. The disposal of each sample is recorded on the client's COC form, in LIMS, or referenced in the project file. Sample disposal procedures and documentation are described in operation-specific SOPs. STL's routine

sample retention period is at least thirty days after the analytical report is issued to the client, unless otherwise specified by the client.

For Nuclear Regulatory Commission (NRC) or state licensed laboratories, a real-time inventory of all radioactive isotopes contained in the laboratory (including radioactive samples), as required by the NRC or state, is maintained by the Radiation Safety Officer (RSO). If the quantities of radioactive materials in-house approach the limits stipulated by the laboratory NRC or state license, appropriate action must be taken to ensure the licensed level is not exceeded. This may involve returning samples to clients immediately.

If samples are returned to the client rather than disposed of by the laboratory, the original COC or a new COC is used to document custody transfer back to the client from the laboratory. A copy of the completed COC is retained in the laboratory project file.

8.5.4 Calibration Procedures and Criteria

All equipment and instruments used at STL operations for quantitative measurements are controlled by a formal calibration program. Table 8.0-1 lists the lab's major analytical instrumentation , and Tables 8.5-6 through 8.5-9 outline calibration requirements. Calibrations may be periodic or operational. These are described in the lab's method SOPs. The Policy P-T-001, "Selection of Data Points Required for an Initial Calibration Curve," is applicable when the number of data points is not described in the method. At a minimum, these calibration procedures shall include:

- Instrument to be calibrated
- Reference standards used for calibration
- Calibration technique (e.g., linear, quadratic)
- Acceptable performance tolerances and corrective actions required if specifications are not met
- Frequency of calibration
- Calibration documentation requirements.

Whenever possible, recognized procedures such as those published by ASTM or the USEPA or procedures provided by manufacturers shall be adopted. If established procedures are not available, a procedure shall be developed considering the type of equipment, stability characteristics of the equipment, required accuracy, and the effect of operation error on the quantities measured.

8.5.4.1 Physical Reference Standards

Physical reference standards associated with periodic calibrations include weights for calibrating balances and certified thermometers for calibrating working thermometers. Whenever possible, physical reference standards shall be calibrated by a body that can provide traceability to nationally or internationally recognized standards. If these standards are not available, the basis for the reference standard shall be documented.

Physical reference standards shall be used only for calibration procedures and shall be stored separately from equipment used for analysis.

8.5.4.2 Chemical Reference Standards and Reagents

Chemical reference standards are generally associated with operational calibration. These standards include reference materials traceable to recognized standards suppliers. This may include vendor-certified materials traceable to national or international standard reference materials (e.g., NIST). This topic is also discussed in the Section on "Procurement of Supplies and Services" (see 5.2.4).

All chemical reference standards maintained in the laboratory for use in calibrations (or as QC spiking solutions) and reagents prepared in the laboratory shall be labeled or referenced to appropriate documentation (hard copy or electronic) with the following information at a minimum:

- A unique identification including concentration (solutions containing several analytes can be identified such that the solution constituents and concentrations can be referenced to a logbook)
- Medium prepared in
- Preparation date
- Expiration date
- Initials of preparer.

Vials containing standard solutions that are not large enough to accommodate labels listing the above information may be referenced to a laboratory logbook/ notebook entry or standards software. The expiration date of the working standard and reagent must not exceed the expiration date of the original material. These records should provide sufficient detail to allow one to reproduce the standard or reagent.

Records for all purchased standards and reagents shall include the date of receipt, the date opened, and, where applicable, the expiration date.

8.5.4.3 Standard Verification

When possible, reference standards are purchased from a STL

preapproved vendor. Standards are verified by quantitation against a second known standard before reporting data. The standard for verification must meet the laboratory's criteria for the independent/second source ICV verification. Therefore, the verification of a new standard initial calibration with a second source ICV meets this verification requirement. Realizing that some "bad acting" analytes may not meet these criteria and must be approved by the QAM before use. Standard spiking solutions and surrogates shall be verified by analyzing an LCS with the new standards and verifying against historical criteria limits. Special standards that are obtained from another source must also be independently verified at the lab. Verification by the laboratory of a reference standard from neat materials is also necessary.

To extend the use of an expired standard, which may not be allowed by all programs, reverification is necessary provided that new analysis produces acceptable data. The verification of an expired standard is performed against a current, independent standard reference material by analyzing within a valid calibration and QC.

Stock and working standards and reagents are checked regularly for signs of deterioration, such as discoloration, formation of precipitates, or change in concentration. Care is exercised in the proper storage and handling of standard and reagent solutions. Standards and reagents are always stored separately from samples.

An independent or second source standard is used to verify initial calibrations. An independent/second source standard is defined as a standard composed of the same target constituents as, but from a different source than those used in the standards for the initial calibration. An independent standard may be a laboratory-prepared or a certified independent standard solution(s). Independence of reference material can be achieved by: (1) purchasing reference materials from two separate vendors, (2) using a different lot from the same vendor that is certified by the vendor as an independent standard or (3) having two separate individuals prepare the calibration and verification standard solutions if independent sources are not available.

8.5.4.4 Periodic Calibration

Periodic calibration is performed at prescribed intervals. In general, equipment that can be calibrated periodically is a distinct, singular purpose unit and is relatively stable in performance. These include balances, micropipettors, counters, thermometers, refrigerators, freezers, and ovens. Equipment employed at STL requiring periodic calibration are listed along with their respective calibration requirements in Tables 8.5-6. NELAC

requires mechanical volumetric dispensing devices (except Class A glassware) to be checked for accuracy or at least a quarterly basis if in use. The laboratory unit has an SOP in place for the calibration of this equipment if in use at their location.

8.5.4.5 Operational and Continuing Calibration

Operational calibration is routinely performed as part of instrument usage, such as the development of a standard calibration curve (see Tables 8.5-7 to 8.5-9). The accuracy of initial calibrations are to be verified prior to sample analysis through the use of an independent standard in situations where the source method requires calibration verification.
Detailed requirements for operational and continuing calibration are contained in method-specific SOPs.

When an initial calibration is not performed on the day of analysis, the validity of the initial calibration verification must be verified prior to sample analyses by a continuing instrument calibration verification with each analytical batch.

- A continuing instrument calibration verification must be repeated at the beginning and end of each analytical batch. The concentrations of the calibration verification shall be varied within the established calibration range on an annual basis for each NELAC accredited analytical method. If an internal standard is used, only one continuing instrument calibration verification must be analyzed per analytical batch.

- Sufficient raw data records must be retained to permit reconstruction of the continuing instrument calibration verification, e.g., test method, instrument, analysis date, each analyte name, concentration and response, and calibration curve or response factor.

- If the continuing instrument calibration verification results obtained are outside the established acceptance criteria, corrective actions must be performed. If routine corrective action procedures fail to produce a second consecutive (immediate) calibration verification within acceptance criteria, then either the laboratory has to demonstrate performance after corrective action with two consecutive successful calibration verifications or a new initial instrument calibration must be performed. If the laboratory has not demonstrated acceptance performance, sample analyses must not occur until a new initial calibration curve is established and verified. However, sample data

associated with an unacceptable calibration verification may be reported as qualified data under the following special conditions:

- When the acceptance criteria for the continuing calibration verification is exceeded high, i.e., high bias, and there are associated samples that are non-detects, then those non-detects may be reported. Otherwise the samples affected by the unacceptable calibration verification shall be reanalyzed after a new calibration curve has been established, evaluated and accepted.

- When the acceptance criteria for the continuing calibration verification is exceeded low, i.e., low bias, those sample results may be reported if they exceed a maximum regulatory limit. Otherwise the samples affected by the unacceptable verification shall be reanalyzed after a new calibration curve has been established, evaluated and accepted.

8.5.4.6 Calibration Failure

Equipment or instruments that fail calibration or become inoperable during use shall be tagged to indicate they are out of calibration. Such instruments or equipment shall be repaired and successfully recalibrated before reuse. Following recalibration or verification, back to control will be documented in the injection/run log and/or maintenance logbook through the routine identification of the required calibration runs specified by the standard operating procedure.

8.5.4.7 Calibration Records

Calibration shall be documented for each piece of equipment subject to calibration. All calibration records (periodic and operational) directly affect data and may not be limited to one project. These records shall be stored in either the quality records or the associated project files. Project files that include sample data shall either include the calibration records or include reference to them.

8.6 Quality Assessment

The effectiveness of the QA practices is measured by the quality of data generated by the laboratory. Procedures are in place to detect, prevent, and correct quality problems and to ensure quality improvement. Items and processes that do not meet established requirements must be investigated to determine their cause. Improvements must be implemented in the operations that will prevent a recurrence of these quality problems

and provide overall quality performance. All phases of laboratory work should be designed with the objective of preventing problems and improving quality on a continuous basis.

8.6.1 Data Quality Assessment

Data quality is judged in terms of precision, accuracy, representativeness, completeness and comparability. The areas of representativeness, comparability, and completeness for an overall project, inclusive of sampling issues, may be beyond the control of the laboratory. The elements over which the laboratory has direct control are precision, accuracy, and completeness relative to analytical testing results.

Precision and accuracy assessments are made as part of the evaluation of laboratory QC data generated during sample preparation and analysis. The QC samples employed at STL Pittsburgh as part of routine sample analysis are summarized in Section 8.4 of this document. Table 8.6-1 shows the precision and accuracy measurements employed. Analytical method SOPs and STL Policy Number QA-003 include information on requirements for the type of QC samples, frequencies, and acceptance criteria. Additionally, the SOPs and Policy describe the appropriate actions to be taken when a QC sample result does not meet acceptance criteria.

8.6.2 Statistical Evaluation of Data

In-house limits for all QC data must be evaluated at least annually and compared to the limits published in the methods for applicable matrices. Method limits will be employed until sufficient QC data are acquired. A minimum of 20 to 30 data points are recommended to establish the in-house QC limits. *If in the judgement of the QA Manager the method limits are sufficiently strict, they may be used in lieu of the in house calculated limits. However, this will be done on a test basis rather than a compound specific basis.* Calculated results of the QC (LCS) samples are evaluated by comparing against control limits (3-sigma).

Control charts are used to develop control limits, trouble-shoot analytical problems, and, in conjunction with the non-conformance system, to monitor for trends. Program-specific data analysis requirements for control charts are followed as required for data generated under those programs. These additional requirements shall be documented in a QAPP or QAS.

Precision and accuracy measurements employed by STL Pittsburgh are shown in Table 8.4-3 through 8.4-7. Calculated results of these QC samples are evaluated using statistical tables or control charts.

8.7 Data Recording Procedures

To ensure data integrity, all documentation of data and records generated or used during the process of data generation must be performed in compliance with SOP Number QA-008, "Data Recording Requirements".

8.8 Data Reduction and Verification Procedures

Data review procedures comprise a set of computerized and manual checks applied at appropriate levels of the measurement process. Data review begins with the reduction or processing of data and continues through verification of the data and the reporting of analytical results. Calculations are checked from the raw data to the final value prior to reporting results for each group of samples. Data reduction can be performed by the analyst who obtained the data or by another analyst. Data verification starts with the analyst who performs a 100 percent review of the data to ensure the work was done correctly the first time. Data verification continues with review by a second reviewer who verifies that data reduction has been correctly performed and that the analytical results correspond to the data acquired and processed. This procedure is outlined in Figure 8.8-1.

8.8.1 Data Reduction and Initial Verification

Data reduction and initial verification may be performed by more than one analyst depending upon the analytical method employed. The preparation and analytical data may be reviewed independently by different analysts. In these instances, each item may not be applicable to the subset of the data verified or an item may be applicable in both instances. It is the responsibility of the analyst to ensure that the verification of data in his or her area is complete. The data reduction and initial verification process must ensure that:

- Sample preparation information is correct and complete including documentation of standard identification, solvent lot numbers, sample amounts, etc.
- Analysis information is correct and complete including proper identification of analysis output (charts, chromatograms, mass spectra, etc.)
- Analytical results are correct and complete including calculation or verification of instrument calibration, QC results, and qualitative and quantitative sample results with appropriate qualifiers
- The appropriate SOPs have been followed and are identified in the project records
- Proper documentation procedures have been followed
- All nonconformances have been documented
- Special sample preparation and analytical requirements have been met.
- The data generated have been reported with the appropriate number of significant figures as defined by the analytical method in the LIMS or otherwise specified by the client.

In general, data will be processed by an analyst in one of the following ways:

- Manual computation of results directly on the data sheet or on calculation pages attached to the data sheets
- Input of raw data for computer processing
- Direct acquisition and processing of raw data by a computer.

If data are manually processed by an analyst, all steps in the computation shall be provided including equations used and the source of input parameters such as response factors (RFs), dilution factors, and calibration constants. If calculations are not performed directly on the data sheet, they may be attached to the data sheets.

Manual integrations are sometimes necessary to produce good chromatography, but must only be performed when necessary. Further discussion of manual integrations and the required documentation is given in Policy Number QA-011, "Acceptable Manual Integration Practices".

For data that are input by an analyst and processed using a computer, a copy of the input shall be kept and uniquely identified with the project number and other information as needed. The samples analyzed must be clearly identified.

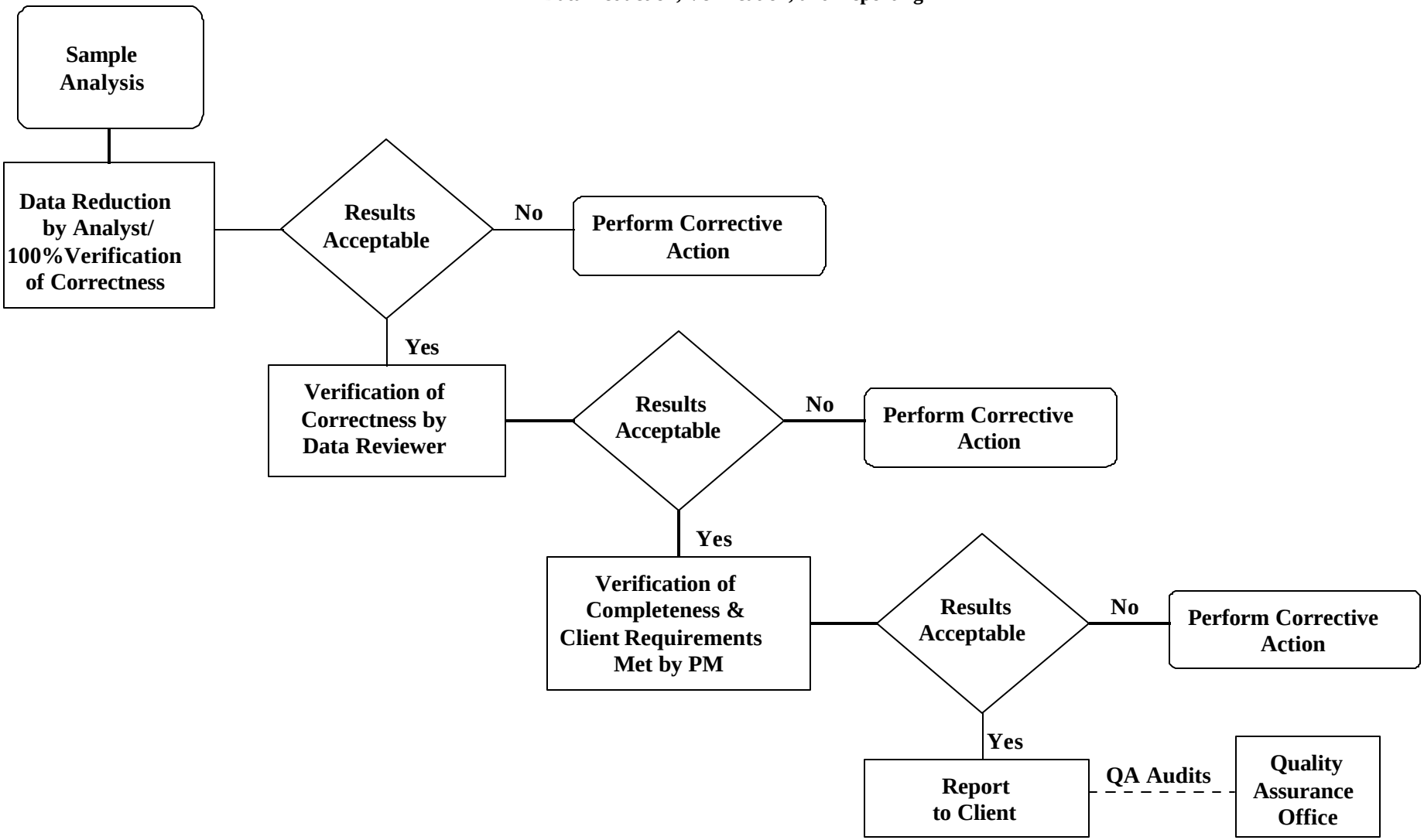
If data are directly acquired from instrumentation and processed, the analyst must verify that the following are correct:

- Project and sample numbers
- Calibration constants and RFs
- Units
- Numerical values used for reporting limits.

Analysis-specific calculations for methods are provided in SOPs. In cases where computers perform the calculations, software must be validated or verified, as described in Section 6.0 of this document, before it is used to process data.

The data reduction is documented, signed and dated by the analyst completing the process. Initial verification of the data reduction by the same analyst is documented on a data review checklist, signed and dated by the analyst. Data review requirements are described in Section 5.3.6 of the QMP.

FIGURE 8.8-1
Data Reduction, Verification, and Reporting



8.8.2 Data Verification

Following the completion of the initial verification by the analyst performing the data reduction, a systematic check of the data that has been fully reduced and checked through Level 1 review is performed by an experienced peer, supervisor, or designee. This check is performed to ensure that level 1 review has been completed correctly and thoroughly. The second level reviewer examines the data signed by the analyst. This review includes an evaluation of all items required in the raw data package. Any exceptions noted by the analyst must be reviewed. Included in this review is an assessment of the acceptability of the data with respect to:

- Adherence of the procedure used to the requested analytical method SOP
- Correct interpretation of chromatograms, mass spectra, etc.
- Correctness of numerical input when computer programs are used (checked randomly)
- Correct identification and quantitation of constituents with appropriate qualifiers
- Numerical correctness of calculations and formulas (checked randomly)
- Acceptability of QC data
- Documentation that instruments were operating according to method specifications (calibrations, performance checks, etc.)
- Documentation of dilution factors, standard concentrations, etc.
- Sample holding time assessment.

This review also serves as verification that the process the analyst has followed is correct in regard to the following:

- The analytical procedure follows the methods and specific instructions given on the project QAS or equivalent summary form
- Nonconforming events have been addressed by corrective action as defined on a nonconformance memo
- Valid interpretations have been made during the examination of the data and the review comments of the initial reviewer are correct
- The package contains all of the necessary documentation for data review and report production and results are reported in a manner consistent with the method used for preparation of data reports.

The specific items covered in the second stage of data verification may vary according to the analytical method, but this review of the data must be documented by signing the same checklist. Data review requirements are described in Section 5.3.6 of the QMP.

8.8.3 Completeness Verification

A third-level review is performed by the PM. This review is required before results are submitted to clients. This review serves to verify the completeness of the data report and to ensure that project requirements are met for the analyses performed. The items to be reviewed are:

- Analysis results are present for every sample in the analytical batch, reporting group, or sample delivery group (SDG)
- Every parameter or target compound requested is reported with either a value or reporting limit
- The correct units and correct number of significant figures are utilized
- All nonconformances, including holding time violations, and data evaluation statements that impact the data quality are accompanied by clearly expressed comments from the laboratory
- The final report is legible, contains all the supporting documentation required by the project, and is in either the standard STL format or in the client-required format.
- Implement checks to monitor the quality of laboratory results using correlation of results for different parameters of a sample (for example, does the TOC results justify the concentration of organic compounds found by GC/MS.)
- A narrative to accompany the final report will be finalized by the PM. This narrative will include relevant comments collected during the earlier reviews.

8.9 Data Reporting

8.9.1 Data Reports

STL Pittsburgh is capable of developing a variety of data deliverable reports. Standard reports will contain:

- Cover Letter/Narrative - Information on sample types, tests performed, any problems encountered, and general comments are provided.
- Analytical Data - Data are reported by sample or by test with the appropriate significant figures and reporting limits, and have been adjusted for dilution, if appropriate. Pertinent information including dates sampled, received, prepared, extracted, and analyzed are provided.
- Laboratory Performance QC Information - The results of LCSs and method blanks analyzed with the project are listed. Any data or QC anomalies are discussed in the narrative.
- Matrix-Specific QC Information - Results of any sample duplicates and MS/MSDs analyzed with the samples as batch QC are reported. Other project-specific QC requested by the client are also reported. The results include supporting information such as amount spiked, percent recovery,

or percent difference/RPD.

- Methodology - Reference for analytical methodology used is cited.
- Other Deliverables - Other deliverables available include disk deliverables, electronic data transfer, sample raw data packages, complete deliverable packages, and custom report formats. Requirements for electronic reporting are defined in Policy CORP-QA-017, "Electronic Reporting".

8.9.2 Final Report Details

STL Pittsburgh will provide paginated reports or a uniquely defined, identifiable certificate/report (i.e. electronic file, CD). The report will include:

a) Report title, name, address and phone number of the laboratory.
b) Name and address of client/project name/client identification number.
c) Description (lab ID of sample).
d) Dates and Time of sample collections (if known), receipt, preparation and analysis.
e) If the required holding time is 48 or less, time of sample preparation and analysis.
f) Method identifiers traceable to all procedures used.
g) Reporting limit.
h) Test result with appropriate units and how reported (wet weight/dry weight). Also identify any results outside of quantitation limits. When required, a statement of the estimated uncertainty of the test result should be added.
i) If appropriate, description of any QC failures or deviations from SOPs.
j) Signature and title of the individual responsible for the report. Electronic signature is acceptable.
k) Date of issue.
l) All subcontract work must be clearly identified, and name and address of outside subcontractor noted.
m) Where relevant, a statement to the effect that the results relate only to the items tested or to the sample as received by the laboratory
n) Where relevant, a statement that the certificate or report shall not be reproduced except in full, without the written approval of the laboratory.

After final report any correction, addition, or deletion must clearly identify its purpose and meet the above reporting requirements as appropriate.

All applicable elements from above should be available for review if not issued in a formal report by an in-house or captive laboratory.

8.9.3 Verbal Results

STL Pittsburgh, as a policy, discourages the release of data verbally or without full data review. If however, the client requests analytical results to be communicated verbally or by facsimile prior to final review, they must be clearly identified as "Preliminary" results. The client must understand that the data have not undergone the required levels of review and may potentially change.

8.9.4 Reporting Analytical Results

Sample results are reported according to analytical method SOPs or client specifications. Normally, the laboratory uses the STL Pittsburgh Reporting Limit (RL) at which any analyte of interest detected at or above that level is reported as a positive value and any analyte of interest not detectable or detected below that level is reported as "not detected" at the RL. The laboratory will normally report results within the calibration, however, any reported results outside of the calibration range will be documented in the final report.

If a QC measurement is out of control and the data is to be reported, data qualifiers are reported with samples associated with failed QC measurements.

The laboratory must certify that the test results meet all NELAC requirements or provide reasons and/or justification if they do not.

In some cases a contract, QAPP, or documented client request may require the laboratory to report sample results in a specified manner. Some examples are given below:

- The laboratory may be requested to report all analytes of interest that are less than the laboratory's RL but are greater than the MDL. This data will be flagged with an appropriate qualifier or noted in the report case narrative. (See precautions in "Establishing Reporting Limits", Policy Number QA-009).
- The laboratory may be requested to report any tentatively identified compounds (TICs). These data will be flagged with an appropriate qualifier.
- The laboratory may be requested to report sample results using an RL that is higher than their normal level. In this case, only the analytes of interest found at or above that level would be reported as positive values. In this case, the laboratory will state the PSRL rather than the RL. All analytes of interest not detected or detectable below that level would be reported as "not detected" at the PSRL.

  In this situation, the laboratory must include documentation in the project file that supports the reporting procedure employed.

It is the responsibility of the laboratory to provide for a reporting system that assures that any problems associated with an analysis are properly documented on a nonconformance memo, communicated to the appropriate STL Pittsburgh staff, and addressed appropriately in the data report.

8.9.5 Reissued Deliverables

If, after issuance of a report, STL Pittsburgh observes any mistake that affects the results reported or the QC interpretation of those results, the client will be notified. After issuance of the report, the laboratory report remains unchanged. Any material amendments to a report after issue made only in the form of a further document, or data transfer must include the statement "Supplement to Test Report" or otherwise identified. For further discussion see SOP CORP-QA-0010.

8.9.6 Client Confidentiality

Data and sample materials provided by the client or at the client's request, and the results obtained by STL, shall be held in confidence, unless such information is generally available to the public or is in the public domain. STL's reports, and the data and information provided therein, are for the exclusive use and benefit of our clients, and are not released to a third party without written consent from the client. Data confidentiality is also discussed Section 3.6.

8.10 Data Validation

Data validation for STL refers to data reviews conducted in accordance with the USEPA CLP "Laboratory Data Validation Functional Guidelines for Evaluating Organic Analyses" and "Laboratory Data Validation Functional Guidelines for Evaluating Inorganic Analyses", or modifications thereof, for non-CLP type analyses.

This form of data validation provides an impartial evaluation of the laboratory's results. Data validation may be requested by the client for a percentage of data and is usually performed by a third party, one which was not involved with the sample analysis. Qualifiers are assigned to data, when required, according to the requirements of the data validation protocol being used.

8.11 Preventive Maintenance and Service

Facilities, instruments, equipment, and parts are subject to wear, deterioration, or change in operational characteristics. Within STL, preventive maintenance, coupled with vendor service agreements, is an organized program of actions taken to maintain facilities and equipment in control.

8.11.1 Analytical Instrumentation and Equipment

The primary purpose of the maintenance program is to prevent instrument and equipment failure and to minimize down time. A properly implemented maintenance program increases the reliability of a measurement system.

Each instrument or piece of equipment shall be uniquely identified. The laboratory maintains the following:

- Instrument/equipment inventory list
- Instrument/equipment major spare parts list or inventory
- External service agreement documents (if applicable)
- Instrument-specific preventive maintenance logbook or file for each functional unit.

The records of routine maintenance and non-routine maintenance shall include at a minimum:

- Name and serial number of the item or equipment
- Details of maintenance performed
- Dates and results of recalibrations/ reverifications indicating return to control
- Analyst initials and the date maintenance was performed whether by the analyst or a contracted service representative.

Any item or equipment that does not perform to specifications or defective shall be taken out of service, and tagged as out of service until it has been repaired and shown by calibration/ verification to perform satisfactorily.

8.11.2 Frequency of Equipment Maintenance

The frequency of maintenance must consider manufacturer's recommendations and previous experience. Frequency of preventive maintenance along with the recommended preventive maintenance schedules are given in Tables 8.11-1 through 8.11-30 for analytical instrumentation and equipment or defined in operation specific routine maintenance SOPs. Frequency of maintenance for the facility systems is documented in the CHP.

8.11.3 Facilities

Another important aspect of the laboratory operation is the existence and maintenance of adequate, safe, and clean facilities including appropriate engineering controls such as proper ventilation, lighting, dust control, hoods, air flow, protection from extreme temperatures, waste disposal, and a source of stable power. The facility floor plan is provided in Figure 8.11.

The maintenance and use of these facilities and proper operations are described in the Chemical Hygiene Plan (CHP). The Laboratory Manager has responsibility for ensuring a properly maintained facility. The Laboratory Director also has the responsibility for ensuring that facilities are available to store samples properly without contamination, work areas are equipped with adequate bench, hood and operational space, and that procedures are in place to ensure the areas are free from chemical and radiological contamination that may affect analytical results.

8.11.4 Facility Security

The laboratory building is a limited access, secure facility. To ensure that only authorized personnel are able to enter the building from an entrance that is not monitored, entry into each building is limited in one or more of the following ways at a minimum:

- The use of key pads or electronic locks activated by swipe or magnetic cards which are issued only to authorized personnel
- Locking doors and issuing keys only to authorized personnel
- Alarm systems to detect unauthorized entrance

During business hours, entry is possible only through the main entrance. This entrance is monitored at all times, usually by a receptionist. All guests are required to sign in by using a visitor logbook.

8.12 Requirements for Ancillary Equipment and Materials

8.12.1 Water

High purity water (e.g., ASTM reagent grade or equivalent water) will be used in all metals, radiological, wet chemistry, and organic analyses. Demonstration of contaminant-free water is shown through the analysis of method blanks consisting of the reagent water on a daily basis for the analyte of interest. This water is obtained by the use of either a commercial ion-exchange deionizing, distillation, or reverse osmosis unit plus an appropriate polishing unit. The resulting water has a maximum conductivity of 1.0 umho-cm at 25°C or a minimum resistivity of 1.0 Mohm at 25°C. Conductivity or resistivity will be monitored and documented daily or on each day that water is dispensed for analytical use.

For volatile analyses the water may be further purified by purging with an inert gas before use to remove potential traces of organic solvents. This is described further in SOP # CORP-MS-0002PT.

8.12.2 Compressed Air and Gases

Ultra high-purity compressed gases from preapproved vendors or in-house gas generators will be used when required for instrumentation. These air and gases must meet the requirements and specifications of the analytical methods performed. In-line filters will be used when appropriate to minimize contamination and moisture from the gases.

8.12.3 Glassware Preparation

Glassware preparation procedures implemented at operating units are designed to ensure that contaminants are not introduced during sample analysis. Procedures describing glassware preparation are detailed in operation-specific SOP PITT-QA-0003.

8.12.4 Chemical Storage

Storage of chemicals shall be conducted in a manner to minimize the potential for fire or release of hazardous material resulting from an unplanned chemical reaction. Refrigerators used for storing flammable liquids must have spark-free interior construction. Flammable solvents shall be stored in appropriate cabinets meeting all necessary codes. All chemicals are stored according to chemical compatibility. Further details regarding chemical storage are provided in the CHP.

8.12.5 Waste Management

The goal of STL's policy for waste management is to ensure that laboratory wastes are disposed of safely and in a manner consistent with applicable federal, state and local regulations. The waste disposal program is designed to assure that minimal harm to people and the environment shall result from the disposal of laboratory chemicals. This goal is accomplished by requiring that the laboratory comply with the procedures presented in the CHP

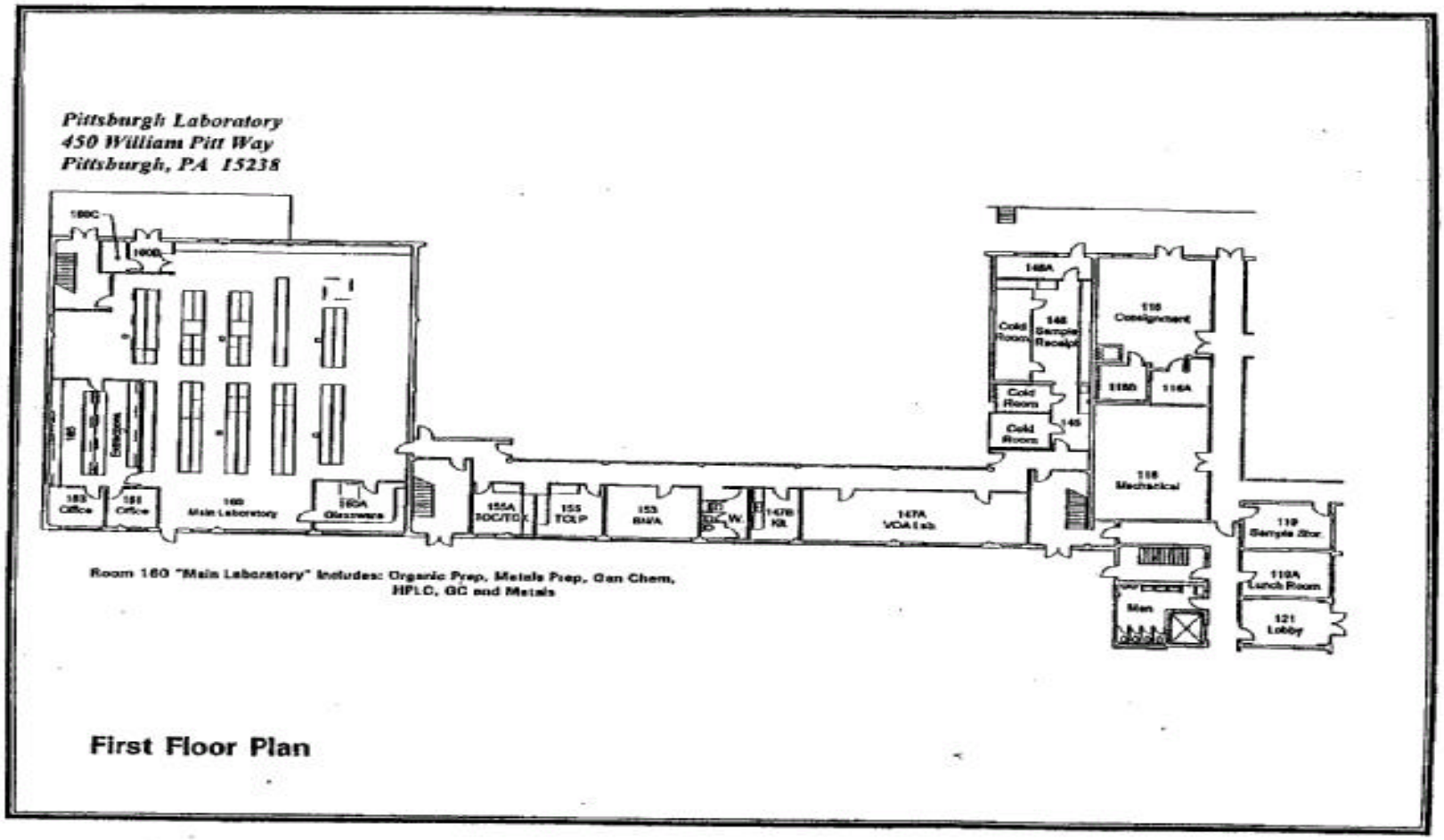

Pittsburgh Laboratory
450 William Pitt Way
Pittsburgh, PA 15238
Cold Room
Cold Room
Cold Room
Mechanical
Men
Lobby
Lunch Room
Room 160 "Main Laboratory" Includes: Organic Prep, Metals Prep, Gen Chem, HPLC, GC and Metals
First Floor Plan

TABLE 8.11-1
Instrument Maintenance Schedule
Ion Chromatograph[1]

As Needed	Daily	Weekly	Monthly	Semi-annually
Clean micromembrane suppressor when decreases in sensitivity are observed.	Check plumbing/leaks.	Check pump heads for leaks.	Check all air and liquid lines for discoloration and crimping, if indicated.	Lubricate left hand piston.
Check fuses when power problems occur.	Check gases.	Check filter (inlet)	Check/change bed supports guard and analytical columns, if indicated.	Clean conductivity cell.
Reactivate or change column when peak shape and resolution deteriorate or when retention time shortening indicates that exchange sites have become deactivated.	Check pump pressure.			Check conductivity cell for calibration.
De-gas pump head when flow is erratic.	Check conductivity meter.			

TABLE 8.11-2
Instrument Maintenance Schedule
LACHAT Auto Analyzer[1]

As Needed	Daily	Monthly	Semi-annually	Annually
Prepare fresh reagents.	Check detector. Clean detector cell and make sure there are no trapped bubbles in detector cell. Check Valves Check Reference source	Replace tubing.	Lubricate pump roller.	Clean pump rollers with steel wool and lubricate.
	Check peristaltic tubing. Check sampler Check auto diluter	Clean pump, diluter, and XYZ Sampler.		
	Clean sample probe shaft.			

TABLE 8.11-3
Instrument Maintenance Schedule
Total Organic Halide Analyzer[1]

Daily	As Needed
Check electrodes for damage, polish the electrodes.	Examine and clean or replace pyrolysis tube.
Replace dehydrating fluid and electrolyte fluid.	Clean titration cell.
Clean quartz boat.	Observe gas flow.
Observe check valves during use for backfeed.	Replace reference electrode fluid.
At end of each day of use, wash out absorption module, empty electrolyte and fill cell with DI water. Empty dehydrator tube	Change quartz wool.
Perform cell performance check.	Replace o-rings and seals.

TABLE 8.11-4
Instrument Maintenance Schedule
High Pressure Liquid Chromatograph[1]

Daily	As Needed
Check level of solution in reservoirs. If adding, verify that solvent is from the same source. If changing, rinse gas and delivery lines to prevent contamination of the new solvent.	Replace columns when peak shape and resolution indicate that chromatographic performance of column is below method requirements.
Check gas supply.	Oil autosampler slides when sample does not advance.
Flush with an appropriate solvent to remove all bubbles.	Rinse flow cell with 1N nitric acid if sensitivity low.
Pre-filter all samples.	Change pump seals when flow becomes inconsistent.
	Repack front end of column Backflush column.

TABLE 8.11-5
Instrument Maintenance Schedule
Flame Atomic Absorption Spectroscopy[1]

Daily	Monthly	As Needed
Verify proper safety precautions are working.	Clean all filters and fans.	Check drain receptacle.
Verify gas box operates properly and safely.	Change capillary tubing	Check background corrector for alignment.
Verify sensitivity using elements in UV/VIS spectrum.	Clean optical windows	Clean burner head.
		Clean nebulizer.
		Clean spray chamber.
		Check sample introduction O-rings.

TABLE 8.11-6
Instrument Maintenance Schedule
Inductively Coupled Argon Plasma/Mass Spectrometry (ICAP/MS)[1]

Daily	Weekly	Monthly	Quarterly	Annually	As Needed
Check sample waste container level.	Check peristaltic pump: proper roller pressure, sample introduction tubing, correct pump rotation, condition of drain tubing.	Clean all filters and fans.	Replace oil in roughing pumps.	Replace oil in turbo-molecular pump.	Check electronic settings for optimum sensitivity: resolution, mass calibration, ion optics, CEM, deflector voltage.
Check quartz torch condition.	Check condition of sampler and skimmer cones.	Check recirculator water level.			
Measure quartz torch for proper alignment.	Check and drain oil mist eliminator on roughing pumps.				
Clean spray chamber and nebulizer.					
Check oil level of roughing pumps.					

TABLE 8.11-7
Instrument Maintenance Schedule
ICP[1]

Daily	Monthly or As Needed	Semi-annually	Annually
Check gases Check that argon tank pressure is 50-60 psi and that a spare tank is available. Check aspiration tubing	Clean plasma torch assembly to remove accumulated deposits.	Change vacuum pump oil.	Notify manufacturer service engineer for scheduled preventive maintenance service.
Check vacuum pump gage. (<10 millitorr)	Clean nebulizer and drain chamber; keep free flowing to maintain optimum performance.	Replace coolant water filter. (may require more or less frequently depending on the quality of water)	
Check that cooling water supply system is full and drain bottle is not full. Also that drain tubing is clear, tight fitting and has few bends.	Clean filters on back of power unit to remove dust.		
Check that nebulizer is not clogged.	Replace when needed: peristaltic pump tubing sample capillary tubing autosampler sipper probe		
Check that capillary tubing is clean and in good condition.	Check yttrium position. Check O-rings Clean/lubricate pump rollers.		
Check that peristaltic pump windings are secure.			
Check that high voltage switch is on.			
Check that exhaust screens are clean.			
Check that torch, glassware, aerosol injector tube, bonnet are clean.			

TABLE 8.11-8
Instrument Maintenance Schedule
Graphite Furnace Atomic Absorption[1]

Daily	Weekly	Monthly	Semi-annually	Annually
Check gas lines and gas supply.	Clean optical windows.	Check coolant level in cooling unit. Add coolant if error message appears.	Change graphite contacts	Notify manufacturer service engineer to clean optics.
Clean contact cylinders.				Check optics
Check tubes and platform; replace if corroded, faking, or if low absorbance results. Check autosampler tubing and alignment. Flush autosampler tubing				
PE4100ZL: clean fume extraction tip, replace fume extraction filter and H_2O trap.				
As needed, trim sampling capillary.				
Check drain lines and waste containers; empty as needed.				
Check acid rinse containers; fill as needed.				

TABLE 8.11-9
Instrument Maintenance Schedule
Cold Vapor Atomic Absorption (Leeman PS 200) [1]

Daily	As Needed	Annually
Change drying tube	Change pump tubing	Change Hg lamp.
Check pump tubing/drain tubing	Check/change Hg lamp	
Check gas pressure	Clean optical cell	
Check aperture reading Check tubing	Lubricate pump	

TABLE 8.11-10
Instrument Maintenance Schedule
Cold Vapor Atomic Absorption (PE 5000) [1]

Daily	As Needed	Monthly
Clean aspirator by flushing with DI water.	Change source lamp	Clean cell in aqua regia.
Check tubing and replace if needed.		Clean aspirator in aqua regia.
Change silica gel in drying tube.		Clean windows with methanol.
Check argon gas supply.		
Adjust lamp.		

TABLE 8.11-11
Instrument Maintenance Schedule
Gas Chromatograph[1]

Daily	As Needed	Quarterly/Semi-annually/Annually
Check for sufficient supply of carrier and detector gases. Check for correct column flow and/or inlet pressures.	Replace front portion of column packing or break off front portion of capillary columns. Replace column if this fails to restore column performance or when column performance (e.g. peak tailing, poor resolution, high backgrounds, etc.) indicates it is required.	Quarterly ELCD: change-roughing resin, clean cell assembly. Quarterly FID: clean detector
Check temperatures of injectors and detectors. Verify temperature programs.	Change glass wool plug in injection port and/or replace injection port liner when front portion of column packing is changed or front portion of capillary column is removed.	Semi-annually ECD: perform wipe test.
Check inlets, septa. Replace septum Clean injector port		Annually ELCD: change finishing resin, clean solvent filter. Annually FID: Replace flame tip ECD: detector cleaning and re-foiling, every five years or whenever loss of sensitivity, or erratic response or failing resolution is observed.
Check baseline level.	Perform gas purity check (if high baseline indicates that impure carrier gas may be in use).	
Check reactor temperature of electrolytic conductivity detector.	Replace or repair flow controller if constant gas flow cannot be maintained.	
	Replace fuse.	
Inspect chromatogram to verify symmetrical peak shape and adequate resolution between closely eluting peaks.	Reactivate external carrier gas dryers.	
Clip column leader	Detectors: clean when baseline indicates contamination or when response is low. FID: clean/replace jet, replace ignitor. NPD: clean/replace collector assembly. PID: clean lamp window monthly or replace as needed, replace seals. ELCD: check solvent flow weekly, change reaction tube, replace solvent, change reaction gas, clean/replace Teflon® transfer line. ECD: follow manufacturers suggested maintenance schedule	
	Reactivate flow controller filter dryers when presence of moisture is suspected.	

TABLE 8.11-11
Instrument Maintenance Schedule
Gas Chromatograph[1]
(Continued)

Daily	As Needed	Quarterly/Semi-annually/Annually
GC (continued)	HP 7673 Autosampler: replace syringe, fill wash bottle, dispose of waste bottle contents.	
	Purge & trap devices: periodic leak checks quarterly, replace/condition traps (when poor response or disappearance of reactive or poorly trapped compounds), clean sample lines, valves (if they become contaminated), clean glassware. Clean sparger weekly. Check purge flow monthly. Bake trap as needed to correct for high background. Change trap annually, or as needed whenever loss of sensitivity, or erratic response or failing resolution is observed.	
	Purge & trap autosamplers: leak check system, clean sample lines, valves. PTA-30 autosampler also requires cleaning the syringes, frits, valves, and probe needles, adjustment of micro switches, replacement of Teflon® valve, and lubrication of components.	

TABLE 8.11-12
Instrument Maintenance Schedule
Mass Spectrometer[1]

Daily	Weekly	As Needed[2]	Quarterly	Semi-Annually	Annually
Check for sufficient gas supply. Check for correct column flow and/or inlet pressure.	Check mass calibration (PFTBA or FC-43)	Check level of oil in mechanical pumps and diffusion pump if vacuum is insufficient. Add oil if needed between service contract maintenance.	Check ion source and analyzer (clean, replace parts as needed)		Replace the exhaust filters on the mechanical rough pump every 1-2 years.
Check temperatures of injector, detector. Verify temperature programs.		Replace electron multiplier when the tuning voltage approaches the maximum and/or when sensitivity falls below required levels.	Check vacuum, relays, gas pressures and flows	Clean rods	
Check inlets, septa.		Clean Source, including all ceramics and lenses - the source cleaning is indicated by a variety of symptoms including inability of the analyst to tune the instrument to specifications, poor response, and high background contamination.	Change oil in the mechanical rough pump. Relubricate the turbomolecular pump-bearing wick.		
Check baseline level.		Repair/replace jet separator.			
Check values of lens voltages, electron multiplier, and relative abundance and mass assignments of the calibration compounds.		Replace filaments when both filaments burn out or performance indicates need for replacement.			

TABLE 8.11-13
Instrument Maintenance Schedule
TRAACS 800 Auto Analyzer [1]

As Needed	Daily	Monthly	Semi-annually	Annually
Replaces air filter when progressive loss of air pressure is observed.	Check air pressure gauge (22 ± 2 psi)	Change all pump tubes (or after 200 hours of pumping time)	(or after 1000 hours of pumping time)	Lightly lubricate the Linear Sample Rails (use semi-fluid lubricant)
Replace air valve tubing when occlusion in tubing is observed	Use recommended washout procedure (at end of analysis operations)	Clean sample probe shaft	Replace pump platens	Replace colorimeter lamp (or after 2500 hours of use)

TABLE 8.11-14
Instrument Maintenance Schedule
Sonicator [1]

Daily	As Needed
Daily when used: Inspect probe tips for inconsistencies (etching/pitting).	Replace probe tip.
	Disassemble and clean sonicator probe tips.
	Tune sonicator assembly.

TABLE 8.11-15
Instrument Maintenance Schedule
Analytical/Top Loading Balances[1]

Daily	Annually
Check using Class S-verified weights once daily or before use Clean pan and weighing compartment	Manufacturer cleaning and calibration.

TABLE 8.11-16
Instrument Maintenance Schedule
Refrigerators/Walk-in Coolers [1]

Daily	As Needed
Temperatures checked and logged.	Refrigerant system and electronics serviced.

TABLE 8.11-17
Instrument Maintenance Schedule
Ovens [1]

Daily	As Needed
Temperatures checked and logged.	Electronics serviced.

TABLE 8.11-18
Instrument Maintenance Schedule
Specific Digital Ion Analyzer[1]

Daily	As Needed
Daily when used: Calibrate with check standards. Inspect electrode daily, clean as needed. Inspect electrode proper levels of filling solutions daily, fill as needed. Clean probe, each use.	Electronics serviced.

TABLE 8.11-19
Instrument Maintenance Schedule
Turbidimeter[1]

Daily	Monthly	As Needed
Daily when used: Adjust linearity on varying levels of NTU standards. Standardize with NTU standards. Inspect cells.	Clean instrument housing	Electronics serviced.

TABLE 8.11-20
Instrument Maintenance Schedule
Dissolved Oxygen Meter[1]

Daily	As Needed
Daily when used: Calibrate with check standards. Check probe membrane for deterioration	Electronics serviced.

Clean and replace membrane with HCl solution.	

TABLE 8.11-21
Instrument Maintenance Schedule
Conductance Meter[1]

Daily	As Needed
Daily when used: Check probe and cables. Standardize with KCl. Inspect conductivity cell	Electronics serviced.

TABLE 8.11-22
Instrument Maintenance Schedule
Chemical Oxygen Demand (COD) Reactor[1]

Daily	As Needed
Daily when used: Calibrate with check standards.	Electronics serviced.

TABLE 8.11-23
Instrument Maintenance Schedule
Spectrophotometer[1]

As Needed	Daily	Monthly	Annually
Dust the lamp and front of the front lens.	Check the zero %A adjustment.	Clean windows	Check instrument manual.
	Clean sample compartment		Perform wavelength calibration.
	Clean cuvettes		Replace lamp annually or when erratic response is observed.
			Clean and align optics.

TABLE 8.11-24
Instrument Maintenance Schedule
pH Meter[1]

As Needed	Daily
Clean electrode.	Inspect electrode. Verify electrodes are properly connected and filled.
Refill reference electrode.	Inspect electrode proper levels of filling solutions. Make sure electrode is stored in buffer.

TABLE 8.11-25
Instrument Maintenance Schedule
Fourier Transform Infrared Spectrometry (FTIR)[1]

Check desiccant every 3 months.
Check KBr window every 3 months.

TABLE 8.11-26
Instrument Maintenance Schedule
Radiological Analysis Equipment[1]

Instrument	Items Checked/Service	Minimum Frequency
Alpha Proportional	Check gas flow	Daily
	Clean sample tray	Weekly
	Check bubbler oil level	Monthly
Beta Proportional	Check gas flow	Daily
	Clean sample holders	Weekly
Liquid Scintillation	Clean sample changer	Weekly
	Check condensate trays	Weekly
	Check air filters	Monthly
Quad aß Proportional	Check gas flow	Daily
	Clean sample holders	Weekly
Gamma Spectroscopy	Check LN_2 level	Bi-weekly
	Replace plastic liner	Weekly
Alpha Spectroscopy	Clean sample holder	As needed
	Change vacuum pump oil	Every six months
LIPA	Clean sample changer	Weekly
	Check laser dye performance	Weekly
Benzene Synthesizer	Check gas tubes	Weekly
	Clean instrument	Monthly
Electrolytic Enrichment	Check electrical leads	Monthly
	Clean system	Monthly
Fluorometer	Clean sample holder	Weekly

TABLE 8.11-27
Instrument Maintenance Schedule
Total Organic Carbon Analyzer (OI 7000)

Daily	As Needed	Weekly	Monthly	Semi-Annually
Check: Oxygen supply Persulfate supply Acid supply Carrier gas flow rate (~ 150 cc/min) IR millivolts for stability (after 30 min. warm-up) Reagent reservoirs	Check injection port septum after 50-200 runs. Tube end-fitting connections after 100 hours or use. Indicating drying tube. NDIR zero, after 100 hours of use. Sample pump, after 2000 hours for use. Digestion vessel/condensation chamber, after 2000 hours of use. Permeation tube, after 2000 hours of use. NDIR cell, after 2000 hours of use.	Check liquid-flow-rate-pump-tubing conditions on autosampler Check injection port septum	Clean digestion vessel Clean condenser column Do the leak test	Change pump tubing

Footnotes to Preventive Maintenance Tables

(1) Refer to manufacturer's instructions for each instrument to identify and perform maintenance operations.
(2) Also see Table 8.11-11 for applicable "As Needed" GC maintenance.

TABLE 8.11-28
Instrument Maintenance Schedule
APCI/ESI LC/MS/MS

Daily	As Needed	Semi-annually	Annually
Check helium sparge supply for adequate pressure	Oil autosampler when it is noisy or picking up the tray	Replace rough-pump oil	Replace turbo-pump oil
Check solvent reservoirs for sufficient level of solvent	Change pump seals		Vacuum system components including fans and fan covers
Verify that pump is primed, operating pulse free	Change filters in autosampler		
Check needle wash reservoir for sufficient solvent	Replace column if excessive pressure or poor performance		
Verify capillary heater temperature	Rinse capillary with MeOH		
Verify vaporizer heater temperature	Clear capillary if clogged		
Verify manifold heater temperature	Rinse and clean corona needle		
Verify manifold pressure (~5 x $10^{-}6$)	Replace sample inlet tube in APCI (10.1 cm)		
Verify fore-pump pressure (~30 to 200mtorr)	Replace fused silica tube in ESI interface		
Verify rough pump and turbo-pump oil levels	Clean lenses		
Verify nitrogen pressure for auxiliary and sheath gasses	Clean skimmer		
Verify that corona and multiplier are functioning			

TABLE 8.11-29
Instrument Maintenance Schedule
Digestion Block

Annually
Check temperature with NIST thermometer

TABLE 8.11-30
Instrument Maintenance Schedule
Flash Point Tester

Daily	As Needed
Check tubing. Clean sample cup each use.	Check thermometer against NIST thermometer, when used.
Check gas.	
Clean flash assembly	
Check stirrer	

Section 9.0 Quality Assessment and Response
Excerpted from Laboratory Quality Manual for STL Pittsburgh

SEVERN TRENT SERVICES

Laboratory Quality Manual for

STL Pittsburgh

450 William Pitt Way
Pittsburgh, PA 15238
(412) 820-8380

Approved by:

4/10/01
Laboratory Director Date

4/10/2001
Technical Director Date

4/10/2001
Quality Assurance Manager Date

Revision 0
September 1, 2000
Controlled Copy Number: _____

9.0 Quality Assessment and Response

9.1 Nonconformances

A nonconformance is an unplanned deviation from an established protocol or plan and in some cases may be exceptionally permitted departures from the documented policies and procedures or from standard specifications. The deviation may be the result of STL's actions as a systematic error, then termed a deficiency. A single isolated event or event beyond the control of STL is termed an anomaly.

Nonconformances can be identified on the basis of internal or external systems or performance audits, sample processing, routine calibration and monitoring of analytical and support equipment, or QC sample analyses. The Technical Director, Operations Manager, Project Manager, QA Manager, Group Leader, and Analyst may be involved in identifying the most appropriate corrective action. If previously reported data are affected, the issue is immediately brought to the attention of QA.

9.1.1 Nonconformance Memo (NCM)

All nonconformances, deficiencies and anomalies, are documented via an electronic process or on a paper form that meets NCM requirements as approved by QA. An allowed exception is log-in conformance problems, which are documented on a Condition Upon Receipt Form (see Section 8.5). A detailed description of the procedure and responsibilities associated with nonconformance documentation, communication, and resolution is described in SOP # CORP-QA-0010.

The Clouseau NCM program, available on the local-area network throughout the laboratory, is the main vehicle for documenting and communicating NCMs. The program allows anyone in the laboratory to document a nonconformance, explain the cause of the problem, and link to the LIMS system to identify the samples and clients involved. The program uses the local e-mail to automatically notify the person's supervisor, the Project Managers associated with the samples, and the QA department. The program is used to document approval and completion of the immediate corrective actions for the samples involved, and can be used to document long-term corrective actions. It provides a place to document resolution of problems with the clients, and it provides routines to query the associated data base to examine trends and prepare management reports. A copy (paper or electronic) of the nonconformance memo will be kept in the project files along with the data it refers to. A copy, paper or electronic, shall also be kept in the quality files.

9.2 Client Complaints

Client inquiries and complaints are generally received through the PM or Customer Services Manager. Typically, the PM or CSM communicates with the client to determine the details of the inquiries, including technical data problems, deliverable issues, turn-around-time problems, etc. Technical and deliverable issues are coordinated by the PM and usually involve input from operations, QA, and management staff. A formal written response to the client is coordinated by the PM, but may on occasion be delivered by the CSM or the Account Manager. Details of the types and levels of complaints and required documentation are provided in Section 4.8 of the QMP. Client complaints are recorded as a type of NCM in the Clouseau database, which are summarized in the monthly QA Reports to Management (see Section 9.6 for more about the monthly QA reports).

9.3 Corrective Actions

Corrective actions are measures taken to rectify conditions adverse to quality and, where possible, to prevent their reoccurrence. Investigations of potential problems and corrective actions should be timely, determine the root cause, and evaluate any propagation of the error or problem. Whenever a systematic error is discovered that affects the accuracy or defensibility of results reported to STL's clients, Corporate QA involvement followed by written client notification will be part of the corrective action.

Corrective actions should be implemented with an understanding of the technology and work activities associated with the quality element, with appropriate training of STL associates and vendors, and should be monitored for progress and success. Depending on the nature of the problem, the corrective action employed may be formal or informal. In either case, occurrence of the problem, the corrective action employed, and verification that the problem has been eliminated must be documented properly. On-the-spot actions are used to correct minor problems, such as recalibration, retuning, or a minor repair (e.g., replacement of a minor part) of a malfunctioning instrument or the correction of poor analytical technique being used by an analyst. These occurrences are documented in the appropriate injection, run, or analysis logbooks. Similarly, routine instrument maintenance, malfunctions, and power failures are also documented in the appropriate instrument maintenance logbooks. These events do not require a formal NCM process, provided reported analytical results are not affected. Corrective actions specific to quality controls for analytical methods are discussed in the operational-specific SOPs.

9.3.1 Monitoring Corrective Actions

All formal corrective action documentation is maintained by the QA department, either in the Clouseau data base or in paper files. The QA department reviews all corrective actions and selects one or more of the significant corrective actions for inclusion in the annual systems audit. The QA department may also implement a spot assessment audit.

The purpose of these audits is to monitor the implementation of the corrective action and to determine whether the action taken has been effective in overcoming the issue identified.

9.4 Internal Audits

Internal audits are performed to assess the degree of adherence to established policies, procedures and standards. These assessments are conducted by STL personnel who are independent of the area being evaluated. Audits can identify areas for improvement with regard to compliance with policies, procedures and standards. Audits also provide a means for correction prior to system failure.

Audits and assessments are generally conducted through the use of checklists and relevant reference documents. The findings of all audits and assessments are documented as is the laboratory response and any corrective actions. Follow-up checks are performed and the status of implementation of corrective actions is documented for all categories of audits and assessments. This cycle continues until all issues are closed.

9.4.1 Audit Types and Frequency

The following types of audits are performed at STL Pittsburgh:

Figure 9.4-1 Audit Types and Frequency

Audit Type	Performed By	Frequency
Systems Audits	QA Department or designee	Annual per lab section
Data Audits	QA Department	5% of all report packages
Spot Assessment	QA Department or designee	As needed to monitor specific issues
Proficiency Testing	Coordinated by QA Dept.	Two samples per year per program as required by NELAC

Note that some programs, e.g., AFCEE, require data audits conducted by QA at a higher frequency.

9.4.2 Systems Audits

Facility systems audits are comprehensive technical and systems evaluations covering each operational and support area at least once per year. Generally, a rotating schedule is established throughout the year to ensure adequate coverage of all areas. This schedule can change as situations in the lab warrant. The objectives and schedule of the

audit are communicated to the lab groups being assessed in advance of the audit. At the completion of the audit, a debriefing is held to outline the findings, including identification of positive performance, to discuss areas of deficiencies, and to answer questions. The audit report issued by the QA Manager within 21 calendar days of the audit. The audit report is addressed to the area supervisor and/or manager, and copied to the General Manager and Laboratory Director. Written audit responses are required within 21 calendar days of the date of the audit report. The audit response from the lab areas must follow the format of the original audit report, and is sent from the respondents to all individuals copied on the audit report. Where a corrective action requires longer than 21 days to complete, the target date for the corrective action is stated and evidence of corrective action is submitted to the QA department in the agreed upon time frame.

9.4.3 Data Audits

Data audits are routinely performed and documented to ensure that project records meet project requirements as described in method SOPs, project plans, or other documented requirements. The data audit is used to identify any lab errors that may have occurred. Significant issues found in the course of the audit are brought to the attention of appropriate personnel for clarification, and overseeing correction of final reports if necessary. QA staff are required to perform data audits on 5% of report packages, or more as required by individual national programs. Data audits include spot-checking manual integrations to determine if they are appropriate and documented according to policy QA-011. Errors found in client project reports are revised and the revision sent to the client (also see Section 8.9.5).

9.4.4 Spot Assessments

Spot assessments, equivalent to special audits in the STL QMP, are conducted on as needed basis, generally as a follow up to specific issues such as client complaints, validator concerns, corrective actions, control chart or NCM trends, proficiency testing results, data audits, or external audit issues. Spot assessments are focused on a specific issue. The frequency, report format, distribution, and timeframes are tailored to address the nature of the issue.

9.4.5 Proficiency Testing

Proficiency testing samples (PTs) are analyzed to verify the ability of the laboratory to correctly identify and quantitate compounds in PT samples. PT samples may be supplied internally or externally as single-blind or double-blind samples. They can be used to assess if a deficiency has been corrected, they can be used to document the proficiency of the analyst perform the analysis, or they can be used to assess the overall performance of an analytical method.

PT samples are handled and tested in the same manner as environmental samples - it is not acceptable to run multiple replicates that would not otherwise be performed, it is not acceptable to average multiple results, and PT results cannot be shared among labs in advance of the close of the study. PT test sample data is archived using the same requirements as for project and raw data record retention.

9.4.5.1 External PT Samples

STL Pittsburgh participates in a number of PT studies, as shown in Table 9.4-1. The primary one being the NELAC PT program, which involves a minimum of two PT rounds each year for NELAC field of testing for which the lab is maintaining certification. In addition, under the 12/99 SDWA requirements, the laboratory also analyzes annually a PT sample for each drinking water method, where more than one method is used for a given analyte.

9.4.5.2 Internal PT Samples

Each STL facility performing chemical analyses also participates in a double-blind performance evaluation annually. An external vendor is contracted to submit double blind samples to the STL labs. Both the level of customer service and the accuracy of the test results is assessed objectively by the external contractor. The PT contractor provides a detailed report to the Corporate QA Manager and to each of the STL facilities.

9.5 External Audits

STL Pittsburgh is regularly audited by clients and external regulatory authorities. STL is available for these audits, and makes every effort to provide the auditors with the personnel, documentation and assistance they require. STL recommends that all audits be scheduled with the QA department so that all necessary personnel are available on the day of the audit. All deficiencies reported to the laboratory must be responded to within the time frame specified by the auditors. It is the responsibility of the QA Manger to coordinate the response to the audit report. The development and implementation of the corrective actions is the responsibility of the operations management of the affected areas. All responses must be approved by the Laboratory Director or Operations Manger prior to submitting the final response. It is the responsibility of the QA Manager to verify implementation of the corrective actions and inform the responsible manager of the closure of all deficiencies from the audit.

9.6 Management Reviews

9.6.1 Quality Reports to Management

A monthly QA report is prepared by the QA Manager and forwarded to the Laboratory Director, the General Manager, and the Corporate QA Manager. The

reports include metrics (i.e., frequency and number of revised reports, frequency and number of client complaints) to assess the effectiveness of the Quality System. The contents of the monthly report include:

- Audits
  Results of internal systems audits performed
  Results of external systems audits hosted
  Data audits performed, percent of total packages per month plus any issues
- Revised Reports / Client Complaints
  Frequency of revised reports
  Total number of client complaints, issues, and resolution
- Certification / Parameter Changes
- Proficiency Testing
  Score for each PT as a percentage of maximum score
  Note repeat failures and/or significant problems
- Miscellaneous QA and Operational Issues
  Narrative outling improvements, regulatory compliance issues, general concerns, and assistance required from management

This information is compiled by the Corporate QA Manager together with similar information from and about other STL laboratories, which is then presented in a report to the STL Chief Operating Officer.

9.6.2 Management Review of QA Systems

The Laboratory Director will conduct annual evaluations the status of the quality systems in the laboratory to review their suitability and effectiveness, and to introduce necessary changes or improvements. The evaluation shall consider:

- The suitability of policies and procedures
- Reports from managerial and supervisory personnel
- The outcome of recent internal audits
- Corrective and preventative actions
- Assessments by external bodies
- The results of interlaboratory comparisons and proficiency tests
- Status of QA documents
- Reviews of QA related requirements in RFPs, SOWs, SAPs, and QAPjPs
- Changes in the volume and type of work and the effects on QA systems
- Client feedback
- Complaints
- Quality control activities
- Resources and staff training

QAMP

Quality Assurance Management Plan

QUALITY MANAGEMENT PLAN
Revision: 4

January 2001

Approved by:

President: _____ Date: __1-24-01__
Rachel Brydon Janetta

Chief Operating Officer: _____ Date: __1-24-01__
Dr. Keith C. Wheatstone

General Manager,
Operational and Technical
Services: _____ Date: __1-24-01__
Dr. James W. Andrews

Quality Assurance Director: _____ Date: __1-24-01__
Deborah A. Loring

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1. Introduction, Purpose, and Scope

1.1. Severn Trent Laboratories (STL) Overview

STL is a part of Severn Trent Services Inc. (STS), a major group of U.S. based companies with 5,000 employees throughout the U.S., Europe and Asia. Both companies are owned by Severn Trent Plc., a British water, waste and utility services company, one of the top publicly traded companies in the United Kingdom, employing some 13,500 people.

STL offers a broad range of environmental testing services provided by over two thousand professionals in the US. STL's testing capabilities include chemical, physical, and biological analyses of a variety of matrices, including aqueous, solid, drinking water, waste, tissue, air and saline/estuarine samples. Specialty capabilities include dioxin and furan analysis, air toxics, radiological testing, geotechnical testing, tissue preparation and analysis, aquatic toxicology, asbestos analysis, microscopy services, High Resolution Mass Spectrometry (HRMS), Inductively Coupled Plasma/MS (ICP/MS), Liquid Chromatography/MS (LC/MS), and on-site technologies including mobile laboratories. STL facility locations and contact information are outlined in Table 1.

1.2. Quality Assurance Policy

It is STL's policy to:

- provide high quality, consistent, and objective environmental testing services that meet all federal, state, and municipal regulatory requirements.
- generate data that are scientifically sound, legally defensible, meet project objectives, and are appropriate for their intended use.
- provide STL clients with the highest level of professionalism and the best service practices in the industry.
- build continuous improvement mechanisms into all laboratory, administrative, and managerial activities.
- maintain a working environment that fosters open communication with both clients and staff.

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Table 1 STL Facility Locations

STL Austin
14046 Summit Drive
Suite 111
Austin, TX 78728
Phone: 512-244-0855
Fax: 512-244-0160

STL Baltimore
19 Loveton Circle
Sparks, MD 21152
Phone: 410-771-4920
Fax: 410-771-4407

STL Billerica
149 Rangeway Road
N. Billerica, MA 01862
Phone: 978-667-1400
Fax: 978-667-7871

STL Buffalo
10 Hazelwood Drive
Suite 106
Amherst, NY 14228
Phone: 716-691-2600
Fax: 716-691-7991

STL Burlington
208 South Park Drive
Suite 1
Colchester, VT 05446
Phone: 802-655-1203
Fax: 802-655-1248

STL Connecticut
128 Long Hill Cross Road
Shelton, CT 06484
Phone: 203-929-8140
Fax: 203-929-8142

STL Chicago
2417 Bond Street
University Park, IL 60466
Phone: 708-534-5200
Fax: 708-534-5211

STL ChromaLab
1220 Quarry Lane
Pleasanton, CA 94566-4756
Phone: 925-484-1919
Fax: 925-484-1096

STL Corpus Christi
1733 N. Padre Island Drive
Corpus Christi, TX 78408
Phone: 361-289-2673
Fax: 361-289-2471

STL Denver
4955 Yarrow Street
Arvada, CO 80002
Phone: 303-421-6611
Fax: 303-431-7171

STL Edison
777 New Durham Road
Edison, NJ 08817
Phone: 732-549-3900
Fax: 732-549-3679

STL Houston
6310 Rothway Drive
Suite 130
Houston, TX 77040
Phone: 713-690-4444
Fax: 713-690-5646

STL Knoxville
5815 Middlebrook Pike
Knoxville, TN 37921
Phone: 865-291-3000
Fax: 865-584-4315

STL Los Angeles
1721 South Grand Avenue
Santa Ana, CA 92705
Phone: 714-258-8610
Fax: 714-258-0921

STL Miami
10200 USA Today Way
Miramar, FL 33025
Phone: 954-431-4550
Fax: 954-431-1959

STL Mobile
900 Lakeside Drive
Mobile, AL 36693
Phone: 334-666-6633
Fax: 334-666-6696

STL Newburgh
315 Fullerton Avenue
Newburgh, NY 12550
Phone: 845-562-0890
Fax: 845-562-0841

STL North Canton
4101 Shuffel Drive NW
North Canton, OH 44720
Phone: 330-497-9396
Fax: 330-497-0772

STL On-Site Technology
Westfield Executive Park
53 Southampton Road
Westfield, MA 01085
Phone: 413-572-4000
Fax: 413-572-3707

STL Pensacola
3355 McLemore Drive
Pensacola, FL 32514
Phone: 850-474-1001
Fax: 850-478-2671

STL Pittsburgh
450 William Pitt Way
Building 6
Pittsburgh, PA 15238
Phone: 412-820-8380
Fax: 412-820-2080

STL Richland
2800 George Washington Way
Richland, WA 99352
Phone: 509-375-3131
Fax: 509-375-5590

STL Sacramento
880 Riverside Parkway
West Sacramento, CA 95605
Phone: 916-373-5600
Fax: 916-372-1059

STL St. Louis
13715 Rider Trail North
Earth City, MO 63045
Phone: 314-298-8566
Fax: 314-298-8757

STL Savannah
5102 LaRoche Avenue
Savannah, GA 31404
Phone: 912-354-7858
Fax: 912-351-3673

STL Tallahassee
2846 Industrial Plaza Dr.
Tallahassee, FL 32301
Phone: 850-878-3994
Fax: 850-878-9504

STL Tampa East
5910 H Breckenridge Pkwy.
Tampa, FL 33610
Phone: 813-621-0784
Fax: 813-623-6021

STL Tampa West
6712 Benjamin Road
Suite 100
Tampa, FL 33634
Phone: 813-885-7427
Fax: 813-885-7049

STL Valparaiso
2400 Cumberland Drive
Valparaiso, IN 46383
Phone: 219-464-2389
Fax: 219-462-2953

STL Westfield
Westfield Executive Park
53 Southampton Road
Westfield, MA 01085
Phone: 413-572-4000
Fax: 413-572-3707

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1.3. Management Commitment to Quality Assurance

STL management is committed to providing the highest quality data and the best service in the environmental testing industry. To ensure that the data produced and reported by STL meet the requirements of its clients and comply with the letter and spirit of municipal, state and federal regulations, STL maintains a Quality System that is clear, effective, well communicated, and supported at all levels in the company.

STL Mission Statement
We enable our customers to create safe and environmentally favorable policies and practices, by leading the market in scientific and consultancy services. We provide this support within a customer service framework that sets the standard to which others aspire. This is achieved by people whose professionalism and development is valued as the key to success and through continued investments in science and technology.

1.4. Purpose

The purpose of the Quality Management Plan (QMP) is to describe the STL Quality System and to outline how that system enables all employees of STL to meet the Quality Assurance (QA) policy. The QMP also describes specific QA activities and requirements and prescribes their frequencies. Roles and responsibilities of management and laboratory staff in support of the Quality System are also defined in the QMP.

1.5. Scope

The requirements set forth in this document are applicable to all STL facilities. Where the document uses the terms “must” and “shall”, this denotes required activities. Where a practice is described, this denotes guidelines as to how those activities are generally performed.

Each STL facility has the responsibility and authority to operate in compliance with regulatory requirements of the jurisdiction in which the work is performed. Where this QMP conflicts with those regulatory requirements, the regulatory requirements of the jurisdiction shall hold primacy. The facility’s Laboratory Quality Manual (LQM) shall take precedence over the QMP in those cases. Secondarily, each STL facility has the responsibility and authority to operate in compliance with documented client requirements, where they do not conflict with regulatory requirements. STL shall not enter any client agreements that conflict with regulatory requirements in the jurisdiction

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in which the work is performed. Where documented client agreements conflict with this QMP, but meet the regulatory requirements of the jurisdiction in which the work is performed, the client agreements shall supercede requirements in this QMP.

STL operates under the regulations and guidelines of the following federal programs:

Air Force Center for Environmental Excellence (AFCEE)
US Army Corp of Engineers, Hazardous, Toxic and Radioactive Waste (USACE HTRW)
Clean Air Act (CAA)
Clean Water Act (CWA)
Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA)
Department of Energy (DOE)
Marine Protection, Research, and Sanctuaries Act (MPRSA)
Navy Facilities Engineering Service Center (NFESC)
National Pollution, Discharge, and Elimination System (NPDES)
Nuclear Regulatory Commission (NRC)
Occupational Safety and Health Administration (OSHA)
Resource Conservation and Recovery Act (RCRA)
Safe Drinking Water Act (SDWA)
Toxic Substances Control Act (TSCA)

STL also provides services under various state and local municipal guidelines. A current Table of Analytical Services and list of certifications for each facility is provided in STL's Corporate Statement of Qualifications.

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2. References

The following references were used in preparation of this document and as the basis of the STL Quality System:

EPA Guidance for the Preparation of Standard Operating Procedures (SOPs) for Quality Related Documents, US EPA, Office of Research and Development, EPA QA/G-6, November 1995.

EPA Requirements For Quality Management Plans, EPA QA/R-2, US EPA Management Staff, Washington, DC, Draft Interim Final, August 1994.

EPA Requirements for Quality Assurance Project Plans, EPA QA/R-5, US EPA Quality Staff, Washington, DC, Interim Final, November 1999.

EPA Quality Manual for Environmental Programs, 5360, US EPA Office of Research and Development, National Center for Environmental Research and Quality Assurance, Quality Assurance Division, July 1998.

General Requirements for the Competence of Testing and Calibration Laboratories, ISO/IEC 17025, December 1999.

Good Automated Laboratory Practices, EPA 2185, 1995.

Quality Assurance Project Plan, HQ Air Force Center for Environmental Excellence, Version 3.0, March 1998.

National Environmental Laboratory Accreditation Conference, Constitution, Bylaws, and Standards, EPA600/R-98/151, US EPA Office of Research and Development, July 1999.

Navy Installation Restoration Laboratory Quality Assurance Guide, Interim Guidance Document, Naval Facilities Engineering Service Center, February 1996.

Navy Installation Restoration Chemical Data Quality Manual, Navy IR CDQM, June 1998.

Quality Systems Manual for Environmental Laboratories, Department of Defense, Version 1, October 2000.

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Shell for Analytical Chemistry Requirements, US Army Corps of Engineers, December 1998.

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3. Terms and Definitions

Accuracy: the degree of agreement between a measurement and true or expected value, or between the average of a number of measurements and the true or expected value.

Audit: a systematic evaluation to determine the conformance to specifications of an operational function or activity.

Batch: environmental samples, which are prepared and/or analyzed together with the same process, using the same lot(s) of reagents. A preparation batch is composed of one to 20 environmental samples of a similar matrix, meeting the above mentioned criteria. Where no preparation method exists (example, volatile organics, water) the batch is defined as environmental samples that are analyzed together with the same process and personnel, using the same lots of reagents, not to exceed 20 environmental samples. An analytical batch is composed of prepared environmental samples, extracts, digestates or concentrates that are analyzed together as a group. An analytical batch can include prepared samples originating from various environmental matrices and can exceed 20 samples.

Chain of Custody (COC): an unbroken trail of accountability that ensures the physical security of samples, data and records.

Clean Air Act: legislation in 42 U.S.C. 7401 et seq., Public Law 91-604, 84 Stat. 1676 Pub. L. 95-95, 91 Stat., 685 and Pub. L. 95-190, 91 Stat., 1399, as amended.

Comprehensive Environmental Response, Compensation and Liability Act (CERCLA/Superfund): legislation (42 U.S.C. 9601-9675 et seq., as amended by the Superfund Amendments and reauthorization Act of 1986 (SARA), 42 U.S.C. 9601et seq.

Compromised Sample: a sample received in a condition that jeopardizes the integrity of the results. See Section 4.7.1 for a description of these conditions.

Confidential Business Information (CBI): information that an organization designates as having the potential of providing a competitor with inappropriate insight into its management, operation or products.

Confirmation: verification of the presence of a component using an additional analytical technique. These may include second column confirmation, alternate wavelength,

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derivatization, mass spectral interpretation, alternative detectors, or additional cleanup procedures.

Corrective Action: action taken to eliminate the causes of an existing non-conformance, defect or other undesirable situation in order to prevent recurrence.

Data Audit: a qualitative and quantitative evaluation of the documentation and procedures associated with environmental measurements to verify that the resulting data are of acceptable quality.

Demonstration of Capability (DOC): procedure to establish the ability to generate acceptable accuracy and precision.

Equipment Blank: a portion of the final rinse water used after decontamination of field equipment; also referred to as Rinsate Blank and Equipment Rinsate.

Document Control: the act of ensuring that documents (electronic or hardcopy and revisions thereto) are proposed, reviewed for accuracy, approved for release by authorized personnel, distributed properly and controlled to ensure use of the correct version at the location where the prescribed activity is performed.

Federal Insecticide, Fungicide and Rodenticide Act (FIFRA): legislation under 7 U.S.C. 135 et seq., as amended.

Federal Water Pollution Control Act (Clean Water Act, CWA): legislation under 33 U.S.C. 1251 et seq., Public Law 92-50086 Stat. 816.

Field Blank: a blank matrix brought to the field and exposed to field environmental conditions.

Field of Testing (FOT): a field of testing is based on NELAC's categorization of accreditation based on program, matrix, analyte.

Good Laboratory Practices (GLP): formal regulations for performing basic laboratory operations outlined in 40 CFR Part 160 and 40 CFR Part 729 and required for activities performed under FIFRA and TSCA.

Holding Time: the maximum time that a sample may be held before preparation and/or analysis as promulgated by regulation or as specified in a test method.

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Instrument Blank: a blank matrix that is the same as the processed sample matrix (i.e. extract, digestate, condensate) and introduced onto the instrument for analysis.

Internal Chain of Custody: an unbroken trail of accountability that ensures the physical security of samples, data and records. Internal Chain of Custody refers to additional documentation procedures implemented within the laboratory that includes special sample storage requirements, and documentation of all signatures and/or initials, dates, and times of personnel handling specific samples or sample aliquots.

Instrument Detection Limit (IDL): the minimum amount of a substance that can be measured with a specified degree of confidence that the amount is greater than zero using a specific instrument. The IDL is associated with the instrumental portion of a specific method only, and sample preparation steps are not considered in its derivation. The IDL is a statistical estimation at a specified confidence interval of the concentration at which the relative uncertainty is ±100%. The IDL represents a range where qualitative detection occurs on a specific instrument. Quantitative results are not produced in this range.

Laboratory Control Sample (LCS): a blank matrix spiked with a known amount of analyte(s), processed simultaneously with, and under the same conditions as, samples through all steps of the analytical procedure.

Laboratory Quality Manual (LQM): a document stating the quality policy, quality system and quality practices of the laboratory. The LQM may include by reference other documentation relating to the laboratory's quality system.

Limit of Detection (LOD): the minimum amount of a substance that an analytical process can reliably detect.

Matrix: the substrate of a test sample. Common matrix descriptions are defined in Table 2.

Matrix Duplicate (MD): duplicate aliquot of a sample processed and analyzed independently; under the same laboratory conditions; also referred to as Sample Duplicate; Laboratory Duplicate.

Matrix Spike (MS): field sample to which a known amount of target analyte(s) is added.

Matrix Spike Duplicate (MSD): a replicate matrix spike.

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Table 2 Matrix Descriptions

Matrix	Description
Air	Air samples as analyzed directly or as adsorbed into a solution or absorption matrix and desorbed.
Aqueous	Aqueous sample excluded from the definition of Drinking Water or Saline/Estuarine source. Includes surface water, groundwater and effluents.
Drinking Water	Aqueous sample that has been designated a potable water source.
Saline	Aqueous sample from an ocean or estuary, or other salt-water source such as the Great Salt Lake.
Liquid	Liquid with <15% settleable solids.
Solid	Soil, sediment, sludge or other matrices with ≥15% settleable solids.
Waste	A product or by-product of an industrial process that results in a matrix not previously defined.
Tissue	Sample of a biological origin such as fish tissue, shellfish, or plant material. Such samples shall be grouped according to origin.

Method Blank: a blank matrix processed simultaneously with, and under the same conditions as, samples through all steps of the analytical procedure.

Method Detection Limit (MDL): the minimum amount of a substance that can be measured with a specified degree of confidence that the amount is greater than zero using a specific measurement system. The MDL is a statistical estimation at a specified confidence interval of the concentration at which the relative uncertainty is ±100%. The MDL represents a range where qualitative detection occurs using a specific method. Quantitative results are not produced in this range.

Non-conformance: an indication, judgement, or state of not having met the requirements of the relevant specifications, contract, or regulation.

Precision: an estimate of variability. It is an estimate of agreement among individual measurements of the same physical or chemical property, under prescribed similar conditions.

Preservation: refrigeration and/or reagents added at the time of sample collection to maintain the chemical, physical and/or biological integrity of the sample.

Proficiency Testing: determination of the laboratory calibration or testing performance by means of inter-laboratory comparisons.

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Proficiency Test (PT) Sample: a sample, the composition of which is unknown to the analyst, that is provided to test whether the analyst/laboratory can produce analytical results within specified performance limits. Also referred to as Performance Evaluation (PE) Sample.

Proprietary: belonging to a private person or company.

Quality Assurance (QA): an integrated system of activities involving planning, quality control, quality assessment, reporting and quality improvement to ensure that a product or service meets defined standards of quality with a stated level of confidence.

Quality Assurance Project Plan (QAPP): a formal document describing the detailed quality control procedures by which the quality requirements defined for the data and decisions pertaining to a specific project are to be achieved.

Quality Control (QC): the overall system of technical activities, the purpose of which is to measure and control the quality of a product or service.

Quality Control Sample: a control sample, generated at the laboratory or in the field, or obtained from an independent source, used to monitor a specific element in the sampling and/or testing process.

Quality Management Plan (QMP): a formal document describing the management policies, objectives, principles, organizational authority, responsibilities, accountability, and implementation plan of an agency, organization or laboratory to ensure the quality of its product and the utility of the product to its users.

Quality System: a structured and documented management system describing the policies, objectives, principles, organizational authority, responsibilities, accountability, and implementation plan of an organization for ensuring quality in its work processes, products (items), and services. The quality system provides the framework for planning, implementing, and assessing work performed by the organization and for carrying out required QA/QC.

Quantitation Limit (QL): the minimum amount of a substance that can be quantitatively measured with a specified degree of confidence and within the accuracy and precision guidelines of a specific measurement system. The QL can be based on the MDL, and is generally calculated as 3-5 times the MDL, however, there are analytical techniques and methods where this relationship is not applicable. Also referred to as Practical

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Quantitation Level (PQL), Estimated Quantitation Level (EQL), Limit of Quantitation (LOQ).

Raw Data: any original information from a measurement activity or study recorded in laboratory notebooks, worksheets, records, memoranda, notes, or exact copies thereof and that are necessary for the reconstruction and evaluation of the report of the activity or study. Raw data may include photography, microfilm or microfiche copies, computer printouts, magnetic/optical media, including dictated observations, and recorded data from automated instruments. Reports specifying inclusion of “raw data” do not need all of the above included, but sufficient information to create the reported data.

Record Retention: the systematic collection, indexing and storing of documented information under secure conditions.

Reference Standard: a standard, generally of the highest metrological quality available at a given location, from which measurements made at that location are derived.

Reporting Limit (RL): The level to which data is reported for a specific test method and/or sample. The RL is generally related to the QL. The RL must be minimally at or above the MDL.

Resource Conservation and Recovery Act (RCRA): legislation under 42 USC 321 et seq. (1976).

Safe Drinking Water Act (SDWA): legislation under 42 USC 300f et seq. (1974), (Public Law 93-523).

Sampling and Analysis Plan (SAP): a formal document describing the detailed sampling and analysis procedures for a specific project.

Selectivity: the capability of a measurement system to respond to a target substance or constituent.

Sensitivity: the difference in the amount or concentration of a substance that corresponds to the smallest difference in a response in a measurement system using a certain probability level.

Spike: a known amount of an analyte added to a blank, sample or sub-sample.

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Standard Operating Procedure (SOP): a written document which details the method of an operation, analysis or action whose techniques and procedures are thoroughly prescribed and which is accepted as the method for performing certain routine or repetitive tasks.

Storage Blank: a blank matrix stored with field samples of a similar matrix.

Systems Audit: a thorough, systematic, on-site, qualitative review of the facilities, equipment, personnel, training, procedures, record keeping, data validation, data management, and reporting aspects of a total measurement system.

Test Method: defined technical procedure for performing a test.

Toxic Substances Control Act (TSCA): legislation under 15 USC 2601 et seq., (1976).

Traceability: the property of a result of a measurement that can be related to appropriate international or national standards through an unbroken chain of comparisons.

Trip Blank: a blank matrix placed in a sealed container at the laboratory that is shipped, held unopened in the field, and returned to the laboratory in the shipping container with the field samples.

Verification: confirmation by examination and provision of evidence against specified requirements.

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4. Management Requirements

4.1. Organization and Management

4.1.1. Organization

STL's organizational structure is presented in Figure 1. Corporate employees are located at various STL facilities as outlined in the organizational structure. A QA Manager shall be designated at each STL facility. The facility QA Manager has an indirect reporting relationship to the QA Director.

4.1.2. Roles and Responsibilities

President

The President of STL, Inc. has overall management responsibility and authority for Severn Trent's laboratory division, including responsibility for budgeting, resource allocation, long term planning, sales, marketing, and final approval on all management and administrative policies and management plans. The President authorizes the QMP and as such, sets the standards for the Quality System.

Chief Operating Officer (COO)

The COO is responsible for daily management of all STL facilities. The COO's responsibilities include allocation of personnel and resources, long term planning, and development of technical policies and management plans. The COO authorizes the QMP and is responsible for ensuring that business and technical operations are conducted in accordance with its requirements.

General Manager, Operational and Technical Services

The General Manager of Operational and Technical Services is responsible for the functional areas of Quality Assurance, Information Technology, Environmental Health and Safety, and Technical Services. The GM's responsibilities include authorization of Manuals, Policies and Procedures, providing support and direction to the Managers of these areas, and supporting the COO in decisions regarding long term planning, resource allocation, and capital expenditures.

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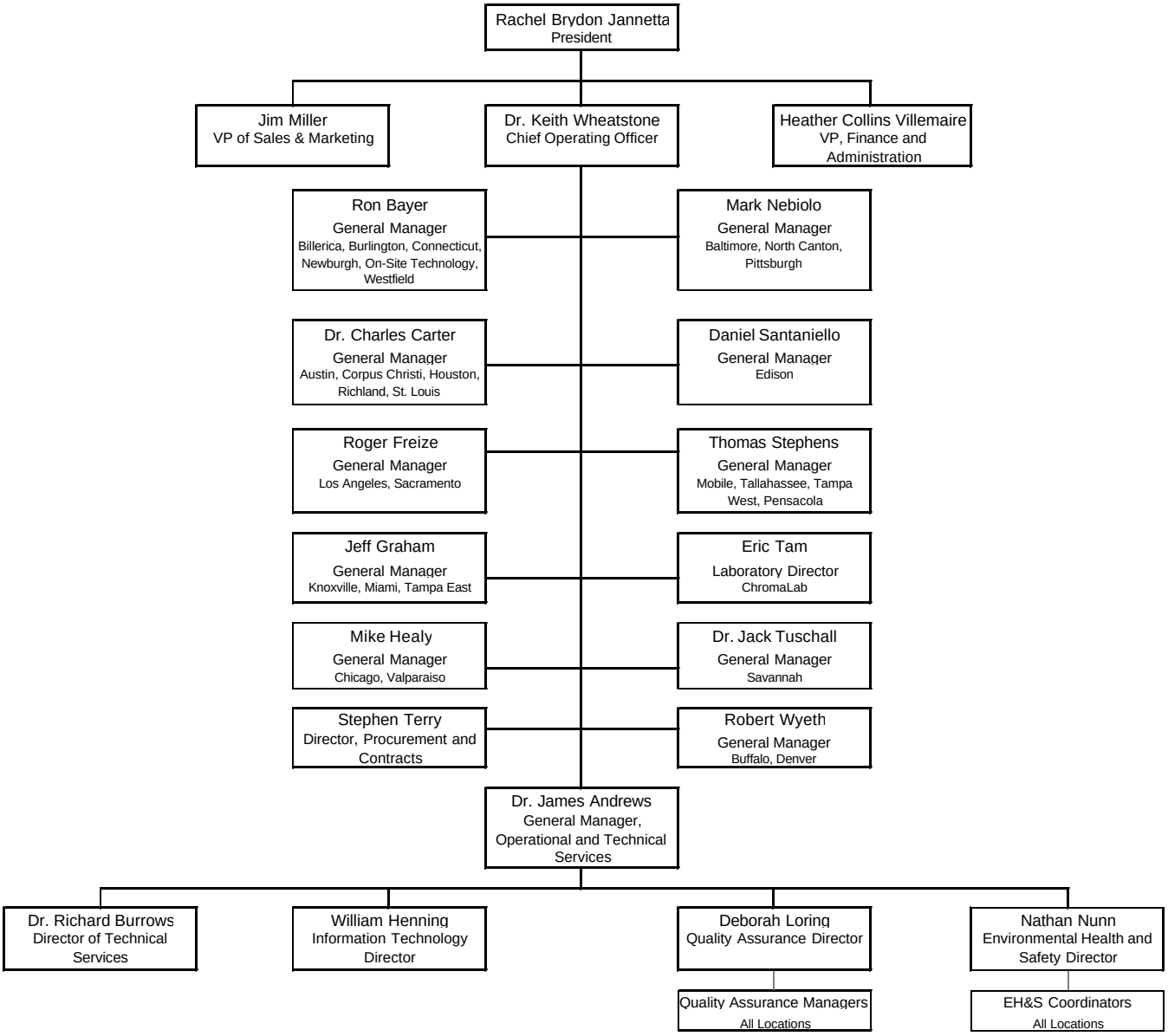
Figure 1 STL Organizational Chart



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QA Director

The QA Director is responsible for establishing, implementing and communicating STL's Quality System. The QA Director monitors compliance with the QMP, provides regulatory and technical updates to the STL facilities, assists in development of management plans and technical policies to be approved by the COO, and coordinates employee training within STL. The QA Director is available to any employee in STL to resolve data quality or ethical issues. The QA Director is independent of operational functions.

Director of Technical Services

The Director of Technical Services is responsible for establishing, implementing and communicating STL's Technical Policies, Standard Operating Procedures, and Manuals. Other responsibilities include conducting technical assessments as required, acting as a technical resource in national contracts review, coordinating new technologies, establishing best practices throughout STL, advising STL staff on technology advances, innovations, and applications, and organizing and running STL's technical committee.

Information Technology (IT) Director

The IT Director is responsible for establishing, implementing and communicating STL's IT Policies, Standard Operating Procedures, and Manuals. Other responsibilities include coordinating new technologies, development of electronic communication tools such as STL's intranet and internet sites, ensuring data security and documentation of software, ensuring compliance with Good Automated Laboratory Practices (GALP), and assistance in establishing, updating, and maintaining Laboratory Information Management Systems (LIMS) at the various STL facilities.

Environmental Health and Safety (EH&S) Director

The EH&S Director is responsible for establishing, implementing and communicating STL's Environmental Health and Safety Policies, Standard Operating Procedures, and Manuals. Other responsibilities include conducting EH&S assessments as required, acting as a resource for all STL facilities to ensure EH&S compliance, coordinating safety committees, providing guidance to the EH&S Coordinator at various STL facilities, and advising STL facilities on new EH&S regulations.

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General Manager (GM)

The GM is directly responsible for the daily operations of one or more operating facilities within STL. The GM's responsibilities include allocation of personnel and resources, long term planning, setting goals, and achieving the financial, business, and quality objectives of STL. The GM ensures timely compliance with corporate management directives, policies, and management systems reviews.

Laboratory Director

The Laboratory Director oversees the daily operations of the laboratory. The Laboratory Director's responsibilities include supervision of staff, setting goals and objectives for both the business and the employees, and achieving the financial, business, technical and quality objectives of the facility. The Laboratory Director ensures timely compliance with audits and corrective actions, and is responsible for maintaining a working environment which encourages open, constructive problem solving and continuous improvement.

QA Manager

The QA Manager is responsible for ensuring that the laboratory's quality system and LQM meet the requirements set forth in the QMP, providing Quality Systems training to all new personnel, maintaining a Laboratory Quality Manual (LQM), and performing systems, data, special, and external audits. The QA Manager oversees the maintenance of QC records, maintains certifications, submits monthly QA Reports, and assists in reviewing new work as needed. The QA Manager shall have the final authority to accept or reject data, and to stop work in progress in the event that procedures or practices compromise the validity and integrity of analytical data. The QA Manager is available to any employee at the facility to resolve data quality or ethical issues. The QA Manager shall be independent of laboratory operations.

Technical Director

The Technical Director(s) of a laboratory has overall responsibility for a defined portion of the technical operations of the laboratory, and may or may not be the Laboratory Director. The Technical Director solves day to day technical issues, provides technical training and guidance to staff, project managers, and clients,

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investigates technical issues identified by QA, and directs evaluation of new methods.

Each LQM has further descriptions of roles and responsibilities at the facility level.

4.2. Quality System

4.2.1. Objectives of STL Quality System

The goal of the STL Quality System is to ensure that business and technical operations are conducted with the highest standards of professionalism in the industry.

To achieve this goal, it is necessary to provide STL clients with not only scientifically sound, well documented, and regulatory compliant data, but also to ensure that STL provides the highest quality service available in the industry. A well-structured and well-communicated Quality System is essential in meeting this goal. STL's Quality System is designed to minimize systematic error, encourage constructive, documented problem solving, and provide a framework for continuous improvement within the organization.

The QMP is the basis and outline for STL's Quality System and contains requirements and general guidelines under which all STL facilities shall conduct their operations.

4.2.2. Laboratory Quality Manual (LQM)

Each STL facility shall have an LQM that further describes the specific QA program at the laboratory.

Each STL facility's LQM shall address:

1. Table of Contents, lists of references and glossaries, and appendices.
2. Quality policy statement, including objectives and commitments, by facility management.
3. Organization and management structure of the laboratory, its place in the STL organization and relevant organizational charts.
4. Relationship between management, technical operations, support services and the quality system.

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5. Record retention procedure.
6. Document control procedure.
7. Job descriptions of essential staff and reference to job descriptions of other staff.
8. Identification of the laboratory's approved signatories.
9. Procedure for achieving traceability of measurements.
10. List of test methods under which the laboratory performs its testing.
11. Procedure for reviewing new work.
12. Reference to the calibration and/or verification test procedures used.
13. Sample handling procedure.
14. Reference to the major equipment, reference standards, facilities and services used by the laboratory in conducting tests.
15. Reference to procedures for calibration, verification and maintenance of equipment.
16. Reference to verification practices including inter-laboratory comparisons, proficiency testing programs, use of reference materials and internal QC practices.
17. Procedures for feedback and corrective action when testing discrepancies are detected, or departures from policies and procedures occur.
18. Procedure for exceptionally permitting departures from documented policies and procedures or from standard specifications.
19. Procedure for handling client complaints.
20. Procedure for protecting client confidentiality and proprietary rights.
21. Procedure for audits and data review.
22. Procedure for establishing that personnel are adequately experienced and trained.
23. Reference to procedures for reporting analytical results.

4.3. Document Control

4.3.1. Document Type

The following documents, at a minimum, must be controlled at each STL Facility:

- Laboratory Quality Manual
- Standard Operating Procedures (SOP)
- Quality Management Plan

4.3.2. Document Control Procedure

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Security and control of documents are necessary to ensure that confidential information is not distributed and that all current copies of a given document are from the latest applicable revision. Unambiguous identification of a controlled document is maintained by identification of the following items in the document header: Document Name, Document Number, Revision Number, Effective Date, Number of Pages. Controlled documents are authorized by Management and/or the QA Department. Controlled documents are marked as such and records of their distribution are kept by the QA Department. Document control maybe achieved by either electronic or hardcopy distribution.

Controlled documents shall be available at all locations where the operational activity described in the document is performed.

4.3.3. Document Revision

Changes to documents occur when a procedural change warrants a revision of the document. When an approved revision of a controlled document is ready for distribution, obsolete copies of the document shall be replaced with the current version of the document. The previous revision of the controlled document must be archived by the QA Department.

4.3.4. Official Documents

The STL Corporate Operations staff issues Corporate Manuals, Standard Operating Procedures, and Policies. These are collectively termed “Official Documents” and encompass the Policies and Procedures that all STL facilities are required to employ. A detailed description of the procedure for issuing, authorizing, controlling, distributing, and archiving Official Documents is found in Corporate SOP S-Q-001.

4.4. Request, Tender, and Contract Review

4.4.1. Contract Review

For many environmental sampling and analysis programs, testing design is site or program specific and does not necessarily “fit” into a standard laboratory service or product. It is STL’s intent to provide both standard and customized environmental testing services to our clients. To ensure project success, technical staff shall perform a thorough review of technical and QC requirements contained

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in contracts. Contracts are reviewed for adequately defined requirements and STL's capability to meet those requirements.

Contract review shall include a review of the client's requirements in terms of compound lists, test methodology requested, sensitivity, accuracy, and precision requirements. The STL representative ensures that the laboratory's test methods are suitable to achieve these requirements and must ensure that the laboratory holds the appropriate certifications and approvals to perform the work. The review also includes the laboratory's capabilities in terms of turnaround time, capacity, and resources to provide the services requested, as well the laboratory's ability to provide the documentation, whether hardcopy or electronic. If the laboratory cannot provide all services but intends to subcontract such services, whether to another STL facility or to an outside firm, this must be documented and discussed with the client prior to contract approval.

All contracts entered into by STL shall be reviewed and approved by the appropriate personnel at the facility or facilities performing the work. Any contract requirement or amendment to a contract communicated to STL verbally must be documented and confirmed with the client in writing. Any discrepancy between the client's requirements and STL's capability to meet those requirements is resolved in writing before acceptance of the contract. Contract amendments, initiated by the client and/or STL, are documented in writing for the benefit of both the client and STL.

All contracts, Quality Assurance Project Plans (QAPPs), Sampling and Analysis Plans (SAPs), contract amendments, and documented communications become part of the permanent project record as defined in Section 4.12.1.

4.4.2. Project Specific Quality Planning

Communication of contract specific technical and QC criteria is an essential activity in ensuring the success of site specific testing programs. To achieve this goal, STL assigns a Project Manager (PM) to each client. The PM is the first point of contact for the client. It is the PM's responsibility to ensure that project specific technical and QC requirements are effectively communicated to the laboratory personnel before and during the project.

Each STL facility shall have established procedures in order to ensure that communication is inclusive and effective. These include project memos, designation and meetings of project teams, and meetings between the laboratory

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staff and the client. STL has found it very effective to invite the client into this process. STL strongly encourages our clients to visit the laboratories and hold formal or informal sessions with employees in order to effectively communicate ongoing client needs as well as project specific details for customized testing programs.

4.4.3. Data Quality Objectives

Data Quality Objectives (DQO) are qualitative and quantitative statements used to ensure the generation of the type, quantity, and quality of environmental data that will be appropriate for the intended application. Typically, DQOs are identified before project initiation, during the development of QAPPs and SAPs. The analytical DQOs addressed in this section are precision, accuracy, representativeness, completeness, and comparability.

The components of analytical variability (uncertainty) can be estimated when QC samples of the right types and at the appropriate frequency are incorporated into measurement process at the analytical laboratory. STL incorporates numerous QC samples to obtain data for comparison with the analytical DQOs and to ensure that the measurement system is functioning properly. The QC samples and their applications, described in Section 5.8.2, are selected based on regulatory, method- or client-specific requirements. Analytical laboratory QC samples for inorganic, organic, and radionuclide analyses may include calibration blanks, instrument blanks, method blanks, LCS, calibration standards, MS, MSD, surrogate spikes, and yield monitors.

The DQOs discussed below ensure that data are gathered and presented in accordance with procedures appropriate for its intended use, that the data is of known and documented quality, and are able to withstand scientific and legal scrutiny.

Precision is an estimate of variability. It is an estimate of agreement among individual measurements of the same physical or chemical property, under prescribed similar conditions. Precision is expressed either as Relative Standard Deviation (RSD) for greater than two measurements or as Relative Percent Difference (RPD) for two measurements. Precision is determined, in part, by analyzing data from aggregate LCS results, MS, MSD, and MD. For radiochemical determinations, counting statistics can also provide an estimate of uncertainty.

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Precision also refers to the measurement of the variability associated with the entire process, from sampling to analysis. Total precision of the process can be determined by analysis of duplicate or replicate field samples and measures variability introduced by both the laboratory and field operations.

Accuracy is the degree of agreement between a measurement and the true or expected value, or between the average of a number of measurements and the true or expected value. It reflects the total error associated with a measurement.

Both random and systematic errors can affect accuracy. For chemical properties, accuracy is expressed either as a percent recovery (R) or as a percent bias (R - 100). Accuracy is determined, in part, by analyzing data from LCS, MS, and MSD. For radiochemical determinations, counting statistics can also provide an estimate of uncertainty.

Representativeness is the degree to which data accurately and precisely represent a characteristic of a population, a variation in a physical or chemical property at a sampling point, or an environmental condition. Data representativeness is primarily a function of sampling strategy; therefore, the sampling scheme must be designed to maximize representativeness. Representativeness also relates to ensuring that, through sample homogeneity, the sample analysis result is representative of the constituent concentration in the sample matrix. STL makes every effort to analyze an aliquot that is representative of the original sample, and to ensure the homogeneity of the sample before sub-sampling.

Completeness is defined as the percentage of measurements that are judged valid or useable. Factors negatively affecting completeness include the following: sample leakage or breakage in transit or during handling, loss of sample during laboratory analysis through accident or improper handling, improper documentation such that traceability is compromised, or sample result is rejected due to failure to conform to QC specifications. A completeness objective of greater than 90% of the data specified by the statement of work is the goal established for most projects.

Comparability is a measure of the confidence with which one data set can be compared to another. To ensure comparability, all laboratory analysts are required to use uniform procedures (e.g. SOPs) and a uniform set of units and calculations for analyzing and reporting environmental data.

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4.5. Subcontracting

Subcontracting must be arranged with the documented consent of the client, in a timely response which shall not be unreasonably refused. All QC guidelines specific to the client's analytical program are transmitted to the subcontractor and agreed upon before sending the samples to the subcontract facility. The originating laboratory shall obtain proof of certification from the subcontract facility, and retain in STL records. Where applicable, specific QC guidelines, QAPPs, and/or SAPs are transmitted to the subcontract laboratory. Samples are subcontracted under formal Chain of Custody (COC).

Subcontract laboratories may receive an on-site audit by a representative of STL's QA staff if it is deemed appropriate by the QA Manager. The audit involves a measure of compliance with the required test method, QC requirements, as well as any special client requirements. The originating laboratory may also perform a paper audit of the subcontractor, which would entail reviewing the LQM, the last two PT studies, and a copy of any recent regulatory audits with the laboratory's responses.

Intra-company subcontracting may also occur between STL facilities. Intra-company subcontracting within STL must be arranged with the documented consent of the client, in a timely response which shall not be unreasonably refused. The originating laboratory is responsible for communicating all technical, quality, and deliverable requirements as well as other contract needs.

Project reports from both STL and external subcontractors are discussed in Section 5.9.4.

4.6. Purchasing Services and Supplies

Evaluation and selection of suppliers and vendors is done, in part, on the basis of the quality of their products, their ability to meet the demand for their products on a continuous and short term basis, the overall quality of their services, their past history, and competitive pricing. This is achieved through evaluation of objective evidence of quality furnished by the supplier, which can include certificates of analysis, recommendations, and proof of historical compliance with similar programs for other clients. To ensure that quality critical consumables and equipment conform to specified requirements, all purchases from specific vendors are approved by a member of the supervisory or management staff.

Chemical reagents, solvents, glassware, and general supplies are ordered as needed to maintain sufficient quantities on hand. Purchasing guidelines for equipment and reagents

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meet with the requirements of the specific method and testing procedures for which they are being purchased.

4.7. Service to the Client

4.7.1. Sample Acceptance Policy

Each STL facility shall maintain a sample acceptance policy that describes compromised sample receipt. Samples shall be considered "compromised" if the following conditions are observed upon sample receipt:

- Cooler and/or samples are received outside of temperature specification.
- Samples are received broken or leaking.
- Samples are received beyond holding time.
- Samples are received without appropriate preservative.
- Samples are received in inappropriate containers.
- COC does not match samples received.
- COC is not properly completed or not received.
- Breakage of any Custody Seal.
- Apparent tampering with cooler and/or samples.
- Headspace in volatiles samples.
- Seepage of extraneous water or materials into samples.
- Inadequate sample volume.
- Illegible, impermanent, or non-unique sample labeling.

When "compromised" samples are received, it must be documented in the project records and the client must be contacted for instructions. If the client decides to proceed with analysis, the project report shall clearly indicate any of the above conditions and the resolution.

4.7.2. Client Confidentiality and Proprietary Rights

Data and sample materials provided by the client or at the client's request, and the results obtained by STL, shall be held in confidence (unless such information is generally available to the public or is in the public domain or client has failed to pay STL for all services rendered or is otherwise in breach of the terms and conditions set forth in the STL and client contract) subject to any disclosure required by law or legal process. STL's reports, and the data and information provided therein, are for the exclusive use and benefit of client, and are not released to a third party without written consent from the client.

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4.8. Complaints

Client complaints shall be documented, communicated to management, and addressed promptly and thoroughly. Client complaints are documented by the employee receiving the complaint. The documentation can take the form of a corrective action report (as described in Section 4.10) or in a format specifically designed for that purpose. The Laboratory Director, PM, Customer Service Manager, and QA Manager are informed of all client complaints, and assist in resolving the complaint.

The nature of the complaint is identified, documented, and investigated, and an appropriate action is determined and taken. In cases where a client complaint indicates that an established policy or procedure was not followed, the QA department is required to conduct a special audit to assist in resolving the issue. A written confirmation, or letter to the client, outlining the issue and response taken is strongly recommended as part of the overall action taken.

The number and nature of client complaints shall be reported to the QA Director in the QA Monthly report submitted by each facility. The overall number of complaints received per facility is tracked and the appropriateness of the response to client complaints is assessed. Monitoring and addressing the overall level and nature of client complaints and the effectiveness of the solutions is part of the Management Systems Review.

4.9. Control of Non-conformances

Each STL facility shall have a procedure to control and document non-conformances. Non-conformances include any out of control occurrence. Non-conformances may relate to client specific requirements, procedural requirements, or equipment issues. All non-conformances in the laboratory are documented at the time of their occurrence.

All non-conformances that affect a sample and/or sample data become part of the affected project's permanent record. When appropriate, reanalysis is performed where QC data falls outside of specifications, or where data appears anomalous. If the reanalysis comes back within established tolerances, the results are approved. If the reanalysis is still outside tolerances, further reanalysis or consultation with the Supervisor, Manager, PM, Laboratory Director, or QA Manager for direction may be required. All records of reanalysis are kept with the project files.

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Where non-conformances specifically affect a client's sample and/or data, the client shall be informed and action must be taken. Action can take the form of reporting and flagging the data, and including a description of the non-conformance in the project narrative or cover letter.

4.10. Corrective Action

4.10.1. General

Each STL facility shall maintain an established, documented corrective action process. Each corrective action is thoroughly investigated, and the investigation, outcome of the investigation, action taken, and follow-up is documented. Corrective action reports are reviewed, approved, and maintained by the QA department.

4.10.2. Initiation

Any employee in STL shall be authorized to initiate a corrective action. The initial source of corrective action can also be external to STL (i.e. corrective action because of client complaint, regulatory audit, or proficiency test). When a problem that requires corrective action is identified, the following items are identified by the initiator on the corrective action report: the nature of the problem, the name of the initiator, and the date. If the problem affects a specific client project, the name of the client and laboratory project number is recorded, and the PM is informed immediately.

4.10.3. Cause Analysis

The corrective action process must be embarked upon as a joint, problem solving, constructive effort. Identification of systematic errors, or errors that are likely to occur repetitively due to a defect or weakness in a system, is particularly valuable in maintaining an environment of continuous improvement in laboratory operations.

When a corrective action report is initiated, the initiator works with the affected employee(s) and/or department(s) to identify the root cause of the problem. An essential part of the corrective action process is to identify whether the problem occurred due to a systematic or isolated error.

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If the initiator of the corrective action report is uncertain as to what would constitute appropriate corrective action or is unable to resolve the situation, the problem is identified to the Supervisor, Manager, Laboratory Director or the QA Manager who provides assistance in the corrective action process.

The root cause of the problem and associated cause analysis is documented on the corrective action form.

4.10.4. Corrective Action

Once the root cause of a problem is identified, the initiator and affected employee(s) and/or department(s) examine potential actions that will rectify the present problem to the extent possible, and prevent recurrence of future, similar occurrences. An appropriate corrective action is then recommended. The corrective action must be appropriate for the size and nature of the issue.

If the corrective action concerns a specific project related issue, the PM or Customer Service Manager approves the corrective action before its implementation.

Implementation of the corrective action and the date of implementation are documented on the corrective action report.

If a corrective action is related to a specific project report, included in the project file. An essential part of the corrective action process is communication and awareness of the problem, the cause, and the action taken to prevent future occurrences and/or rectify the immediate problem.

4.10.5. Monitoring Corrective Action

All corrective action reports are maintained by the QA Department. The QA department reviews all corrective actions and selects one or more of the more significant corrective actions for inclusion in the annual systems audit. The QA Department also may implement a special audit. The purpose of inclusion of the corrective action process in both routine and special audits is to monitor the implementation of the corrective action and to determine whether the action taken has been effective in overcoming the issue identified.

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4.11. Preventative Action

Each STL facility shall maintain an established, documented preventative action process. Preventative action is defined as noting and correcting a problem before it happens, because of a weakness in a system, method, or procedure. Preventative action includes analysis of the Quality System to detect, analyze, and eliminate potential causes of non-conformances. When potential problems are identified, preventative action is initiated to effectively address the problem to eliminate or reduce the risk identified. The preventative action process takes the same format as the corrective action process.

4.12. Records

4.12.1. Record Types

Record types are described in Table 3.

Table 3 STL Record Types

Raw Data	Controlled Documents	QC Records	Project Records	Administrative Records
See Section 3. Terms and Definitions	LQM	Audits/ Responses	COC Documentation	Accounting
	QMP	Certifications	Contracts and Amendments	EH&S Manual, Permits, Disposal Records
	SOPs	Corrective Action	Correspondence	Employee Handbook
		Logbooks*	QAPP	Personnel files, Employee Signature & Initials, Training Records
		Method & Software Validation, Verification data	SAP	
		Standards Certificates	Telephone Logbooks	Technical and Administrative Policies

*Examples of Logbook types: Maintenance, Instrument Run, Preparation (standard and samples), Standard and Reagent Receipt, Archiving, Balance Calibration, Temperature.

4.12.2. Record Retention

Table 4 outlines STL's standard record retention time. For raw data and project records, record retention shall be calculated from the date the project report is issued. For other records, such as Controlled Documents, QC, or Administrative Records, the retention time is calculated from the date the record is formally

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retired. Records related to the programs listed in Table 5 have lengthier retention requirements and are subject to the requirements in Section 4.12.3.

Table 4 STL Record Retention

Record Type		Archival Requirement
Raw Data	All*	5 Years from project completion
Controlled Documents	All*	5 Years from document retirement date
QC	All*	5 Years from archival
Project	All*	5 Years from project completion
Administrative	Personnel/Training	7 years
	Accounting	See Accounting and Control Procedures Manual

* Exceptions listed in Table 5.

Table 5 Special Record Retention Requirements

Program	Retention Requirement
Colorado – Drinking Water	10 years
Commonwealth of MA – All environmental data 310 CMR 42.14	10 years
FIFRA – 40 CFR Part 160	Retain for life of research or marketing permit for pesticides regulated by EPA
Housing and Urban Development (HUD) Environmental Lead Testing	10 years
Louisiana – All	10 years
Michigan Department of Environmental Quality – all environmental data	10 years
Minnesota – Drinking Water	10 years
Navy Facilities Engineering Service Center (NFESC)	10 years
NY Potable Water NYCRR Part 55-2	10 years
OSHA - 29 CFR Part 1910	30 years
Pennsylvania – Drinking Water	10 years
TSCA - 40 CFR Part 792	10 years after publication of final test rule or negotiated test agreement

4.12.3. Programs with Longer Retention Requirements

Some regulatory programs have longer record retention requirements than the STL standard record retention time. These are detailed in Table 5 with their

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retention requirements. In these cases, the longer retention requirement must be implemented and noted in the archive. If special instructions exist such that client data cannot be destroyed prior to notification of the client, the container or box containing that data is marked as to who to contact for authorization prior to destroying the data.

4.12.4. Archives and Record Transfer

Archives must be indexed such that records are accessible on either a project or temporal basis. Archives are protected against fire, theft, loss, deterioration, and vermin. Electronic records are protected from deterioration caused by magnetic fields and/or electronic deterioration. Access to archives is controlled and documented. On-site and/or off-site facilities may be used.

STL ensures that all records are maintained as required by the regulatory guidelines and per the QMP upon facility location change or ownership transfer. Upon STL facility location change, all archives are retained by STL in accordance with the QMP. Upon ownership transfer, record retention requirements shall be addressed in the ownership transfer agreement and the responsibility for maintaining archives is clearly established.

4.13. Internal Audits

4.13.1. Audit Types and Frequency

A number of types of audits shall be performed at STL. Audit type and frequency are categorized in Table 6.

Table 6 Audit Types and Frequency

Audit Type	Performed by	Frequency
Systems	QA Department or Designee	Annual
Data	QA Department	5% of all projects or as agreed upon with Corporate QA
Special	QA Department or Designee	As Needed

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4.13.2. Systems Audits

Facility systems audits are technical in nature and are conducted on an ongoing basis by the QA Manager or his/her designee at each facility. Systems audits cover all departments of the facility, both operational and support.

The audit report is issued by the QA Manager of the facility within 21 calendar days of the audit. The audit report is addressed to the Department Supervisor and/or Manager, and copied to the General Manager and Laboratory Director.

Written audit responses are required within 21 calendar days of audit report issue. The audit response follows the format of the audit report, and corrective actions and time frames for their implementation are included for each deficiency. The audit response is directed to all individuals copied on the audit report. Where a corrective action requires longer than 21 days to complete, the target date for the corrective action implementation is stated and evidence of the corrective action is submitted to the QA Department in the agreed upon time frame.

4.13.3. Data Audits

Data audits are focussed to assess the level of customer service, method compliance, regulatory compliance, accuracy and completeness of test results and reports, documentation, and adherence to established QC criteria, laboratory SOPs, technical policy, and project specific QC criteria.

A data auditing frequency target of 5% has been established. The QA Department provides feedback and/or corrections and revisions to project reports where necessary. Data audits must include spot-checking of manual integrations by QA personnel in order to determine that the manual integration is appropriate and documented according to Section 5.3.6.

Records of the data audits shall be kept, and the frequency of data audits shall be included in the monthly QA report. In performing data audits, it is essential that data be assessed in terms of differentiating between systematic and isolated errors. Upon noting anomalous data or occurrences in the data audits, the QA Department is responsible for seeking clarification from the appropriate personnel, ascertaining whether the error is systematic or an isolated error, and overseeing correction and/or revision of the project report if necessary. Errors found in client project reports are revised and the revision sent to the client. The

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QA Department is also responsible for assisting in the corrective action process where a data audit leads to identification of the need for permanent corrective action.

Where specific clients and regulatory programs require more frequent data auditing, the individual facility must meet the data auditing frequency for that program.

4.13.4. Special Audits

Special audits are conducted on an as needed basis, generally as a follow up to specific issues such as client complaints, corrective actions, proficiency testing results, data audits, systems audits, validation comments, or regulatory audits. Special audits are focussed on a specific issue, and report format, distribution, and timeframes are designed to address the nature of the issue.

4.14. External Audits

STL facilities are routinely audited by clients and external regulatory authorities. STL is available for these audits and makes every effort to provide the auditors with the personnel, documentation, and assistance required by the auditors. STL recommends that the audits be scheduled with the QA Department so that all necessary personnel are available on the day of the audit.

4.15. Management Reviews

4.15.1. QA Reports to Management

A monthly QA report shall be prepared by the QA Manager and forwarded to the Laboratory Director, the General Manager, and the QA Director. The reports include statistical results that are used to assess the effectiveness of the Quality System. The format of the monthly report is shown in Figure 2.

A Corporate QA Monthly Report containing a compilation of the Facility QA reports statistics, information on progress of the Corporate QA program, and a narrative outlining significant occurrences and/or concerns shall be prepared by the QA Director and forwarded to the General Manager of Operational and Technical Services and the COO.

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4.15.2. Management Systems Review

Each STL facility shall perform a management systems review at least annually. The management systems review ensures that the laboratory's quality system is adequate to satisfy the laboratory's policies and practices, regulatory requirements, certification, accreditation, approval requirements, and client expectations. Management systems reviews are accomplished through monthly quality assurance reporting, goal setting and an annual LQM review.

Figure 2 Monthly QA Report Format

1.	Audits Internal systems audits performed. External systems audits performed. Data audits performed (in percent).
2.	Revised Reports/Client Complaints Revised reports in percent. Total number of client complaints, reason, and resolution.
3.	Certifications/Parameters Changes
4.	Proficiency Testing Score for each PT as a percent. Note repeat failures and/or significant problems.
5.	Miscellaneous QA and Operational Issues Narrative outlining improvements, regulatory compliance issues, general concerns, and assistance required from Corporate QA.

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5. Technical Requirements

5.1. Personnel

5.1.1. General

STL management believes that its highly qualified and professional staff is the single most important aspect in assuring the highest level of data quality and service in the industry.

STL staff consists of over two thousand professionals and support personnel that include the following positions:

- General Manager
- Customer Service Manager
- Quality Assurance Manager
- Laboratory Director
- Technical Director
- Laboratory Manager
- Department Supervisor
- Information Technology Manager
- Human Resources Manager
- Project Manager
- Department Manager
- Analyst
- Sample Custodian
- Technician
- Quality Assurance Specialist
- Data Review Specialist
- Information Technology Specialist

5.1.2. Training

STL is committed to furthering the professional and technical development of employees at all levels. Minimum training requirements for STL employees are outlined in Table 7.

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Table 7 STL Employee Minimum Training Requirements

Required Training	Time Frame*	Employee Type
Environmental Health & Safety	Month 1	All
Quality Assurance	Quarter 1	All
Demonstration of Capability (DOC)	Prior to unsupervised method performance	Technical

*From date of initial employment unless otherwise indicated.

Technical training is accomplished within each laboratory by management to ensure method comprehension. All new personnel shall be required to demonstrate competency in performing a particular method by successfully completing a Demonstration of Capability (DOC) before conducting analysis independently on client samples.

DOCs are performed by analysis of four replicate QC samples. Results of successive LCS analyses can be used to fulfill the DOC requirement. The accuracy and precision, measured as average recovery and standard deviation (using n-1 as the population), of the 4 replicate results are calculated and compared to those in the test method (where available). If the test method does not include accuracy and precision requirements, the results are compared to target criteria set by the laboratory. The laboratory sets the target criteria such that they reflect the DQOs of the specific test method or project. A DOC Certification Statement is recorded and maintained in the employee's training or personnel file. Figure 3 shows an example of a DOC Certification Statement.

The following evidence must be on file at the laboratory for each technical employee:

- DOC.
- The employee has read and understood the latest version of the laboratory's quality documentation.
- The employee has read and understood the latest, approved version of all test methods and/or SOPs for which the employee is responsible.
- Annual evidence of continued DOC that may include successful analysis of a blind sample on the specific test method, or a similar test method, or an annual DOC, or four successive, successful LCS.

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Figure 3 Example Demonstration of Capability Certification Statement

Demonstration of Capability
Certification Statement

Date: Matrix:
Laboratory Name: Method:
Laboratory Address:
Analyst Name:

We the undersigned certify that:

1. The analyst identified above, using the cited test method, which is in use at this facility for the analysis of samples under the National Environmental Laboratory Accreditation Program, has met the Demonstration of Capability.
2. The test method was performed by the analyst identified on this certification.
3. Copies of the test method and SOP are available for all personnel on site.
4. The data associated with the DOC are true, complete and representative.
5. All raw data (including a copy of this certification form) necessary to reconstruct and validate these analyses have been retained at the facility, and that the associated information is available for review by authorized inspectors.

Laboratory Manager/Supervisor Signature Date

5.1.3. Ethics Policy

Establishing and maintaining a high ethical standard is an important element of a Quality System. In order to ensure that all personnel understand the importance the company places on maintaining high ethical standards at all times; STL has established an Ethics Agreement (Figure 4). Each employee shall sign the Ethics Agreement, signifying agreed compliance with its stated purpose.

Ethics is also a major component of the STL QA training program. Each employee must be trained in ethics within three months of hire in a standardized QA training program that includes an overview of regulatory programs and program goals, a review of the ethics statement, and group discussions about data integrity and data misrepresentation. Employees must be trained as to the legal and environmental repercussions that result from data misrepresentation. A data integrity hotline is maintained by STL and administered by the QA Director.

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Figure 4 STL Ethics Agreement

It is the policy of STL to incorporate the highest standard of quality with all analytical programs by adhering to the following practices:

STL will only offer environmental analyses for which it can consistently demonstrate compliance with high quality, traceable and legally defensible performance standards. All STL staff is committed to the practice of complete honesty in the production and reporting of data.
Staff who are aware of misrepresentation of facts or data manipulation to bypass established QA/QC requirements, are required to immediately inform their supervisor or any member of the upper management.

All employees are asked to sign a copy of the statement below upon their first day of employment.

I, _____(print name) understand that high standards of integrity are required of me with regard to the duties I perform and the data I report in connection with my employment at the Company. I agree that in the performance of my duties at the Company:
I will not intentionally report data values that are not the actual values obtained;
I will not intentionally report the dates, times, sample or QC identifications, or method citations of data analyses that are not the actual dates, times, sample or QC identifications, or method citations;
I will not intentionally misrepresent another individual's work; and
If a supervisor or a member of STL management requests me to engage in or perform an activity that I feel is compromising data validity or quality, I will not comply with the request and report this action immediately to a member of the upper management, up to and including the president of Severn Trent Laboratories Inc.
I will not intentionally report data values that do not meet established quality control criteria as set forth in the Method and/or Standard Operation Procedures, or as defined by Company Policy.

I agree to inform my Supervisor of any accidental reporting of non-authentic data by me in a timely manner. I agree to inform my Supervisor of any accidental or intentional reporting of non-authentic data by other employees. I have read this Ethics Agreement and understand that failure to comply with the conditions stated above will result in disciplinary action, up to and including termination from the Company.

Compliance with this policy of business ethics and conduct is the responsibility of every STL employee. Disregard or failing to comply with this standard of business ethics and conduct could lead to disciplinary action, up to and including possible termination of employment.

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5.2. Facilities

Each STL facility must be secure and access must be controlled and documented. Access is controlled by various measures including locked doors, passwords, electronic access cards, security codes, and staffed reception areas. All visitors sign in and are escorted by STL personnel while at an STL facility.

STL's facilities are designed for efficient, automated high-quality operations. All laboratories are equipped with Heating, Ventilation, and Air Conditioning (HVAC) systems appropriate to the needs of environmental testing laboratories. Environmental conditions in the facilities, such as hood flow, are routinely monitored and documented. Table 8 summarizes the square footage at each STL facility.

All STL facilities are equipped with structural safety features. Each employee is familiar with the location, use, and capabilities of general and specialized safety features associated with their workplace. STL also provides and requires the use of protective equipment including safety glasses, protective clothing, gloves, respirators, etc.

5.3. Test Methods

5.3.1. Method Selection

Most of the test methods performed at STL originate from test methods published by a regulatory agency such as the US EPA and other state and federal regulatory agencies. These include, but are not limited to, the following published compendiums of test methods:

Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, US EPA, January 1996.

Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act, and Appendix A-C; 40 CFR Part 136, USEPA Office of Water.

Methods for Chemical Analysis of Water and Wastes, EPA 600 (4-79-020), 1983.

Methods for the Determination of Inorganic Substances in Environmental Samples, EPA-600/R-93/100, August 1993.

Methods for the Determination of Metals in Environmental Samples, EPA/600/4-91/010, June 1991.

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Table 8 STL Laboratory Square Footage

Facility	Square Footage
STL Austin	43,000
STL Baltimore	17,000
STL Billerica	10,000
STL Buffalo	32,000
STL Burlington	36,000
STL Chicago	51,000
STL ChromaLab	21,000
STL Connecticut	17,000
STL Corpus Christi	12,000
STL Denver	54,000
STL Edison	30,000
STL Houston	28,000
STL Knoxville	29,000
STL Los Angeles	27,000
STL Miami	9,000
STL Mobile	14,000
STL Newburgh	8,000
STL North Canton	53,000
STL Pensacola	18,000
STL Pittsburgh	30,000
STL Richland	33,000
STL Sacramento	66,000
STL Savannah	55,000
STL St. Louis	31,000
STL Tallahassee	22,000
STL Tampa East	11,000
STL Tampa West	12,000
STL Valparaiso	7,000
STL Westfield	10,000

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Methods for the Determination of Organic Compounds in Drinking Water, EPA-600/4-88-039, December 1988, Revised, July 1991, Supplement I, EPA-600-4-90-020, July 1990, Supplement II, EPA-600/R-92-129, August 1992.

NIOSH Manual of Analytical Methods, 4th ed., August 1994.

Statement of Work for Inorganics Analysis, ILM04.0, USEPA Contract Laboratory Program Multi-media, Multi-concentration.

Statement of Work for Organics Analysis, OLM03.2, USEPA Contract Laboratory Program, Multi-media, Multi-concentration.

Statement of Work for Organic Analysis, Multi-Media, Multi-Concentration, OLMO4.1, USEPA Contract Laboratory Program, September 1998.

Standard Methods for the Examination of Water and Wastewater, 18th/19th edition; Eaton, A.D. Clesceri, L.S. Greenberg, A.E. Eds; American Water Works Association, Water Pollution Control Federation, American Public Health Association: Washington, D.C.

Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW846), Third Edition, September 1986, Final Update I, July 1992, Final Update IIA, August 1993, Final Update II, September 1994; Final Update IIB, January 1995; Final Update III, December 1996.

Annual Book of ASTM Standards, American Society for Testing & Materials (ASTM), Philadelphia, PA.

National Status and Trends Program, National Oceanographic and Atmospheric Administration, Volume I-IV, 1985-1994.

5.3.2. SOPs

Each STL facility shall maintain an SOP Index for both Method and Process SOPs. Method SOPs are maintained to describe a specific test method. Process SOPs are maintained to describe function and processes not related to a specific test method.

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Method SOPs contain the following information:

Title Page with Document Name, Document Number, Revision Number, Effective Date, Page Numbers and Total # of Pages, Authorized Signatures, Dates and Proprietary Information Statement (Figure 5).

1. Identification of Test Method
2. Applicable Matrix
3. Reporting Limit
4. Scope and Application, including test analytes
5. Summary of the Test Method
6. Definitions
7. Interferences
8. Safety
9. Equipment and Supplies
10. Reagents and Standards
11. Sample Collection, Preservation, Shipment and Storage
12. Quality Control
13. Calibration and Standardization
14. Procedure
15. Calculations
16. Method Performance
17. Pollution Prevention
18. Data Assessment and Acceptance Criteria for Quality Control Measures
19. Corrective Actions for Out-of-Control Data
20. Contingencies for Handling Out-of-Control or Unacceptable Data
21. Waste Management
22. References
23. Tables, Diagrams, Flowcharts and Validation Data

Process SOPs may contain the following information:

Title Page with Document Name, Document Number, Revision Number, Effective Date, Page Numbers and Total # of Pages, Authorized Signatures, Dates and Proprietary Information Statement (Figure 5).

1. Scope
2. Summary
3. Definitions
4. Responsibilities

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5. Safety
6. Procedure
7. References
8. Tables, Diagrams, and Flowcharts

The QA Department is responsible for maintenance of SOPs, archival of SOP historical revisions, maintenance of an SOP index, and records of controlled distribution. SOPs, at a minimum, must undergo periodic review as described the each facility's LQM or SOP. Where an SOP is based on a published method, the laboratory must maintain a copy of the reference method.

Figure 5 Proprietary Information Statement

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 STL 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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SOP Appendix

In some cases, a standard laboratory procedure is modified slightly for a specific client or project at the client or regulatory agency's request. In these cases, an Appendix to the SOP may be attached that indicates the modifications to the SOP which are specific to that project. SOP appendices shall not be used to alter test methods required by regulation such that the modifications would result in non-compliance with the regulation.

5.3.3. Method Validation

Laboratory developed methods are validated and documented according to the procedure described in Section 5.3.5.

5.3.4. Method Verification

Method verification is required when a validated standard test method or a method modification is implemented. The level of activity required for method verification is dependent on the type of method being implemented, or on the level of method modification and its affect on a method's robustness. Method modification often takes advantage of a method's robustness, or the ability to make minor changes in a method without affecting the method's outcome. Method verification may require some, but not all, of the activities described in Section 5.3.5.

5.3.5. Method Validation and Verification Activities

Before analyzing samples by a particular method, method validation and/or method verification must occur. A complete validation of the method is required for laboratory developed methods. While method validation can take various courses, the following activities can be required as part of method validation. Method validation records are designated QC records and are archived accordingly.

<u>Determination of Method Selectivity</u>
Method selectivity is demonstrated for the analyte(s) in the specific matrix or matrices. In some cases, to achieve the required selectivity for an analyte, a confirmation analysis is required as part of the method.

<u>Determination of Method Sensitivity</u>
Sensitivity can be both estimated and demonstrated. Whether a study is required to estimate sensitivity depends on the level of method development required when applying a particular measurement system to a specific set of samples. Where estimations and/or demonstrations of sensitivity are required by regulation or client agreement, such as the procedure in 40 CFR Part 136 Appendix B, under the Clean Water Act, these shall be followed. STL Facilities must have an SOP that details their approach to estimation and/or demonstration of sensitivity.

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A number of procedures that can be used for estimating the LOD and/or MDL are referenced below:

Critical Level Approach (Currie, 1968)
This approach estimates the LOD based on a critical level. The critical level is determined from the standard deviation and population characteristics of successive blank determinations.

Decision Limit Approach (Hubaux and Vos, 1970)
This procedure uses a decision limit and the confidence limits from a least squares fitted regression line to estimate the LOD.

Decision Limit Approach using Non-central t-Distribution (Clayton etal, 1987)
This approach estimates the LOD based on a decision limit. This approach is similar to the Hubaux-Vos method but using a non-centrality parameter of distribution in calculating the LOD.

Method Detection Limit Study – (USEPA, Glaser etal, 1981)
This approach establishes a procedure for estimation of the MDL at a single concentration using a minimum of seven successive determinations of samples or spikes containing the analyte to be determined.

Weighted Least Squares Approach (Gibbons etal, 1997)
This approach for estimating the LOD utilizes spiked samples at a series of concentrations and applies a weighted least squares regression analysis to the resulting data.

Study Design in Estimation of Sensitivity

Two components of study design are crucial to ensuring an accurate estimation of sensitivity. First, when the signal of an analyte is used to estimate the Limit of Detection (LOD), it must be based on data for which qualitative identification criteria have been met. For example, qualitative mass spectral identification criteria must be met prior to using a specific ion in a mass spectrum to generate meaningful values for estimation of LOD based on spiked samples. Proper resolution of analytes must be taken into account in determining whether a LOD can be reasonably estimated.

The second important component of study design is to build appropriate and representative variability into the study. Many methods for estimation of the LOD

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require the measurement of variance. The study design must take into account all factors that influence the variability of a measurement system in the routine operation with which it is to be performed. This would include utilizing different analysts, different lots of reagents, different days (taking into account minor temperature and humidity variations), and utilizing all instruments that are to be used in routine operations, to generate the data that will be used in estimating the LOD.

Relationship of Limit of Detection (LOD) to the Quantitation Limit (QL)

Each laboratory shall have a procedure to relate the QL to the LOD (or MDL if appropriate). An important characteristic of expression of sensitivity is the difference in the LOD and the QL. The LOD is the minimum level at which the presence of an analyte can be reliably concluded. The QL is the minimum level at which both the presence of an analyte and its concentration can be reliably determined. For most instrumental measurement systems, there is a region where semi-quantitative data is generated around the LOD (both above and below the estimated MDL or LOD) and below the QL. In this region, detection of an analyte may be confirmed but quantification of the analyte is unreliable within the accuracy and precision guidelines of the measurement system. When an analyte is detected below the QL, and the presence of the analyte is confirmed by meeting the qualitative identification criteria for the analyte, the analyte can be reliably reported, but the amount of the analyte can only be estimated. If data is to be reported in this region, it must be done so with a qualification that denotes the semi-quantitative nature of the result.

Ongoing Demonstration of Sensitivity

STL facilities may have a procedure for ongoing demonstration of sensitivity. The frequency of analysis of a sensitivity check sample should be determined and addressed for the measurement system and based on both the measurement system’s ability to routinely detect the analyte at the level required and the nature of the decisions that the data will support. The level of the sensitivity check sample should be between the QL and the LOD or MDL. Qualitative identification criteria must be met for all analytes in the check sample to confirm the required or estimated sensitivity. Ongoing sensitivity is demonstrated by the detection of the analytes in the sensitivity check sample. Accuracy and precision requirements should not be applied to the sensitivity check sample, as the level of measurement is semi-quantitative.

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Where a single analyte has been used to represent a group of target analytes in demonstrating sensitivity, it is recommended that the analyte be varied amongst that group in demonstrating ongoing sensitivity.

Determination of Interferences
A determination that the method is free from interferences in a blank matrix is performed.

Determination of Range
Where appropriate, a determination of the applicable range of the method may be performed. In most cases, range is determined and demonstrated by comparison of the response of an analyte in a curve to established or targeted criteria. The curve is used to establish the range of quantitation and the lower and upper values of the curve represent upper and lower quantitation limits. Curves are not limited to linear relationships.

Demonstration of Capability
DOCs are performed prior to method performance.

Determination of Accuracy and Precision
Accuracy and precision studies are generally performed using replicate analyses, with a resulting percent recovery and measure of reproducibility (standard deviation, relative standard deviation) calculated and measured against a set of target criteria.

Documentation of Method
The method is formally documented in an SOP. If the method is a minor modification of a standard laboratory method that is already documented in an SOP, an SOP Appendix describing the specific differences in the new method is acceptable in place of a separate SOP.

Continued Demonstration of Method Performance
Continued demonstration of Method Performance is addressed in the SOP. Continued demonstration of method performance is generally accomplished by batch specific QC samples such as LCS and Method Blanks.

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5.3.6. Data review

All data, regardless of regulatory program or level of reporting, shall be subject to a thorough review which involves a primary, secondary, and completeness review process. All levels of the review must be documented.

Primary Review

The primary review is often referred to as a "bench-level" review. In most cases, the analyst who generates the data (i.e. logs in, prepares and/or runs the samples) is the primary reviewer. In some cases, an analyst may be reducing data for samples run by an auto-sampler set up by a different analyst. In this case, the identity of both the analyst and the primary reviewer is identified in the raw data.

One of the most important aspects of primary review is to make sure that the test instructions are clear, and that all project specific requirements have been understood and followed.

Once an analysis is complete, the primary reviewer must ensure that:

- Sample preparation information is complete, accurate, and documented.
- Calculations have been performed correctly.
- Quantitation has been performed accurately.
- Qualitative identifications are accurate.
- Manual integrations are appropriate.
- Data flags to indicate manual integrations are recorded.
- Manual integrations are authorized by a date and signature or initials of primary analyst.
- Client specific requirements have been followed.
- Method and process SOPs have been followed.
- Method QC criteria have been met.
- QC samples are within established limits.
- Dilution factors are correctly recorded and applied.
- Non-conformances and/or anomalous data have been properly documented and appropriately communicated.
- COC procedures have been followed.
- Primary review is documented by date and initials/signature of primary analyst.

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Any anomalous results and/or non-conformances noted during the Primary Review are communicated to the Supervisor and the PM for resolution. Resolution can require sample reanalysis, or it may require that data be reported with a qualification. Non-conformances are documented per Section 4.9.

Secondary Review

The secondary review shall be a complete technical review of a data set. The secondary review must be documented and the secondary reviewer identified. The following items are reviewed:

- Qualitative Identification
- Quantitative Accuracy
- Calibration
- QC Samples
- Method QC Criteria
- Adherence to method and process SOPs
- Accuracy of Final Client Reporting Forms
- Manual Integrations – Minimal requirement is to spot-check raw data files for manual integration, as verified by date and initials or signature of secondary data reviewer. Some regulatory programs require 100% secondary review of manual integrations.
- Completeness
- Special Requirements/Instructions

If problems are found during the secondary review, the reviewer must work with the appropriate personnel to resolve them. If changes are made to the data, such as alternate qualitative identifications, identifications of additional target analytes, re-quantitation, or re-integration, the secondary reviewer must contact the laboratory analyst and/or primary reviewer of the data so that the primary analyst and/or reviewer is aware of the appropriate reporting procedures.

Completeness Review

The completeness review shall include the generation of a project narrative and/or cover letter which outlines anomalous data and non-compliances using project narrative notes and non-compliance reports generated during the primary and secondary review. The completeness review addresses the following items:

- Is the project report complete?

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- Does the data meet with the client's expectations?
- Were the data quality objectives of the project met?
- Are QC outages and/or non-conformances approved and appropriately explained in the narrative notes?

5.3.7. Data Integrity and Security

This section details those procedures that are relevant to computer systems that collect, analyze, and process raw instrumental data, and those that manage and report data.

Security and Traceability
Access to computer systems that collect, analyze, and process raw instrumental data, and those that manage and report data must be both controlled and recorded. There are various systems at STL to which this applies, which include the Laboratory Information Management System (LIMS), as well as specific systems such as chromatography data systems.

Control of the system is accomplished through limitation of access to the system by users with the education, training and experience to perform the task knowledgeably and accurately. System users are granted privileges that are commensurate with their experience and responsibilities.

Computer access is tracked by using unique login names and passwords for all employees that have access to the computer system. "General" or "multi-user" account access to computer systems that collect, analyze and process raw instrumental data, and those that manage and report data shall not be permitted. Entries and changes are documented with the identity of the individual making the entry, and the time and date. Where a computer system is processing raw instrumental data, the instrument identification number as described in Section 5.4.1 is recorded. Many of these systems have the capability of maintaining audit trails to track entries and changes to the data. This function is activated on any computer system that has that capability.

Verification
All commercially obtained software shall be verified prior to use and after version upgrade. Verification involves assessing whether the computer system accurately performs its intended function. Verification generally is accomplished by comparing the output of the program with the output of the raw data manually processed, or processed by the software being replaced. The records of the

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verification are required to contain the following information: software vendor, name of product, version, comparison of program output and manual output, raw data used to verify the program, date, and name of the individual performing the verification. Records of verification are retained as QC records.

Validation
Software validation involves documentation of specifications and coding as well as verification of results. Software validation is performed on all in house programs. Records of validation include original specifications, identity of code, printout of code, software name, software version, name of individual writing the code, comparison of program output with specifications, and verification records as specified above. Records of validation are retained as QC records.

Auditing
The QA Department systems audit includes review of the control, security, and tracking of IT systems and software.

Version Control
The laboratory shall maintain copies of outdated versions of software and associated manuals for all software in use at the laboratory for a period of five years from its retirement date. The associated hardware, required to operate the software, must also be retained for the same time period.

5.4. Equipment

5.4.1. Equipment Operation

STL is committed to routinely updating and automating instrumentation. STL facilities maintain state of the art instrumentation to perform the analyses within the QC specifications of the test methods. Each STL facility shall maintain an equipment list that must include the following information:

- Identity
- Date Installed
- Manufacturer's Name, Model Number, Serial Number
- Current Location
- Preventative Maintenance Schedule

All equipment is subject to rigorous checks upon its receipt, upgrade, or modification to establish that the equipment meets with the selectivity, accuracy,

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and precision required by the test method for which it is to be used. All manufacturer's operations and maintenance manuals are kept up to date and accessible for the use of the equipment operator. Documentation of equipment usage is maintained using analytical run and maintenance logbooks.

5.4.2. Equipment Maintenance

Each STL facility must employ a system of preventative maintenance in order to ensure system up time, minimize corrective maintenance costs and ensure data validity. All routine maintenance is performed as recommended by the manufacturer and may be performed by an analyst, instrument specialist or outside technician. Maintenance logbooks are kept on all major pieces of equipment in which both routine and non-routine maintenance is recorded. Notation of the date and maintenance activity is recorded each time service procedures are performed. The return to analytical control following instrument repair is documented in the maintenance logbook. Maintenance logbooks are retained as QC records.

Maintenance contracts are held on specific pieces of equipment where outside service is efficient, cost-effective, and necessary for effective operation of the laboratory.

5.4.3. Equipment Verification and Calibration

All equipment shall be tested upon receipt to establish its ability to meet the QC guidelines contained in the test method for which the instrumentation is to be used. This testing shall be documented. Once an instrument is placed in routine service, ongoing instrument calibration is demonstrated at the appropriate frequency as defined in the test method. Any instrument that is deemed to be malfunctioning is clearly marked and taken out of service. When the instrument is brought back into control, this is documented in the instrument maintenance log.

5.5. Measurement Traceability

5.5.1. General

Traceability of measurements shall be assured using a system of documentation, calibration, and analysis of reference standards. Laboratory equipment that are peripheral to analysis and whose calibration is not necessarily documented in a

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test method analysis or by analysis of a reference standard shall be subject to ongoing certifications of accuracy.

At a minimum, these must include procedures for checking specifications for balances, thermometers, temperature, Deionized (DI) and Reverse Osmosis (RO) water systems, automatic pipettes and other volumetric measuring devices. With the exception of Class A Glassware (including glass microliter syringes that have a certificate of accuracy), quarterly accuracy checks are performed for all mechanical volumetric devices. Wherever possible, subsidiary or peripheral equipment is checked against standard equipment or standards that are traceable to national or international standards.

An external certified service engineer services laboratory balances on an annual basis. This service is documented on each balance with a signed and dated certification sticker. Balances are calibrated on each day of use. All mercury thermometers are calibrated annually against a traceable reference thermometer. Temperature readings of ovens, refrigerators, and incubators are checked on each day of use.

Laboratory DI and RO water systems have documented preventative maintenance schedules and the conductivity of the water is recorded on each day of use.

5.5.2. Reference Standards

The receipt of all reference standards must be documented. References standards are labeled with a unique Standard Identification Number, date received, and the expiration date. All documentation received with the reference standard is retained as a QC record and references the Standard Identification Number.

All standards should be purchased with an accompanying Certificate of Analysis that documents the standard purity. If a standard cannot be purchased from a vendor that supplies a Certificate of Analysis, the purity of the standard is documented by analysis. The documentation of standard purity is archived, and references the Standard Identification Number.

All efforts are made to purchase standards that are $\geq$ 97.0% purity. If this is not possible, the purity is used in performing standards calculations.

The accuracy of calibration standards is checked by comparison with a standard from a second source. In cases where a second standard manufacturer is not

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available, a different lot is acceptable for use as a second source. The appropriate Quality Control (QC) criteria for specific standards are defined in laboratory SOPs. In most cases, the analysis of an Initial Calibration Verification (ICV) or Laboratory Control Sample (LCS) is used as the second source confirmation.

5.5.3. Reagents

Reagents are, in general, required to be analytical reagent grade unless otherwise specific in method SOPs. Reagents must be at a minimum the purity required in the test method. The date of reagent receipt and the date the reagent was opened are documented.

5.6. Sampling

Sample representativeness and integrity are the foundations upon which meaningful analytical results rely. Where documented and approved SAPs and/or QAPPs are in place, they must be made available to the laboratory before sample receipt, and approved by laboratory management before sample receipt.

5.7. Sample Handling, Transport, and Storage

5.7.1. General

Chain of Custody (COC) can be established either when bottles are sent to the field, or at the time of sampling. STL can provide all of the necessary coolers, reagent water, sample containers, preservatives, sample labels, custody seals, COC forms, ice, and packing materials required to properly preserve, pack, and ship samples to the laboratory.

Samples are received at the laboratory by a designated sample custodian and a unique Laboratory Project Identification Number is assigned. The following information is recorded for each sample shipment: Client/Project Name, Date and Time of Laboratory Receipt, Laboratory Project Number, and Signature or initials of the personnel receiving the cooler and making the entries.

Upon inspection of the cooler and custody seals, the sample custodian opens and inspects the contents of the cooler, and records the cooler temperature. If the cooler arrival temperature exceeds the required or method specified temperature range by $\pm 2^{o}C$ (for samples with a temperature requirement of $4^{o}C$, a cooler temperature of just above the water freezing temperature to $6^{o}C$ is acceptable);

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sample receipt is considered "compromised" and the procedure described in Section 4.7.1 is followed. All documents are immediately inspected to assure agreement between the test samples received and the COC.

Any non-conformance, irregularity, or compromised sample receipt as described in Section 4.7.1 must be documented and brought to the immediate attention of the client. The COC, shipping documents, documentation of any non-conformance, irregularity, or compromised sample receipt, record of client contact, and resulting instructions become part of the permanent project record.

Samples that are being tested at another STL facility or by an external subcontractor shall be appropriately packaged, and sent out under COC.

Following sample labeling as described in Section 5.7.2, the sample is placed in storage. Sample storage is required to be access controlled. All samples are stored according to the requirements outlined in the test method and in a manner such that they are not subject to cross contamination or contamination from their environment. Unless specified by method or state regulation, a tolerance range of $4 \pm 2^{o}C$ is used. Sample storage temperatures are monitored daily.

5.7.2. Sample Identification and Traceability

Each sample container shall be assigned a unique Sample Identification Number that is cross-referenced to the client identification number such that traceability of test samples is unambiguous and documented. Each sample container is affixed with a sample identification label.

All unused portions of samples, including empty sample containers, are returned to the secure sample control area.

5.7.3. Sub-sampling

Sample preparation procedures must be referenced in each STL facility's LQM and documented in the laboratory SOPs.

5.7.4. Sample Preparation

Sample preparation procedures must be referenced in each STL facility's LQM and documented in the laboratory SOPs.

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5.7.5. Sample Disposal

Each facility shall have an SOP describing sample retention and disposal procedures. Samples should be retained in STL storage facilities for a minimum of 30 days after the project report is sent, however, provisions may be made for earlier disposal of samples once the holding time is exceeded. Some samples are required to be held for longer periods based on regulatory or client requirements (example, ACOE, 60 days after project report is sent). The laboratory must follow the longer sample retention requirements where required by regulation or client agreement. Samples may be returned to the client per written request. Unused portions of samples found or suspected to be hazardous according to state or federal guidelines may be returned to the client upon completion of the analytical work.

Samples shall be disposed of in accordance with federal, state and local regulations. Each facility must have an SOP detailing the disposal of samples, digestates, and extracts.

5.8. Assuring the Quality of Test Results

5.8.1. Proficiency Testing

Each STL facility must analyze Proficiency Test (PT) samples as required for accreditation. As required by NELAC, each STL facility participates in the PT program semi-annually for each PT field of testing for which it is accredited; according to the NELAC PT field of testing published guidelines. Under SDWA, the laboratory also analyzes a PT sample by each method once per year, if the laboratory uses more than one method for the analyte.

In addition to the PT program required for NELAC accreditation, STL participates in a number of additional PT programs, as appropriate for the specific facility.

PT samples must be handled and tested in the same manner (procedural, equipment, staff) as environmental samples. PT test sample data is archived using the requirements for project and raw data record retention.

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Double Blind Performance Evaluation

Each STL facility performing chemical analyses also participates in a double blind performance evaluation annually. An external vendor is contracted to submit double blind samples to the STL facility. Both the level of customer service and the accuracy of the test results are assessed objectively by the external contractor, who provides a detailed report to the QA Director and to each of the STL facilities. This is administered as a double blind program in order to assess all facets of STL operations.

5.8.2. Control Samples

Control samples are analyzed with each batch of samples to monitor laboratory performance in terms of accuracy, precision, sensitivity, selectivity, and interferences. Each regulatory program and each method within those programs specify the control samples that are prepared and/or analyzed with a specific batch. Control samples must be uniquely identified and correlated to unique batches. There are also a number of QC sample types that monitor field sampling accuracy, precision, representativeness, interferences, and the effect of the matrix on the method performed. Control Sample types and typical frequency of their application are outlined in Table 9. Note that frequency and use of control samples vary with specific regulatory, methodology and project specific criteria. Table 9 does not define STL's approach to application of QC samples for each regulatory program or test method.

5.8.3. Calibration

Each STL Facility must define calibration protocols in STL facility SOPs.

5.8.4. Glassware Cleaning

Glassware cleaning must be described in STL facility SOPs.

5.8.5. Permitting Departures from Documented Procedure

Each STL facility must have a procedure that defines the process, documentation, and level of authorization required to permit departures from documented procedures.

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Table 9 Control Samples

Laboratory QC Sample Type	Use	Required Frequency
Laboratory Control Sample (Laboratory Fortified Blank)	Measures accuracy of method in blank matrix	1 per batch of 20 or less samples per matrix type per sample extraction or preparation method[1]
Method Blank	Measures method contribution to any source of contamination	1 per batch of 20 or less samples per matrix type per sample extraction or preparation method[1]
Instrument Blank	Measures instrumental contribution to any source of contamination	As specified in test method
Cleanup Blank	Measures clean up step contribution to any source of contamination	As specified in test method
Storage Blank	Measures storage contribution to any source of contamination (Volatiles only)	As specified in test method or SOP
Control, Brine Control, or Dilution Water	Measures effect of blank water on test organisms (Aquatic toxicology)	As specified in test method and permit
Reference Toxicant	Measure sensitivity of test organisms (Aquatic toxicology)	Annually
Field QC Sample Type	**Use**	Typical Frequency
Matrix Duplicate	Measures effect of site matrix on precision of method	Per 20 samples per matrix or per SAP/QAPP[1,2]
Matrix Spike	Measures effect of site matrix on accuracy of method	Per 20 samples per matrix or per SAP/QAPP[1]
Matrix Spike Duplicate	Measures effect of site matrix on precision of method	Per 20 samples per matrix or per SAP/QAPP[1,2]
Equipment Blank (Equipment Rinsate)	Measures field equipment contribution to any source of contamination	Per SAP/QAPP
Trip Blank	Measures shipping contribution to any source of contamination (Volatiles only)	Per Cooler
Field Blank	Measures field environment contribution to any source of contamination	Per SAP/QAPP
Field Duplicate	Measures representativeness of sampling and effect of site matrix on precision	Per SAP/QAPP

[1] Denotes an STL required frequency
[2] Either an MSD or an MD is required per 20 samples per matrix or per SAP/QAPP.

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Where a departure from a documented SOP, test method, or policy is determined to be necessary, or unavoidable, the departure shall be documented and be authorized by the appropriate level of management, which is defined in the policy. In some instances, it is appropriate to inform the client before permitting a departure. Any such occurrence is documented in the cover letter and/or project narrative.

5.8.6. Development of QC Criteria, Non-Specified in Method/Regulation

Where a method or regulation does not specify acceptance and/or rejection criteria, the laboratory must develop a policy for doing so. The policy must address how the laboratory examines the data user's needs and the demonstrated sensitivity, accuracy and precision of the available test methods in determining appropriate QC criteria.

Data users often need the laboratory's best possible sensitivity, accuracy, and precision using a routinely offered test method, or are unsure of their objectives for the data. For routine test methods that are offered as part of STL's standard services, the laboratory bases the QC criteria on statistical information such as determination of sensitivity, historical accuracy and precision data, and method verification data. The method SOP includes QC criteria for ongoing demonstration that the established criteria are met (i.e. acceptable LCS accuracy ranges, precision requirements, method blank requirements, initial and continuing calibration criteria, etc.).

In some cases, a routine test method may be far more stringent than a specific data user's needs for a project. The laboratory may either use the routinely offered test method, or may opt to develop an alternate test method based on the data user's objectives for sensitivity, accuracy, and precision. In this case, it can be appropriate to base the QC criteria on the data user's objectives, and demonstrate through method verification and ongoing QC samples that these objectives are met.

For example, a client may require that the laboratory to test for a single analyte with specific DQOs for sensitivity, accuracy, and precision as follows: Reporting Limit of 10 ppm, accuracy $\pm$25%, and RSD of less than 30%. The laboratory may opt to develop a method that meets these criteria and document through the Method blank results, MDL study, and LCS results that the method satisfies those

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objectives. In this case, both the method and the embedded QC criteria have been based on the client's DQOs.

In some cases, the data user needs more stringent sensitivity, accuracy, and/or precision than the laboratory can provide using a routine test method. In this case, it is appropriate that the laboratory provide documentation of the sensitivity, accuracy, and precision obtainable to the data user and let the data user determine whether to use the best available method offered by the laboratory, or determine whether method development or further research is required.

5.9. Project Reports

5.9.1. General

All STL Project reports that are generated under NELAC requirements must contain the content as described in Section 5.9.2. The criteria described in Section 5.9.3 and 5.9.4 apply to all Project Reports.

5.9.2. Project Report Content

- Title
- Laboratory name, address, telephone number, contact person
- Unique Laboratory Project Number
- Total Number of Pages (report must be paginated)
- Name and address of Client
- Client Project Name (if applicable)
- Laboratory Sample Identification
- Client Sample Identification
- Matrix and/or Description of Sample
- Dates: Sample Receipt, Collection, Preparation and/or Analysis Date
- Definition of Data Qualifiers
- Reporting Units
- Test Method

The following are required where applicable to the specific test method or matrix:

- Solid Samples: Indicate Dry or Wet Weight
- Whole Effluent Toxicity: Statistical package used

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- If holding time ≤ 48 hours, Sample Collection, Preparation and/or Analysis Time
- Indication by flagging where results are reported below the quantitation limit.

5.9.3. Project Narrative

A Project Narrative and/or Cover Letter shall be included with each project report and at a minimum includes an explanation of any and all of the following occurrences:

- Non-conformances
- "Compromised" sample receipt (see Section 4.7.1)
- Method Deviations
- QC criteria failures

Project Release

The Laboratory Director or his/her designee must authorize the release of the project report with a signature.

Where amendments to project reports are required after issue, these shall be in the form of a separate document and/or electronic data deliverable. The revised report is clearly identified as revised with the date of revision and the initials of the person making the revision. Specific pages of a project report may be revised using the above procedure with an accompanying cover letter indicating the page numbers of the project revised. The original version of the project report must be kept intact and the revisions and cover letter included in the project files.

5.9.4. Subcontractor Test Results

Project reports from external subcontract shall not be altered, and shall be included in original form in the final project report provided by STL. Data from subcontractors' reports may be added to an STL electronic deliverable.

Subcontracted data shall be clearly identified as such, and the name, address, and telephone number for the laboratory performing the test is included in the project report. If the report is being generated under NELAC requirements, all information outlined in Section 5.9.2 are required for both the originating laboratory and the subcontracting laboratory.

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Data subcontracted within STL may be reported on the originating laboratory's report forms provided the following mandatory requirements are met:

- The name, address, and telephone number of the facility are provided.
- Analytical results produced by the STL intra-company subcontractor are clearly identified as being produced by the subcontractor facility.
- The intra-company subcontractor's original report, including the chain of custody is retained by the originating laboratory.
- Proof of certification is retained by the originating laboratory.
- All information as outlined in Section 5.9.2 is included in the final report where the report is required to be compliant with NELAC, for both the originating and subcontracting laboratory.

5.9.5. Electronic Data Deliverables

Electronic Data Deliverables (EDD) are routinely offered as part of STL's services. STL offers a variety of EDD formats including Environmental Restoration Information Management System (ERPIMS), New Agency Standard (NAS), Format A, Excel, Dbase, GISKEY, and Text Files.

EDD specifications are submitted to the IT department by the PM for review and undergo the contract review process in Section 4.4.1. Once the facility has committed to providing diskettes in a specific format, the coding of the format may need to be performed. This coding is documented and validated. The validation of the code is retained as a QC record.

EDDs shall be subject to a secondary review to ensure their accuracy and completeness.

5.9.6. Project Report Format

STL offers a wide range of project reporting formats, including EDDs, short report formats, and complete data deliverable packages modeled on the Contract Laboratory Protocol (CLP) guidelines. More information on the range of project reports available can be obtained by contacting any STL facility. Regardless of the level of reporting, all projects must undergo the levels of review as described in Section 5.3.6.

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QA-001

Standard Operating Procedures

APPROVAL:

Director, Quality Assurance	Vice President, Operations Services

STL Incorporated **POLICY NAME**

COMPANY WIDE **Preparation and Management of Standard Operating Procedures**

Rev. 2, 06/01/98
Supersedes: Revision 1

Policy #: QA-001

OBJECTIVE:

To identify the requirements for the development, review, and management of standard operating procedures (SOPs) and the requirements for control distribution of SOPs.

SCOPE:

To be enforced and followed throughout the company.

POLICY:

1. All routine management, administrative, and operational activities associated with the production of analytical data at facilities of STL Incorporated must be documented using SOPs or supported by written policies. The format of the SOPs shall be determined based on the type of procedure being described. The required formats are provided in the appendix of this policy.

PROPRIETARY INFORMATION STATEMENT

This document has been prepared by and remains the sole property of STL Incorporated. It is submitted to a client or government agency solely for its use in evaluating STL's qualifications in connection with the particular project, certification or approval for which it was prepared, and is to be held proprietary to STL.

The user agrees by its acceptance or use of this document to return it upon STL's request, and not to reproduce, copy, lend or otherwise disclose or dispose of the contents, directly or indirectly, and not to use it for any purpose other than that for which it was specifically furnished. The user also agrees that where consultants or others outside of user's organization are involved in the evaluation process, access to this document shall not be given to those parties, unless those parties also specifically agree to these conditions.

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2. SOPs must be developed, reviewed, approved, implemented, distributed, and maintained using the formats and procedures described in this policy.

   SOPs shall be generated using the appropriate word-processing software specified by STL InformationTechnology (IT) Department in standard, consistent font and type sizes described in the Corporate Identity Documents. All sections shall be numbered according to the outlines provided in the appendices of this policy. Subparagraphs shall be numbered using standard decimal numbering practices (e.g., 1.1, 1.1.1, etc.) as applicable. Each paragraph should be single-spaced with a blank line between paragraphs. The document shall be typed in single column format.

3. The types of SOPs utilized in the laboratory operations include operation-specific SOPs, Corporate method SOPs, method-specific laboratory, and laboratory-specific Corporate method SOPs. An operation-specific SOP must <u>not</u> supersede or alter the content of a corporate SOP unless required by a client or approved by the Corporate QA Director (CQAD). In developing SOPs, the author must review the SOP for consistency with requirements specified in STL's Quality Assurance Management Plan (QAMP), Chemical Hygiene Plan (CHP), policies, method or regulatory requirements and existing SOPs. If clients require the use of a procedure which deviates from an existing corporate or operation-specific SOP, the requirement and use of the alternate SOP must be specified in the project documents (e.g., QAPjP) or in contractual documents. The title, number, and contents of this SOP must clearly indicate that the procedure is developed to meet a specific project's requirements. The approval of the Corproate EH&S Director is required to change any environmental, health or safety requirement based on the requirements in the CHP or corporate EH&S procedures.

4. SOPs must be numbered using the numbering system described in Appendix I. Each page must include the header with the SOP number, the Revision Number, the Revision Date and the page number, including total number of pages, as shown in Appendix II and III. If the document supersedes a previous revision or replaces a different SOP, this is listed on the title page. If no document is superseded, state "None". Approval of operation and corporate SOPs is indicated by signature of the appropriate personnel on the cover sheet of the SOP. The header information and signature requirements are shown in Appendices II, II-A and III. SOPs shall not be used to perform work unless they are <u>controlled</u> <u>copies</u> of the approved document, indicated by the attached and completed signature page. Uncontrolled copies of SOP can be distributed to Operations management for review before the procedure is implemented.

5. SOPs are proprietary of STL and are confidential documents. The proprietary information statement displayed on the signature page of the SOP (see Appendix II, II-A or III) is an integral

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part of the document and must be affixed to each approval page of SOPs. Any use of the SOP without the proprietary information statement shall not be allowed without the approval of Corporate Counsel. STL SOPs are proprietary documents; therefore, they should not be routinely disseminated to clients or other external entities without the permission of the responsible lab manager or QA manager for operation-specific SOPs, Corporate Quality Assurance for QA SOPs and Corporate Technology for Corporate method SOPs. Under special circumstances, SOPs are distributed to external parties as uncontrolled documents as determined by the QAM.

If a method or procedure was developed to meet the specific needs of a client under contract, the SOP is considered the property of the client and may be released to them with the confidentiality statement waived. These SOPs shall not be distributed outside of STL without the written permission of the client.

6. SOPs are normally controlled documents. They shall be distributed for use **internally** as "**controlled"** documents and **externally** as "**uncontrolled"** copies, unless requested as such by the client. Only copies of the complete SOP, including approval signatures, shall be distributed. For example, Department of Energy (DOE) requires controlled copies of SOPs and other laboratory documents.

   Controlled copies are numbered and their distribution documented using a SOP Circulation List (see example in Appendix IV). This form may be computerized and the records maintained in a database. All STL personnel receiving controlled copies of SOPs must document that they have received the SOP(s) using a SOP Circulation List. The printout of a Circulation List will be signed and dated documenting that the SOP was received. The SOP Receipt Form (see example in Appendix V) is an optional form, which may also be used to document SOP receipt.

   SOPs sent to clients or government agencies must be issued by the QA Department as uncontrolled copies, unless specific requirements to provide controlled copies exist. The recipients will need to be tracked only if the documents are controlled. The SOP number, revision number, along with the client name and address and contact person, must be tracked for controlled copies. The uncontrolled copy must be marked "UNCONTROLLED COPY" in the area of the Controlled Copy Number blank on the signature page. Uncontrolled copies are not numbered.

7. The current, approved SOP must be followed each time the covered activity is performed, unless a contract or QAPjP requires a specific version of a SOP. Client agreements which reference specific SOPs should be written where feasible, to incorporate subsequent revisions of these SOPs.

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8. Following the completion of a SOP, each SOP must undergo the required review process before final publication. Each SOP must be reviewed by a representative staff member of the following sections: (1) Operations (i.e., group leader, technical lead, or a qualified peer), (2) appropriate section Supervisor or Manager, (3) QA Department, (4) Environmental, Health and Safety, and (5) the Lab Manager.

9. Work Instructions can be used to document simple procedures and/or project-specific requirements as placards in labs. These documents are not required to undergo the same level of control as officials SOPs. However, Work Instructions (see example in Appendix XI) must be approved by a QA Department representative.

DEFINITIONS:

Document control system: The system of document generation, review, approval and reproduction that will ensure the use of the most current, applicable procedures in all areas.

Controlled copy: Controlled documents distributed with the intention that all updates of that document are provided to the holder of the controlled copy and that the copy is returned when no longer needed or the associate leaves the company. Each copy is marked "Controlled Copy". The copies are numbered and a controlled copy distribution list (e.g., SOP Circulation List) is maintained which includes the holder's name and document number.

Uncontrolled copy: A copy of a controlled document that is issued with no intent to provide the holder with subsequent revisions. Generally, uncontrolled copies are distributed to external clients. The document is marked "Uncontrolled Copy." An uncontrolled copy is not numbered.

PROCEDURES:

I. Format, Development, and Approval of Standard Operating Procedures:

Corporate SOPs are documents developed by STL for use across the company where standardization of procedures is deemed necessary.

A. Corporate Method SOPs:

1. The format for Analytical Method SOPs is described in Appendix VI.

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2. Corporate Method SOPs shall be developed through a team review process. The team shall consist of a Corporate Technical Representative, at least two Operations Representatives from the Operations Regions, and a Quality Assurance Representative. The time frame for completion shall be established by the team and approved by Technology.

3. Corporate Method SOPs shall be reviewed by the members of the Team, an Environmental Health and Safety representative, and sent to each laboratory for review as designated by the laboratory manager. Final approval of corporate method SOPs shall be designated by signature on the cover page by a Technical Specialist, the Director of Quality Assurance, the Director of Environmental Health and Safety, and Management (e.g., Vice President or General Manager of Laboratory Operations).

4. If approved by Technology or Quality Assurance, laboratory-specific modifications deemed necessary shall be made within the body of the appropriate Corporate SOP indicated by the *italic* style. The laboratory-specific Corporate SOP shall include an extension to the Corporate SOP number to represent the STL facility (e.g., CORP-GC-0001AL; CORP-MT-0003DEN, etc.). The laboratory-specific Corporate SOP will maintain the same revision number as the Corporate SOP with the addition of a digit(s) to the right of the decimal point to signify the laboratory-specific revision starting with 0.1. For example, if the Corporate SOP is Revision 1.0, the first laboratory-specific revision should be Revision 1.1. The revision date will reflect the date on which the facility modifications are incorporated into the corporate method SOP. The cover page will be the laboratory-specific format with an additional signature line to indicate the Corporate QA or Technology approval. (See example Appendix II-A.) If a facility chooses to implement the Corporate Method SOP without modifications, no changes to the SOP and revision numbers and approval signatures is necessary. The SOP can be adopted as is.

B. Other Corporate SOPs:

1. The format for corporate SOPs for all procedures other than analytical methods is described in Appendixes VII and VIII.

2. Corporate SOPs for QA procedures shall be developed by the Director of Quality Assurance with the assistance of the corporate QA staff or designated representatives from the QA staff. These documents shall be used to describe implementation of specific QA functions as described in STL's QAMP and QA Policies. Final approval of corporate QA SOPs shall be designated by signature on the cover page by the Director of Quality Assurance, the Director of Environmental Health and Safety, and the Vice President responsible for Quality Assurance.

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3. Corporate SOPs to describe activities and procedures for other functional areas shall be developed by the appropriate staff. Final approval of corporate SOPs shall be designated by signature on the cover page by the Director of Quality Assurance, the Director of Environmental Health and Safety, and the Vice President responsible for that functional area.

C. Operation-Specific SOPs:

1. The format for operation-specific SOPs are described in Appendices VI - VIII.

2. Operation-specific SOPs including method SOPs and other SOPs shall be developed for all procedures that are not described in corporate SOPs. Final approval of operation-specific SOPs shall be designated by signature on the cover page by a Technical Specialist, the QA Manager, the Environmental, Health and Safety Coordinator and the Lab Manager.

II. Document Control for Standard Operating Procedures:

A. Distribution

1. SOPs shall be written and approved according to the procedures described in this policy. Once the SOP has been approved, it must be implemented as written at the facility for which it represents. All individuals required to perform the procedures described by a SOP must read the document and undergo training by the section supervisors or group leaders. For new procedures or major changes to existing procedures, adequate training in addition to reading the SOP must be provided by the section supervisors or group leaders to ensure proper implementation. Such training shall be documented in the associate's training file.

2. Controlled distribution and maintenance of the SOPs is the responsibility of the QA Office. The SOP files consist of the Original Document file and Satellite files. The Original Document file contains copies of all SOPs issued by corporate management and original SOP documents issued by the facility. Satellite, if used, contain photocopies or electronic copies of any SOPs distributed to work areas as may be required. Electronic copies can be kept on public drive as long as security of the documents is maintained, and they are available to the user, if not hard copies must be kept. When the SOP is revised, previous version should be removed from the drive unless still in use. The satellite files may contain all, or an appropriate subset of the corporate and operation-specific SOPs as they apply to a specific function. Distribution of SOPs to associates and/or all satellite files shall be documented. A SOP Circulation Form provided in Appendix IV is an example of the type

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of required documentation. Distribution records may be computerized. All SOPs shall be marked as controlled or uncontrolled copies as described above. Any associate issued one or more personal copies of SOPs shall document the receipt of the SOPs on a SOP Circulation List (Appendix IV). The SOP Receipt Form included in Appendix V can also be used, although this is an optional form.

3. This policy allows for use of electronic forms and electronic distribution of controlled and uncontrolled copies. Electronic receipt can be done via electronic mail (email) using receipt acknowledgment.

B. Revision

1. SOPs must be revised if there is a substantial change in the procedure. In the case of planned analytical methods modifications, an approved revision of the SOP should be in place prior to implementation of the modified procedure in the laboratory. Minor SOP revisions may be documented through the use of the SOP Change Form (see Appendix IX & Appendix X) which also must undergo the same review process. When performing the every two-year review, minor changes must be incorporated into the body of the SOP.

2. It is STL policy to review each SOP <u>every</u> <u>two</u> <u>years</u>. If during the every two-year review, it is determined that no modifications are necessary, a SOP Review Form (Appendix XII) can be used to document the current state of the SOP, extending the life of the document until significant changes occur. This form must be reviewed by the reviewer (a representative of a department) and QA. During this process, the SOP does not need to be reissued with a new revision date and number**.** The SOP revision is updated in the SOP database and the Review Form is maintained in the QA files.

3. The <u>effective date</u> of any quality document, except the QAMP, is the laboratory designated implementation date, the date when controlled copies are distributed and the document is first put into use at a given STL facility. The implementation date is indicated on the title page of the document called Implementation Date, to be completed by the lab. The implementation date is to be filled in by the QAM the time of controlled document distribution. Implementation date is the point after which SOP training, initial performance and MDL studies are complete. The document control systems must include a master list or file that identifies the current revision status of quality documents and records the effective date for each update and version of the documents so that the history of use for each at the facility can be demonstrated.

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4. For operation-specific SOPs, the completed change form must be approved by the technical supervisor, the QA Manager, the Environmental Health & Safety Coordinator, and the Lab Manager, until edited copies are completed. Revisions to corporate SOPs can only be made by the same approval process used for the corporate SOP as indicated by the same signature authorities of the approved SOP.

5. Each revision must be numbered in sequential ascending order. When the revised SOP is distributed to the laboratory, all copies except those required for projects must be collected and destroyed by the **laboratory departments or designee.** The original document of the preceding revision is placed in a historical file and maintained according to the requirements of the Record Retention Policy. For corporate SOPs, each operational unit must maintain a single photocopy of the corporate SOP in the historical file. The original document of the corporate SOP shall be maintained in the Corporate QA historical file.

6. Handwritten changes without the approval of the Section Supervisors or Manager and Quality Assurance department in SOPs are prohibited. Handwritten changes are considered "interim" and are only allowed if each modification or addition is accompanied by the initials and date of the Operations Management using the SOP Change Form. The SOP Change Form can be used to document interim, minor revisions. This form must be approved, including the appropriate signatures, same as the SOP.

RESPONSIBILITIES:

- The QA staff shall be responsible for the document control system for SOPs including maintenance of the original documents and historical files; controlled distribution of new or revised SOPs, documentation of circulation, and issuance of unique, sequential SOP numbers.

- Operations Management shall be responsible for implementation and strict adherence to SOPs.

- Each STL associate shall be responsible for following all SOPs pertaining to activities in his/her work area.

- Supervisors and/or group leaders shall be responsible for replacing superseded SOPs with the new revisions for the documents that are assigned to them.

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LIST OF APPENDICES

I. SOP Numbering System and Typesetting

II. Title Page for Corporate Method SOPs (STL SOPs)

II-A. Title Page for Laboratory-Specific Corporate Method SOP

III. Title Page for Facility SOPs (Operation-Specific SOP)

IV. SOP Circulation Form (also to be used for documenting SOP receipt)

V. SOP Receipt Form (optional)

VI. Format for Analytical Method SOP

VII. Format for SOPs describing Administrative, Non-Method Laboratory Procedures, or Equipment Operation and Maintenance

VIII. Format for Laboratory Reagent/Standard Preparation SOPs

IX. SOP Change Form for operation-specific SOPs

X. SOP Change Form for Corporate Method SOPs

XI. Example Work Instructions Form

XII. Example SOP Review Form

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APPENDIX I

SOP NUMBERING SYSTEM

SOPs are numbered to identify the source and application of the document as follows:

Location-Function-####

where:

Location:		Function:
CORP =	Corporate	QA = Quality Assurance
AK =	Alaska	GC = Gas Chromatography
AUS =	Austin	LC = HPLC
COI =	City of Industry	MS = Mass Spectrometry
DEN =	Denver	MT = Metals
ACS =	Analytical Consulting Services	WC = Wet Chem
KNOX =	Knoxville	ID = Isotope Dilution
NC =	North Canton	IP = Inorganic Prep
PITT =	Pittsburgh	OP = Organic Prep
RICH =	Richland	IT = Information Technology
SAC =	W. Sacramento	HS = Environmental Health and Safety
SANA =	Santa Ana	RB = Radiobioassay
STL =	St. Louis	RC = Radiochemistry
TAMP =	Tampa	RD = Rad Determination/Counting
WEST =	Western Region Labs	AD = Administrative
	(SANA, COI, SAC)	SC = Sample Collection
EHS =	Corporate EH&S	RP = Radiation Protection
		EN = Environmental

= Number assigned sequentially beginning with 0001.

Client-specific SOPs can be identified by a 3-4 letter abbreviation of the client name for the Location field.

Additional location abbreviations and functions can be added with the approval of STL's Director of Quality Assurance.

Facility versions of corporate SOPs must have CORP-Function-XXX and lab location abbreviation at the end.

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APPENDIX II

Controlled Copy
Copy No. _____
Implementation Date:___

SOP No. _____
Revision No. _____
Revision Date _____
Page 1 of _____

STL STANDARD OPERATING PROCEDURE

TITLE: _____

(SUPERSEDES: None)

Prepared by: *(Enter Name of Preparer)* _____

Approved by: _____
Technical Specialist

Approved by: _____
Director, Quality Assurance

Approved by: _____
Director, Environmental Health and Safety

Approved by: _____
Management

Proprietary Information Statement:

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APPENDIX II-A

Controlled Copy
Copy No. _____
Implementation Date:___

SOP No. _____
Revision No. _____
Revision Date _____
Page 1 of _____

LABORATORY-SPECIFIC

STL STANDARD OPERATING PROCEDURE

TITLE:

(SUPERSEDES: None)

Prepared by: *(Enter Name of Preparer)* _____

Approved by: _____
Technical Specialist

Approved by: _____
Quality Assurance Manager

Approved by: _____
Environmental, Health and Safety Coordinator

Approved by: _____
Laboratory Manager

Approved by: _____
Corporate Technology and/or Corporate Quality Assurance

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APPENDIX III

Controlled Copy
Copy No. _____
Implementation Date:___

SOP No. _____
Revision No. _____
Revision Date _____
Page 1 of _____

STL OPERATION-SPECIFIC STANDARD OPERATING PROCEDURE

TITLE: _____

(SUPERSEDES:)

Prepared by: *(Enter Name of Preparer)* _____

Approved by: _____
Technical Specialist

Approved by: _____
Quality Assurance Manager

Approved by: _____
Environmental, Health and Safety Coordinator

Approved by: _____
Laboratory Manager

Proprietary Information Statement:

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APPENDIX IV

EXAMPLE

STANDARD OPERATING PROCEDURE
CIRCULATION LIST

Distributed Copies

Name/Location	SOP No.	SOP Title	Revision #/Date	Supersedes	Control Copy No.*	Date Distributed	Date Returned

I have been issued the listed SOP(s). I understand that I must comply with the instructions of this SOP to perform my work for this process. I shall document any deviations which occur from this SOP and bring them to the attention of my supervisor. I understand that, at any time, I can bring to the attention of my supervisor or the QA Department any questions which I have during the performance of my duties according to this SOP.

Signed_____ Date_____

Name (please print) _____

* U = Uncontrolled copy

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APPENDIX V

OPTIONAL

EXAMPLE

STANDARD OPERATING PROCEDURE
RECEIPT

I have been issued the listed SOP(s). I understand that I must comply with the instructions of this SOP to perform my work for this process. I shall document any deviations which occur from this SOP and bring them to the attention of my supervisor. I understand that, at any time, I can bring to the attention of my supervisor or the QA Department any questions which I have during the performance of my duties according to this SOP.

SOP No.:	Title	Rev. No.	Rev. Date	Control Copy No.

Signed _____ Date _____

Name (please print) _____

(CAN BE DONE IN ELECTRONIC FORMAT)

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APPENDIX VI

SOP FORMAT
ANALYTICAL METHOD SOP

1.0 SCOPE AND APPLICATION

Identify the procedure.
List the analytes and CAS number. (If more than 5 analytes, attach as appendix.)
Identify type of samples for which procedure is applicable.
State sensitivity range/working range of the procedure.
List DQO's measured in method.
{This method contains details on Precision and Accuracy in [Matrix]}
Optional - List associated QuantIMs method codes if applicable

2.0 SUMMARY OF METHOD

Summarize the method in a few paragraphs. The purpose of the summary is to provide a succinct overview of the technique to aid the reviewer or data user in evaluating the method and the data. List sample volume, extraction, digestion, concentration and other preparation steps employed, the analytical instrumentation and detector system(s) and the techniques used for quantitative determinations.

3.0 DEFINITIONS

Method Specific terms only or variations which differ from more commonly used terms (e.g., batch). Others refer to glossary in QAMP.

4.0 INTERFERENCES

State known interferences
Describe effect of Interferents.

5.0 SAFETY

Include Health and Safety precautions describing personal protective equipment (PPE) required for the safe performance of this procedure along with any pertinent sample and chemical handling cautions and warnings. The following standard text must be used.

NOTE: Statements in parentheses {} are optional and may be left out **ONLY** if they are known not to apply to the procedure.

For the Safety section of SOPs that may not directly involve laboratory operations, use the following paragraph:

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Normal office dependent safety precautions must be taken in performing this SOP. If personnel are required to perform any portion of the procedure in laboratory areas, appropriate personal protective equipment and precautions must be utilized.

For the Safety section of SOPs describing laboratory activities, use the following text:

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

Eye protection that satisfies ANSI Z87.1 (as per the Chemical Hygiene Plan), laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately. {VITON gloves may be worn when halogenated solvents are used for extractions or sample preparation. Nitrile gloves may be used when other solvents are handled. Latex gloves should not be worn when handling organic solvents. [Note: VITON is readily degraded by acetone.]

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

{Chemicals that have been classified as **carcinogens**, or **potential carcinogens**, under OSHA include: (insert list of chemicals <u>specific to the procedure</u>, for example, benzene, chloroform, methylene chloride, PCBs, etc.)}

{Chemicals known to be **flammable** are: (insert a list of chemicals <u>specific to the procedure</u>, for example, benzene, methanol, etc.)}

{The following materials are known to be **corrosive**: (insert a list of corrosive materials <u>specific to the procedure</u>, for example, sulfuric acid, hydrofluoric acid, sodium hydroxide, etc.)}

{The following materials are known to be **oxidizing agents**: (insert a list of any oxidizing agents <u>specific to the procedure</u>, for example, potassium permanganate, potassium persulfate, etc.)}

{**Mercury** is a highly toxic compound that must be handled with care. The analyst must be aware of the handling and clean-up techniques before using this material.}

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{**DIAZOMETHANE is an extremely toxic gas with an explosion potential. Since the explosion potential is catalyzed by imperfections in glass, generation of diazomethane must be carried out in glassware free from etches, cracks, chips, and which does not have ground glass joints. Solutions of diazomethane will be kept at temperatures below 90°C. Diazomethane must be generated and handled in a fume hood.** [Note: Diazomethane has not been classed as a carcinogen under the current OSHA definition.]}

{**Magnesium sulfate** has been reported to be a **reproductive toxin**. This toxicity classification should be given to other materials as necessary.}

{Hearing protection is required when ultrasonic digestion is carried out.}

{The following materials are known as sources of radiation: insert a list of radioactive materials specific to the procedure, for example, ^{232}U. ^{229}Th, etc.)

NOTE: Other specific information and specific hazards of other chemicals used in the procedure may be included at this point.

Exposure to chemicals must be maintained **as low as reasonably achievable**, therefore, unless they are known to be non-hazardous, all samples must be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

It is recommended that neat standards be purchased only as a last resort. The preparation of standards from neat materials and reagents {as well as glassware cleaning procedures that involve solvents such as methylene chloride} should be conducted in a fume hood with the sash closed as far as the operations will permit. Standards in solution may be diluted in the open lab when syringes and the like are used.

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

6.0 EQUIPMENT AND SUPPLIES

Use generic language wherever possible. However, for specific equipment such as GC columns, do not assume equivalency of equipment that was not specifically evaluated, and clearly state what equipment and supplies were tested. Include all measurement glassware and equipment. Clearly specify all measurement devices (pipettes, grades, etc.). List additional

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general glassware required to perform the procedure; this should not be so specific to limit substitutions.

7.0 REAGENTS AND STANDARDS

Provide sufficient details on the concentration and preparation of reagents and standards to allow the work to be duplicated, but avoid lengthy discussions of common procedures. If standards prep is in another SOP, simply reference - do not repeat in method SOP. As a reminder, hazards for specific chemicals or operations (e.g., preparation of dilute acids) may be included in parentheses the first time a reagent is used. Include any special safety requirements for handling a solution/neat material.

8.0 SAMPLE COLLECTION, PRESENTATION AND STORAGE

Describe the following:
Sample Collection
Shipment
Preservation
Storage Conditions
Holding Times

9.0 QUALITY CONTROL

Use tables summarizing the types and frequency of QC and the applicable corrective actions in the event that QC are unacceptable. Refer to QA-003 as a reference.

10.0 CALIBRATION AND STANDARDIZATION

Discuss initial calibration and tune (GC/MS and ICP/MS) procedures.
Include initial and continuing calibration verification procedures .
Discuss requirements for retention time window generation for GC and IC analyses.
Discuss corrective actions.
Include performance specifications.

11.0 PROCEDURE

Provide a general description of the sample processing and instrumental analysis steps. Discuss those steps that are essential to the process to enable the analyst to perform the task but avoid unnecessarily restrictive instructions. Include specific safety instructions for extremely hazardous or dangerous steps.

Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described. Any routine method deviations must be noted in Section 17.

12.0 DATA ANALYSIS AND CALCULATIONS

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Describe Qualitative and Quantitation Limits of the Method. Provide equations and give example calculation.

Show calculations for final sample results from instrument data and for QC criteria (RPD, %Recovery). Discuss confirmation requirements. Discuss data review. (Include data review checklist in Section 17 Miscellaneous.)

13.0 METHOD PERFORMANCE

Differentiate routine analytes from all possible analytes. [Two tables - routine and possible by method should be in the Appendix.] List reporting limits in Appendix. Training/Performance Requirements of Analysts must be stated (see boilerplate below).

Training Qualification:

The group/team leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience.

14.0 POLLUTION PREVENTION

Describe aspects of this method that minimize or prevent pollution. {Example: "This method uses the Corning accelerated one-step extractor concentrator that uses only 100 ml of solvent versus 500 ml by other procedures."}

15.0 WASTE MANAGEMENT

Waste generated in the procedure must be segregated and disposed according to the facility hazardous waste procedures. The Environmental Health and Safety Coordinator or Director should be contacted if additional information is required. Operation-specific information on waste management shall be contained in this section. Specific waste streams and disposal requirements must be included.

16.0 REFERENCES

Reference Method(s) first, then STL/Operation-Specific SOPs with other references at end.

17.0 MISCELLANEOUS (TABLES, APPENDICES, ETC.)

This section is <u>required</u> for each SOP. Information, in addition to that cited below, may be presented as part of this section. (These are <u>not</u> to be added as additional <u>sections</u>.)

The following items can be included:

1. Deviations from referenced method.
2. List of other SOPs cross-referenced in SOP.
3. Operation-specific information (if applicable) required to implement SOP.
4. Tables or figures referenced in body of SOP.
5. Record Management and Documentation. (Sample benchsheets, logbook pages, data review checklists, etc.).
6. Method appendices.
7. Procedure Flow Diagram, if applicable (mandatory last page(s)).

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APPENDIX VII
SOP FORMAT

SOPs Describing Administrative, Non-Method Laboratory Procedures, or Equipment Operation and Maintenance SOPs

(Example: Facility Security, Balance Calibration, Sample Log-In, etc.)

1.0 Purpose

General description of the activity described in the SOP

2.0 Responsibilities

Describes functionally who is responsible for specific aspects of the activity, by title or function.

3.0 Safety

Describes pertinent safety information. Include Health and Safety precautions describing personal protective equipment required for the safe performance of this procedure along with any pertinent sample and chemical handling cautions and warnings. For detailed language, see Analytical Method Format - Section 5.0.

4.0 Procedure

Detailed steps required to perform the procedure. Discuss those steps that are essential to the process to enable the associate to perform the task, but avoid unnecessarily restrictive instructions. The following language must be included in the procedure section:

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

5.0 Definitions

Include procedure specific terms which differ from more commonly used terms and are not described in the glossary of the STL QAMP.

6.0 Appendices

Include any additional information, tables, flowcharts, etc.

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APPENDIX VIII
SOP FORMAT

Laboratory Reagent or Standard Preparation SOP

1.0 Reagent or standard name and its use

2.0 Safety

3.0 Constituents and concentration

4.0 Shelf Life

5.0 Procedure description including preparation, documentation and verification requirements

6.0 Appendices (optional)

Any additional information may be included as an appendix.

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APPENDIX IX

SOP CHANGE FORM FOR LABORATORY-SPECIFIC SOPS
STL_____ SOP CHANGE FORM

SOP NUMBER:
SOP TITLE:
SOP SECTIONS AFFECTED BY CHANGE:
REASON FOR ADDITION OR CHANGE:
CHANGE EFFECTIVE FROM:
CHANGE OR ADDITION (SPECIFY SECTION; USE ADDITIONAL SHEETS IF NECESSARY)
SUBMITTED BY/DATE:
***APPROVED BY:**
Technical Reviewer Signature **Date:**
Environmental Health & Safety Signature **Date:**
QA Signature **Date:**
Management Signature **Date:**

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APPENDIX X

SOP CHANGE FORM FOR CORPORATE-METHOD SOPS

SOP CHANGE FORM

SOP NUMBER:
SOP TITLE:
SOP SECTIONS AFFECTED BY CHANGE:
REASON FOR ADDITION OR CHANGE:
CHANGE EFFECTIVE FROM:
CHANGE OR ADDITION (SPECIFY SECTION; USE ADDITIONAL SHEETS IF NECESSARY)
SUBMITTED BY/DATE:
APPROVED BY:

Technical Reviewer Signature	Date
Environmental Health & Safety Signature	Date
QA Signature	Date
Management Signature	Date

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APPENDIX XI

EXAMPLE
WORK INSTRUCTIONS FORM

STL Inc.

WORK INSTRUCTIONS

CLIENT:	**EFFECTIVE DATE:**
PROJECT:	**SITE: N/A**
APPROVED BY:	**DATE:**

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APPENDIX XII

EXAMPLE
SOP REVIEW FORM

STL Inc.
SOP REVIEW FORM

SOP NUMBER:	
SOP TITLE:	
The subject SOP has undergone the required peer/management review. No modifications are necessary at this point. The SOP will be reviewed two years from the date indicated below.	
REVIEWED BY/DATE:	
***APPROVED BY:**	
_____ Technical Review Signature	_____ Date
_____ Environmental Health and Safety Signature	_____ Date
_____ QA Manager Signature	_____ Date
_____ Management Signature	_____ Date

*Must be same signature authorities of SOP being revised.

Control Copy Number: _____

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QA-003

Quality Control Program

APPROVAL:

Director, Quality Assurance | Vice President, Operations Services

STL Incorporated

POLICY NAME

COMPANY-WIDE

STL Quality Control Program

Rev. 2, 07/13/98
Supersedes: Revision 1

Policy #: QA-003

OBJECTIVE:

This policy describes the **STL** program of routine analytical quality control (QC) activities. The objective is to generate QC data that demonstrate that the analytical process is in control and that the data meet client and method requirements.

SCOPE:

This policy is to be enforced and followed throughout the company.

POLICY:

1.0 Assessments of QC data relative to control limits determine the acceptability of sample test results. Whenever control criteria are not met, the data must be evaluated to determine appropriate corrective action. The initial evaluation is made by the analyst, frequently in

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conjunction with data review software and /or senior analysts or supervisors. Further technical evaluation of the data or data review software output is conducted by second-party data reviewers. Corrective action decisions, particularly whether or not to reanalyze samples, should be done in consultation with the client to the extent possible when operating under project-specific QA plans. Requirements for assessment and corrective action are described in the attachments to this policy. Details concerning technical data review and documentation of the reviews are described in "Technical Data Review Requirements" (Policy QA-012).

2.0 STL standard QC program is to be communicated to the client prior to acceptance of work. At the same time, every effort must be made to understand clients' special project requirements. Generally, laboratory project managers serve as a liaison between the clients and the laboratory staff to ensure that requirements are properly communicated in writing to both parties. In the event that alternative QC procedures are not specified by our clients, these standard QC protocols must be followed to ensure the generation of legally and scientifically defensible analytical data.

3.0 Successful implementation of this QC program requires that it is clearly understood by all **STL** staff. Training based on this policy will be conducted at each **STL** facility and provided to new personnel as appropriate for their functions.

4.0 STL QC program applies to the following regulatory programs:

4.1 RCRA and SW-846 Methods - All routine analytical projects performed using SW-846 methods must comply with the requirements described in STL Quality Assurance Management Plan (QAMP, Tables 8.4-2 through 8.4-6) and Attachment I to this policy. The Quality Control sections of analytical standard operating procedures (SOPs) referencing SW-846 methods must be consistent with the requirements in Attachment I

4.2 CWA and 40 CFR Part 136 Listed Methods - Any analytical work conducted in support of an NPDES permit or other Clean Water Act compliance activities, must meet the quality control specifications shown in STL QAMP tables 8.4-2 through 8.4-6. The quality control requirements for the specific methods listed in the QAMP define the minimum requirements that must be given in laboratory analytical SOPs.

4.3 CERCLA and CLP Methods - Projects performed using USEPA Contract Laboratory Program (CLP) methods must comply with the quality control specifications shown in STL Quality Assurance Management Plan (QAMP) table 8.4-7. The quality control sections of the SOPs referencing CLP protocols must be consistent with the QAMP and the relevant CLP Statement of Work.

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4.4 Other Programs or Projects with Clearly Defined QC Requirements

4.4.1 The differences between STL standard QC program and special project requirements must be specified in project documents. These documents may include Quality Assurance Project Plans (QAPjPs), Quality Assurance Program Plans (QAPPs), Sampling and Analysis Plans (SAPs), project-specific Quality Assurance Summaries (QASs), SOPs, contracts, or other approved documents.

4.4.2 Documents describing special project requirements must be reviewed and approved by appropriate QA and operations staff.

4.4.3 If the special project requirements appear to result in modifications that contradict federal or state regulatory requirements, the variance must be noted in writing and communicated to the client. A record of this communication must be retained as a permanent part of the project file.

4.4.4 Any special client's project requirements must be communicated to STL analysts in advance of releasing samples for analysis, and the work must be clearly differentiated in the analytical documentation, otherwise Attachment I requirements will be followed.

4.5. Projects Without Specific QC Requirements

Any projects for which no specific QC program is specified, regardless of the source of the analytical methods being used, must follow the requirements shown in Attachment I.

4.6 Radiochemistry QC

General QC requirements for radiochemistry analyses are provided in Attachment II.

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ATTACHMENT I
STL QUALITY CONTROL PROGRAM

1.0 Introduction

This quality control (QC) program is based on the requirements in "Test Methods for Evaluating Solid Waste", USEPA SW-846, Third Edition with promulgated updates. It applies whenever SW-846 analytical methods are used. It also applies in whole or in part whenever project requirements fail to specify some aspect of QC practices described here. It does not apply when other well defined QC programs (e.g. CLP, CLP-like, AFCEE, ACOE, or NFESC) are specified. This policy represents STL base QC program for environmental analyses.

Details concerning instrument calibrations, tunes, and QC that are required for specific methods (e.g., interference check samples for ICP and isotopic spikes for dioxin procedures) are not given here. Refer to the method standard operating procedures (SOPs) for information about the frequency, assessment and corrective action required for additional QC elements.

2.0 Definitions

2.1 QC Batch - The QC batch is a set of up to 20 field samples plus associated laboratory QC samples that are similar in composition (matrix) and that are processed within the same time period using the same reagent and standard lots.

2.2 Surrogates - Surrogates are organic compounds similar in chemical behavior to the target analytes, but that are not normally found in environmental samples. Surrogates are added to all samples in a batch to monitor the effects of both the matrix and the analytical process on accuracy.

2.3 Method Blank - The method blank (MB) is a control sample prepared using the same reagents used for the samples. As part of a QC batch, it accompanies the samples through all steps of the analytical procedure. The method blank is used to monitor the level of contamination introduced to a batch of samples as a result of processing in the laboratory.

2.4 Instrument/Calibration Blank - The instrument blank is prepared using the same solvents and reagents (e.g. hexane, methylene chloride, or reagent water) used to dilute the prepared sample extracts or digests. Unlike the method blank, it is analyzed without being subject to the preparation steps of the analytical procedure. It is used to monitor laboratory or reagent contamination introduced at the instrumental analysis phase of work. For procedures without a separate preparation step, an instrument blank is equivalent to the method blank, and serves the same purpose.

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2.5 Laboratory Control Sample - A laboratory control sample (LCS) is prepared using a well characterized matrix (e.g. reagent water or Ottawa sand) that is spiked, with known amounts of representative analytes. Alternate matrices (e.g. glass beads) may be used for soil analyses when Ottawa sand is not appropriate. As part of a QC batch, it accompanies the samples through all steps of the analytical process. The LCS is used to monitor the accuracy of the analytical process independent of possible interference effects due to sample matrix.

2.6 Matrix Spike and Matrix Spike Duplicate

2.6.1 Matrix Spike - A matrix spike (MS) is a replicate portion of one field sample in the QC batch that is spiked with known amounts of target analytes. An MS is spiked with the same analytes at the same concentrations that are added to the LCS. As part of the QC batch, it accompanies the field samples through all steps of the analytical process.

2.6.2 Matrix Spike Duplicate - A matrix spike duplicate (MSD) consists of an additional portion of the same sample used to prepare the MS. This portion is spiked and processed exactly as is the MS.

2.6.3 The MS and MSD results are used to determine the effect of the sample matrix on the precision and accuracy of results. Due to the potential variability of the matrix of each sample, the MS and MSD results may not have immediate bearing on any samples except the one spiked.

2.7 Sample Duplicate - A sample duplicate (DU) is a second aliquot of an environmental sample, taken from the same sample container when possible, that is processed with the first aliquot of that sample. That is, sample duplicates are processed as independent samples within the same QC batch. The sample and DU results are compared to determine the effect of the sample matrix on the precision of the analytical process. As with the MS/MSD results, the sample/DU precision results are not necessarily representative of the precision for other samples in the batch.

2.8 Duplicate Control Sample - Duplicate laboratory control samples (LCS/LCSD, also called a DCS pair) consist of a pair of LCSs analyzed within the same QC batch to monitor precision and accuracy independent of sample matrix effects. This QC sample is prepared at the request of the client and/or when insufficient sample volume is received to prepare and analyze an MS/MSD pair. DCS is intended to provide information regarding the precision of the measurement process.

3.0 Batch QC Elements & Batch Processing

3.1 A QC batch is designed to determine the quality of the analytical results obtained for a

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group of up to 20 field samples in terms of accuracy and precision. With some exceptions as described in Sections 3.6 through 3.8 below, the minimum QC elements for each QC batch are

- one method blank (MB),
- one laboratory control sample (LCS),
- one matrix spike (MS), and
- one matrix spike duplicate (MSD).

3.2 The identity of each QC batch must be documented and traceable, i.e., each batch of field samples must be clearly associated with the applicable QC samples.

3.3 To the extent possible, samples that require a preparation step should be analyzed together with their associated QC samples. If the samples in a given QC batch require separate analytical runs, the minimum batch QC in each run is an acceptable MB or instrument/calibration blank. To the extent possible, the QC samples should not be analyzed independent of the field samples on a different instrument.

3.4 For analytical procedures that do not include a separate extraction or digestion (e.g., volatile organic analysis by purge and trap), the QC batch must be analyzed sequentially using the same instrument and instrument configuration within the same calibration event. That is, the same calibration curve, calibration factors, or response factors must be in effect throughout the analysis.

3.5 Field QC samples (e.g., trip blanks, equipment rinsates, and field duplicates) count as individual samples, therefore, they add to the QC batch count. Samples that require simple reanalysis (e.g., dilutions to adjust a sample extract to the working range of the instrument), as opposed to reextraction or digestion and reanalysis, do not count as additional samples in the QC batch. For procedures without a separate preparation, a reanalysis within the same calibration event (as defined in Section 3.4) does not add to the batch count.

3.6 MS/MSD pairs are not the only acceptable means of demonstrating precision.

3.6.1 As requested by clients or required by some methods, batch precision may also be demonstrated through the analysis of sample duplicates (DUs). However, the client should be advised that a DU is less likely to provide usable precision statistics depending on the likelihood of finding concentrations below reporting limits.

3.6.2 A duplicate LCS (DCS) may be used to demonstrate method batch precision independent of client's matrix when the client has not supplied sufficient sample quantity to prepare an MS, MSD or DU, if requested by the client.

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3.6.3 On-going monitoring of LCS results can be used to determine long-term (a.k.a., between batch) precision and accuracy for a method.

3.7 Some methods including isotope-dilution methods, pH and ignitability for example, do not use all of the QC elements listed in Section 3.1. Method exceptions to these requirements are listed in the QC tables of STL QAMP and in the laboratory's analytical SOPs.

3.8 Deviations from these QC elements must either be noted in project planning documents (QAPPs, QAPjPs, SAPs, SOWs, QAS, or equivalent) or in a NCM.

4.0 Data Evaluation and Corrective Action

4.1 General Guidelines

4.1.1 Any QC component that is outside of established control limits is considered an out-of-control event. All out-of-control events must be documented and the associated data evaluated. Depending on the specific circumstances, evaluation can lead to a variety of actions. The following sections and the flowcharts describe the appropriate corrective action for the most common QC failures. However, it is not possible to address all possible data evaluation scenarios in this policy. <u>The guiding principle for all evaluations is that the data and corrective action decisions must be defensible using STL policies, procedures or scientific evidence, and justified in the project records.</u>

4.1.2 If reanalysis for QC failures is conducted and the second analysis confirms a QC problem that is outside of the laboratory's control, further testing is not necessary. The problem must be documented and the data properly qualified in the project report.

4.1.3 QC failures that are not corrected by reanalysis are documented in NCMs or using an electronic anomaly system as described in SOP # CORP-QA-0010. This does not include QC failures due to sample matrix interferences (particularly MS, MSD and surrogate failures). These failures are a function of the method used and are normally outside of the laboratory's control; trending via NCMs is not required. Other forms (for example, data review checklists) may be used to document matrix QC failures.

4.1.4 When ongoing, systematic problems are identified, work must stop until it can be demonstrated that the system is in control again.

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4.2 Method Blank (MB) Evaluation (also see Figure 1)

4.2.1 Acceptance Criteria
All analyte concentrations in the MB must be less than or equal to the project reporting limit.

4.2.2 Corrective Action for MB Failure
The general corrective action requirement is first reanalysis of the MB, and if not resolved then repreparation and reanalysis of all samples in the QC batch.

The following special situations, while requiring documentation, may allow qualified data to be reported without reanalysis:

- method blank contaminant analyte concentration found in samples is less than the RL,
- analyte concentration in samples is greater than 20 times MB concentration, or
- the analyte is a common laboratory contaminant (see below) and the MB concentration is less than five times the RL for organic analyses or less than two times the RL for inorganic analyses.

Common Laboratory Contaminants:

Analyte	**Method**
Methylene Chloride	Volatile Organics (GC or GC/MS)
Acetone	Volatile Organics (GC or GC/MS)
2-Butanone	Volatile Organics (GC or GC/MS)
Phthalate Esters	Semi-Volatile Organics (GC or GC/MS)
Copper	Metals (ICP or GFAA)
Zinc	Metals (ICP or GFAA)
Iron	Metals (ICP or GFAA)
Lead	Metals (Trace ICP or GFAA)

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4.3 Laboratory Control Samples (LCS) Evaluation (also see Figure 2)

4.3.1 Acceptance Criteria

The LCS recovery for the control analytes must be within established control limits. The percent recovery is calculated as follows:

$$\text{LCS Percent Recovery} = \frac{X}{t} \times 100$$

Where: X = observed concentration
t = concentration of spike added

4.3.2 Corrective Action for LCS Failure

- check calculations,
- check instrument performance,
- reanalyze the LCS, and if still outside of control limits,
- reprepare and reanalyze all samples in the QC batch.

Notes: 1. It is acceptable to report the data, if the LCS recovery is out high and analyte of concern was not detected in any of the samples. Successful MS/MSD and surrogate recoveries may also provide evidence of control of accuracy, but this would be decided on a case-by-case basis and only with client approval.

2. In the case of volatile analyses, if the LCS fails, it may be reprepared and reanalyzed within the same tune period.

3. In the case where all target requested analytes are within control, but some other LCS compounds are out of control, the LCS may still be considered acceptable for reporting.

4.4 Duplicate Laboratory Control Samples (LCS/LCSD or DCS) Evaluation (also see Figure 2)

4.4.1 Acceptance Criteria

The recovery for each spike of the pair must be within established control limits. The formula used to calculate LCSD recoveries is the same as the formula for LCS spike recoveries. If a batch includes samples requiring LCS control and samples requiring DCS control, the LCS used will be the first LCS that passes control criteria.

The relative percent difference (RPD) for the pair is calculated as follows:

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$$\text{RPD} = \left[\frac{|X_1 - X_2|}{\frac{(X_1 + X_2)}{2}} \right] \times 100$$

Where: X_1 = first observed concentration

X_2 = second observed concentration

4.4.2 Corrective Action for LCS/LCSD Recovery (Accuracy) Failure

- check calculations,
- check instrument performance,
- reanalyze and/or reprepare and reanalyze all samples in the QC batch.

Note: If either LCS/LCSD spikes fails and the batch cannot be reanalyzed, the failure must be documented and noted in the final report.Also see notes under Section 4.3.2.

4.4.3 Corrective Action for LCSD Precision Failure

- check calculations;
- check instrument performance;
- if the RPD is out of control but both accuracy recoveries are within acceptance criteria, prepare an NCM, and qualify report.

Note: Because LCS/LCSD limits are based on the standard deviation of data collected over time and include long-term precision, it would be unusual to fail precision limits while meeting accuracy limits. If this occurs with any frequency, control limits should be reevaluated.

4.5 Surrogate Evaluation (also see Figure 3)

4.5.1 Acceptance Criteria

Surrogate recoveries must be within established control limits. Method QC (MB, LCS, and/or LCSD) results are not acceptable unless the surrogate recoveries for those QC samples are within control limits. If MS/MSD, DU or field samples require dilutions beyond the threshold stated in the analytical SOPs, routine surrogate control limits do not apply and recoveries are not evaluated. This should be noted in the final report. The recovery is calculated as follows:

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$$\text{Surrogate Percent Recovery} = \frac{X}{t} \times 100$$

Where: X = observed concentration
t = concentration of surrogate added

4.5.2 Corrective Action

4.5.2.1 Surrogate Failures in MB, LCS, or LCSD

- check calculation and instrument performance,
- reanalyze QC sample and/or reanalyze all samples in the QC batch.

Note: Unless otherwise specified by the client, it may be possible to report qualified results if method QC surrogate recoveries are biased high and analytes were not detected in the field samples. However, all other QC requirements would have to be met and the failure would have to be noted in the final report.

4.5.2.2 Surrogate Failures in Field Samples or MS/MSD

- check calculation and instrument performance;
- evaluate objective evidence of matrix interference (e.g. heterogeneous sample, interfering compounds seen on chromatograms, or interference demonstrated by prior analyses);
- document the failure and note it on the final report;

Note: Some client programs require reanalysis to confirm matrix interferences. Check special project instructions for this corrective action.

4.6 Matrix Spike and Matrix Spike Duplicates (MS/MSD) Evaluation (also see Figure 4)

4.6.1 Acceptance Criteria
MS and MSD recoveries and RPD should be within established control limits. If MS or MSD samples require dilutions beyond the threshold stated in the analytical SOPs, routine control limits do not apply and recoveries are not evaluated, but this should be noted in the final report. The MS and MSD recoveries are calculated as follows:

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$$\text{MS or MSD Percent Recovery} = \left[\frac{X_s - X}{t}\right] \times 100$$

Where: X = observed concentration in unspiked sample
X_s = observed concentration in spiked sample
t = concentration of spike added

Notes: 1. If sample result is ND, $X = 0$ when no values reported below RL. If sample result is reported as a value <RL, X = reported value.
2. CLP forms software uses observed recovery, not concentrations.

RPD is defined in Section 4.4.1.

4.6.2 Corrective Action for MS/MSD or MS/MSD RPD Failure (assuming that the LCS is in control)

- check calculation and instrument performance,
- consider objective evidence of matrix interference (e.g. heterogeneous sample, interfering compounds seen on chromatograms, or interference demonstrated by prior analyses);
- document the failure and note on final report;

Note: Some client programs require reanalysis to confirm matrix interferences. Check special project requirements for this corrective action.

4.7 Sample Duplicate (DU)

4.7.1 Acceptance Criteria
The RPD for the sample and its duplicate must be within established control limits. The RPD is the same as for the MS/MSD (see 4.6.1 above).

4.7.2 Corrective Action for DU Failure

- check calculation and instrument performance,
- document the QC failure and note on the final report.

5.0 Establishing QC Acceptance Limits

5.1 Selecting the Data Set
For new procedures, published method limits can be used until sufficient QC data are acquired (minimum of 20 to 30 data points recommended). However, the published limits may not be appropriate if they are based on a single-operator or single-laboratory study. In this case, the QA Manager may establish default limits until enough data is collected for laboratory established limits to be determined. For existing procedures, data collected

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over several months to a year or more can be used. Control tables or control charts are used together with the calculated mean and standard deviation to determine if the data set being considered are free of trends and are representative. If it appears that the data include gross outliers, outlier tests such as the Grubbs Test, Dixon Test (for 20 or fewer data points), or Rule-of-Huge-Error Test can be used to justify eliminating individual data points. Laboratory established limits must be reevaluated at least annually.

5.2 Calculating Laboratory Statistical Performance

Accuracy: mean recovery $\pm 3s$
Precision: zero to (mean RPD + 3s)

Where: s = standard deviation

If there are insufficient MS/MSD data available to calculate limits, LCS/LCSD limits may be used. If there are insufficient sample surrogate recovery data available to calculate limits, method limits may be used, if available. For methods, matrices, and/or analytes with very limited data, interim limits should be established using available data or by analogy to similar methods or matrices.

5.3 Setting Control Limits

The working control limits to be used by the laboratory are based on evaluation of the calculated laboratory statistical performance and available interlaboratory limits provided in the reference methods. Note that some SW-846 methods only supply single-operator or single-laboratory method performance data, which should be used for guidance only and may not be appropriate for routine lab operation.

The control limits should be evaluated for systematic trends and consistency of the performance of the analytical procedure at least annually or whenever new patterns of performance are observed in the laboratory data (i.e. new methods, equipment, etc.). When evaluating current "laboratory-generated limits" against historical "laboratory-generated limits", the laboratory QA manager should investigate any significant changes in "laboratory-generated mean" and "laboratory-generated range" and should attempt to identify the cause before making any changes to the laboratory limits. If the recalculated limits are consistent with the historical limits, the historical limits may remain unchanged.

Notes:
1. Laboratory-generated mean = statistical mean (i.e. $\Sigma x_i / n$)
   Laboratory-generated range = statistical ranges indicated in the previous section
2. If the laboratory-generated mean is within ± 10% of the historical mean, the two means are not significantly different and no investigation of cause of change would be necessary.
3. If the in-house calculated data lead to limits that are significantly tighter than both the guidance limits and/or the calibration acceptance criteria for the method, the laboratory

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can default to using the laboratory-generated mean ± calibration acceptance limit. Unreasonably tight statistical limits can result from the exclusion of unacceptable results from the database. If investigation demonstrates that this is happening, the laboratory's data entry systems should be improved. The lab should employ a statistical test for outlier values before excluding data points. (Reiterations of outlier tests lead to narrower limits and should be used with caution.)

4. If the decision is to use guidance limits from the method, the laboratory should investigate procedural improvements leading to better performance.

6.0 Reporting QC Data

The QC data routinely reported includes the LCS, method blank and surrogate standards. Matrix QC are reported on a project or client basis, and clients are encouraged to identify on the custody forms specific samples to be used for matrix spiking. Client reporting requirements are negotiated and documented as part of the project records. Ultimately, all reporting decisions should accommodate the client's requirements.

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Figure 1 - Method Blank Evaluation

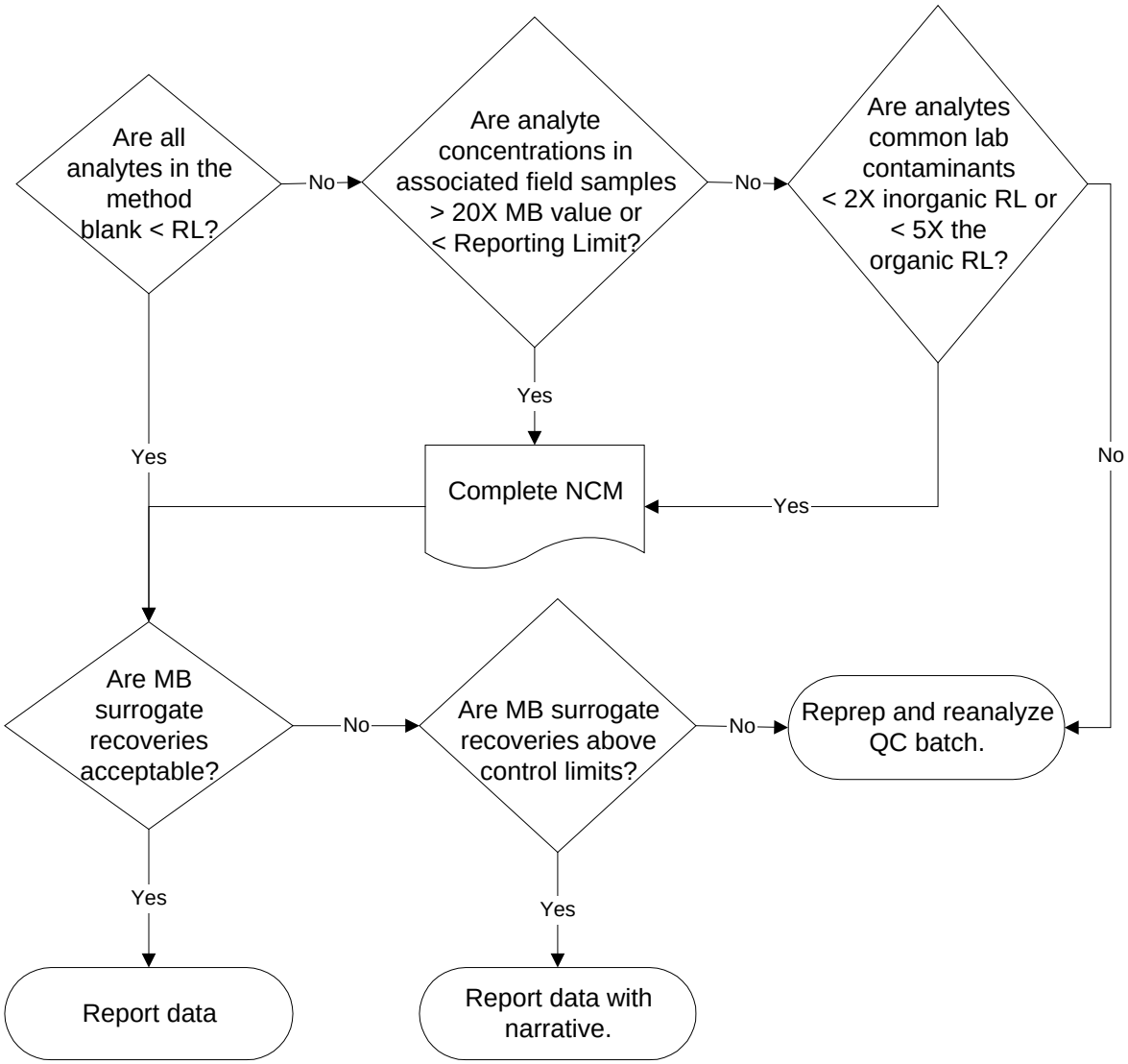

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Figure 2 - LCS/LCSD Evaluation

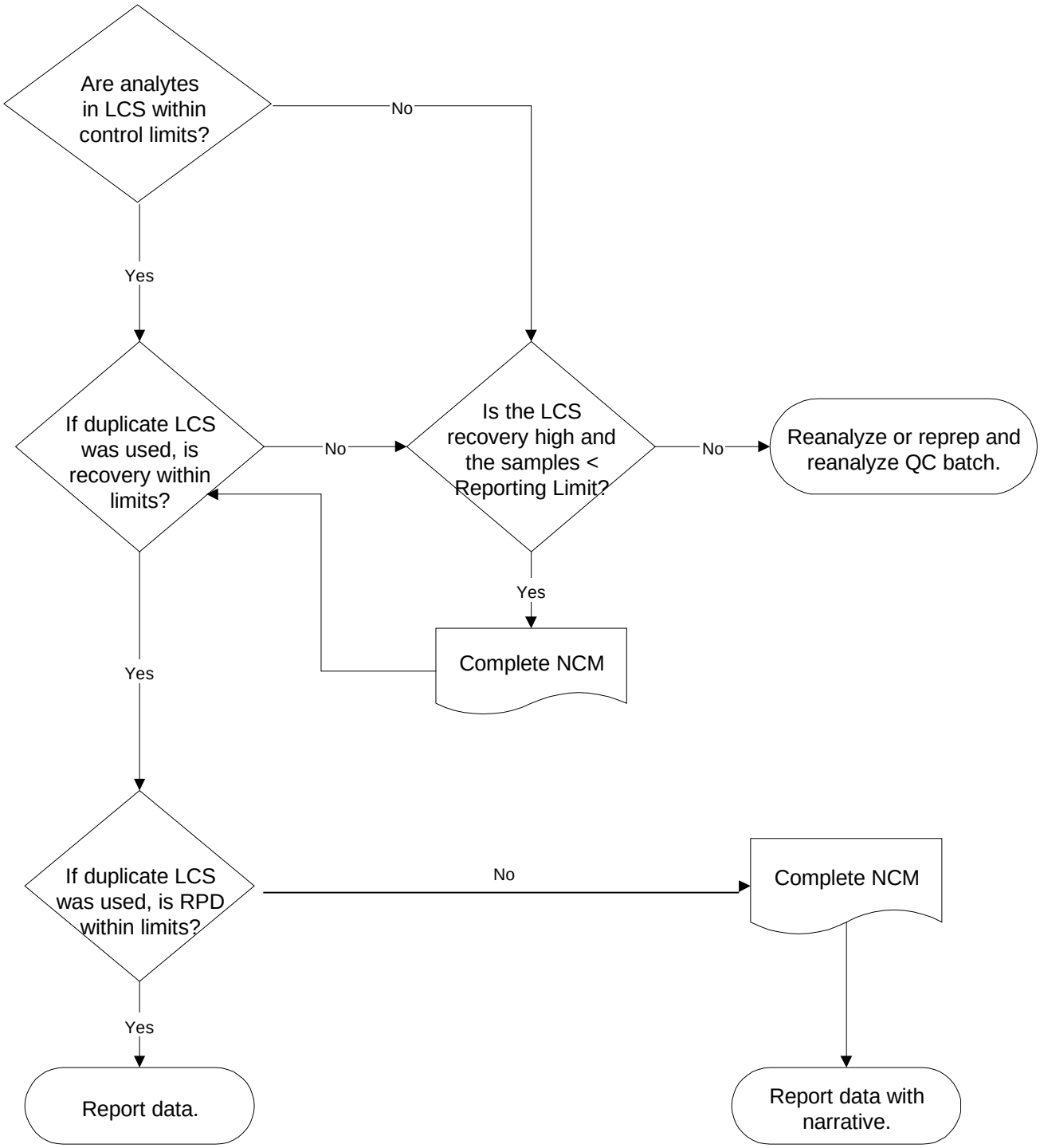

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Figure 3 - Surrogate Evaluation

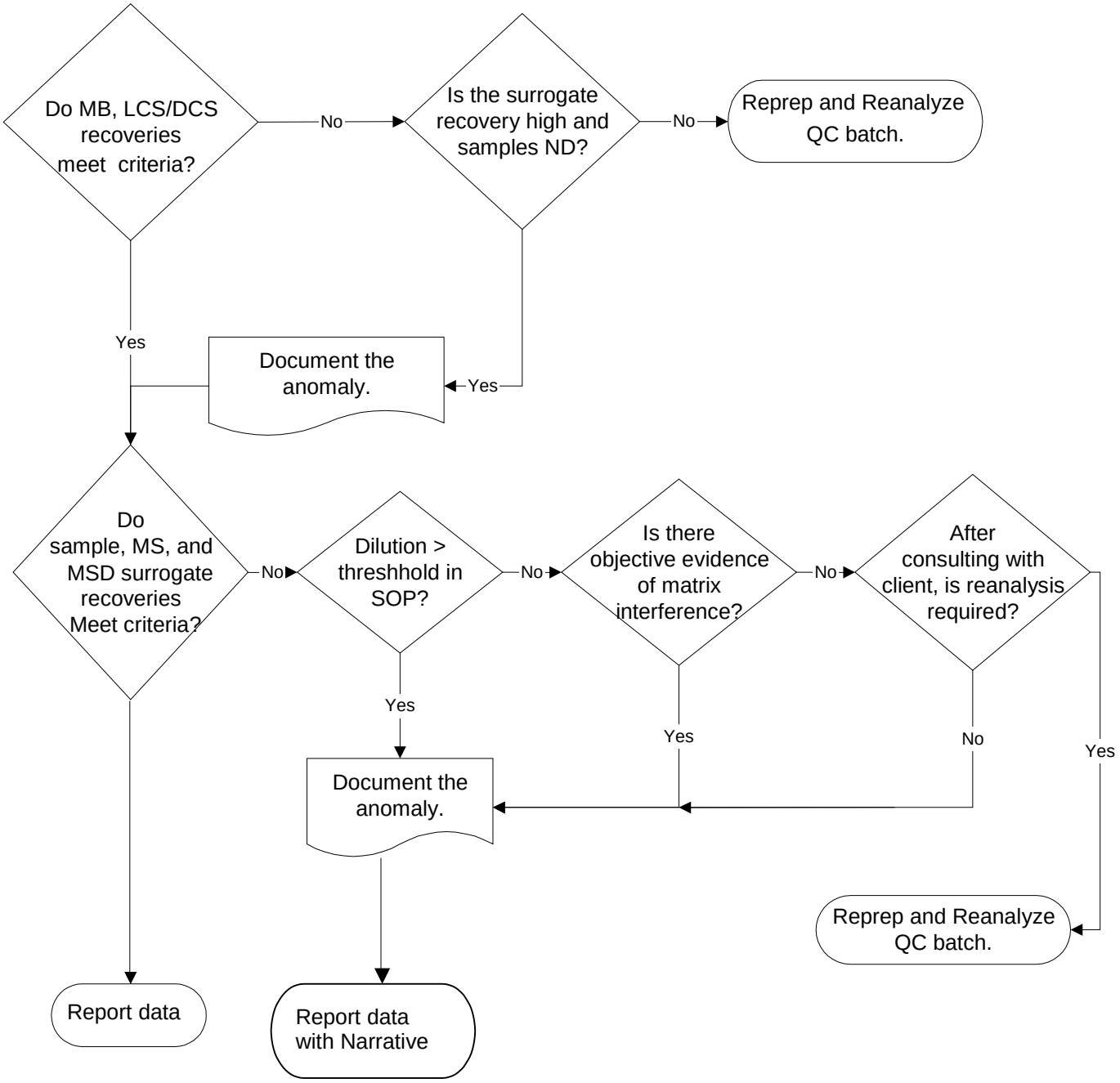

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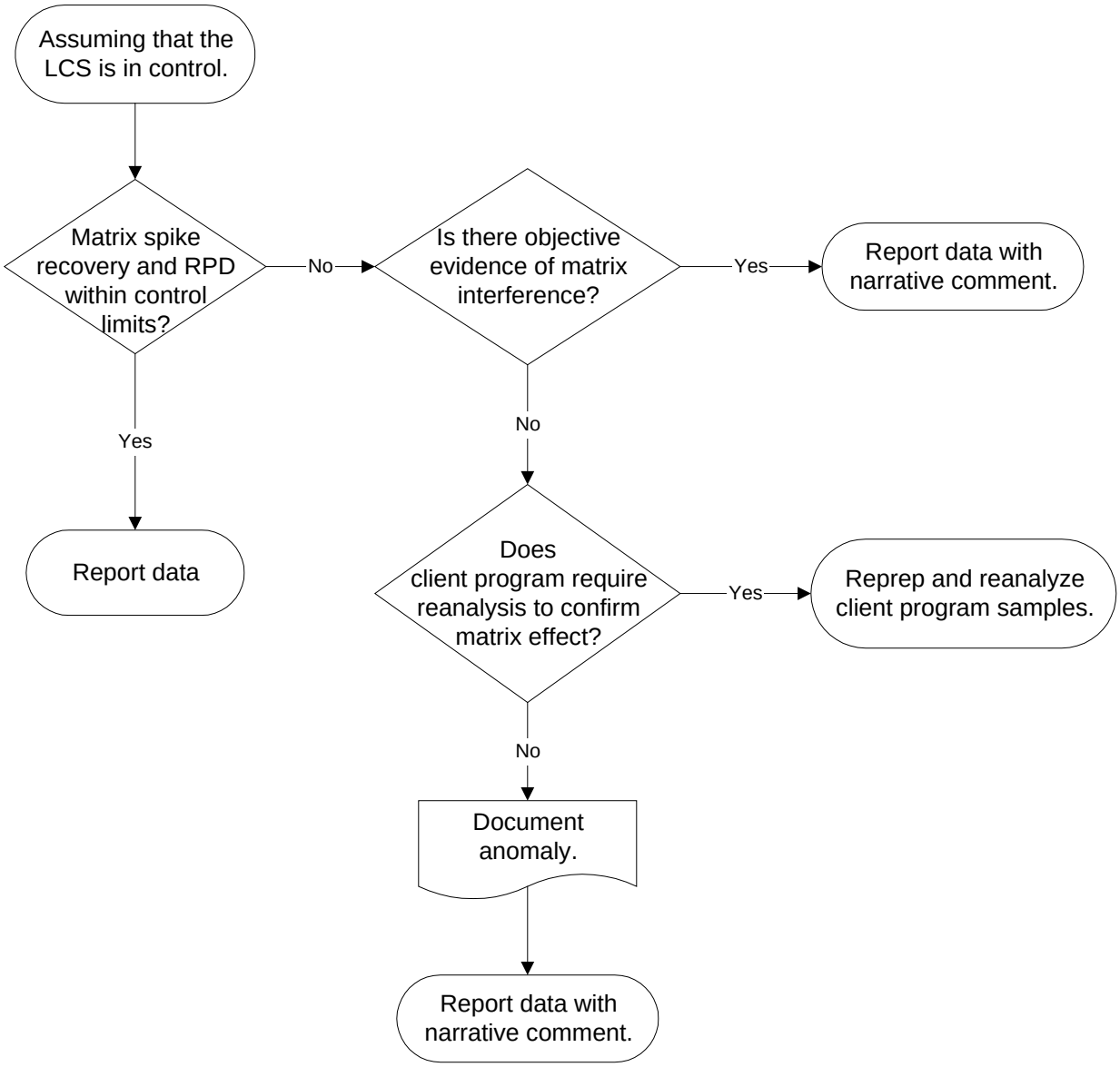
Figure 4 - Matrix Spike/Matrix Spike Duplicate Evaluation



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ATTACHMENT 2
STL RADIOCHEMISTRY QUALITY CONTROL PROGRAM

1.0 Introduction

This Attachment describes the general quality control (QC) program in place to support radiochemical analyses performed in STL laboratories. Due to the lack of a national QC program, which has been deemed to be the industry standard for radiochemistry, individual procedures may vary in their requirements. The program defined here should be taken as the minimum QC program. The details of the implementation and acceptability of the program are described in laboratory SOPs. The requirements of this Attachment may be superseded by a project Scope of work or QA program.

All data produced by the STL radiochemistry laboratories shall be reviewed by procedures described in the STL QAMP and facility SOPs. The review will be documented using a data review checklist.

2.0 Quality Control Samples

2.1 Sample batches (defined in Attachment 1 of this policy) will be accompanied by laboratory prepared QC samples. The minimum QC samples required in a batch are as follows:

2.1.1 Method Blanks: carried through the entire preparation and analysis procedure, one for each batch.

2.1.2 Laboratory Control Samples: prepared and/or analyzed with the samples, one for each batch.

2.1.3 Sample Duplicates: one for each batch, assuming sufficient sample is received.

2.2 Additional Quality Control Samples may include matrix spikes and matrix spike duplicates (matrix spike duplicates will replace sample duplicates) which are performed when contractually required. Matrix spikes are not prepared for samples which are counted directly and are subject to homogenization restrictions, such as solid samples for gamma or alpha/beta analysis.

2.3 Tracers and carriers are added to every sample, blank, and QC sample when required by the analytical method. Tracers are radioisotopes usually with the same atomic number as the target analytes, when available. Carriers are non-radioactive compounds added to assist in isolation of the target analyte(s). Both tracers and carriers, when standardized can be used to correct counting results for actual recovery of the analyte when available radioactive tracers are NIST traceable.

3.0 Acceptability Criteria/Corrective Action

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3.1 In the absence of specific client instructions, the following criteria apply. However, individual cases allow for exceptions as stated below:

3.1.1 Re-counts - Client and/or QC samples are recounted if the acceptance criteria have not been met as indicated on the Data Review Checklist and as deemed necessary by the team leader/designee. Additionally, any blank, spike or client sample may be recounted to verify a result. If the re-count result is found to be within limits, the Data Reviewer accepts the re-count data. If the re-count result is found not to be within limits, the affected samples may need to be reanalyzed.

3.1.2 Reanalysis - If sample reanalysis is necessary and/or the client provides permission, the affected samples and associated quality control samples shall be reanalyzed providing sufficient sample is available. The data of the reanalysis set shall be reviewed using the same criteria as the original data set.

3.2 Method Blank: In general, method blanks may not contain concentrations of the analyte(s) of interest above the Reporting Limit (RL) or Client-Required Detection Limit (CRDL). Specific client requirements may require other criteria for the method blank. The occurrence of an unacceptable method blank requires investigation into the source of the contamination, followed by reanalysis of the associated batch of samples with an acceptable method blank unless the activity levels of the samples are significantly higher than the blank and or the MDA or MDC. The method blank may be water for all matrices unless client requirements specify otherwise

3.3 Yield Monitors: - For QC and sample data where gravimetric (chemical) or tracer recoveries are used for yield correction, the yield of the sample must meet, in the absence of specific limits, a yield monitor recovery greater than or equal to 20% and less than or equal to 115%. Unacceptable yields for method blanks or LCS require investigation and reanalysis of the associated sample batch with acceptable QC sample yields. Unacceptable yields for a sample require reanalysis of the sample in a batch with acceptable QC sample yields. Samples may be reported with unacceptable yield only if repeat analyses indicate that a matrix effect exists that prevents acceptable yield.

3.4 Laboratory Control Sample: Criteria for acceptability of Laboratory Control Samples are set by each procedure, and may utilize historical LCS recovery data. The occurrence of an unacceptable LCS requires investigation into the source of the nonconformance, followed by reanalysis of the associated batch of samples with an acceptable LCS.

3.5 Duplicate Samples: Acceptability criteria for duplicate sample results are stated in laboratory Standard Operating Procedures, and may utilize historical duplicate RPD data. Data associated with duplicate analyses that exceed the RPD criteria are evaluated for usability, and if reported without corrective action, are flagged and noted in client reports.

3.6 Matrix Spike Recoveries: Acceptable matrix spike recovery is determined from laboratory historical data. Control limits are established for acceptability for each method and matrix at

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least annually. Samples with unacceptable matrix spike recoveries are flagged and noted in client reports unless the recovery can be shown to be due to laboratory error.

4.0 MDAs/MDCs

4.1 All radiochemical results are reported with both a sample-specific Minimum Detectable Activity (MDA) or Minimum Detectable Concentration (MDC) and an associated error. Formulas for calculating the MDA or MDC and the error are given in the Standard Operating Procedures. If the sample MDA/MDC is greater than the RL or CRDL, the Data Reviewer shall examine the sample volume/weight, counting time, and detector efficiency. The Data Reviewer shall decide if the sample should be recounted, reanalyzed, or the data accepted. If the sample activity exceeds the achieved MDA/MDC, no further action is necessary.

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QA-005

Determination of Method Detection Limits for Chemical Tests

APPROVAL:

Director, Quality Assurance

Vice President, Operations Services

STL Incorporated **POLICY NAME**

COMPANY WIDE **Determination of Method Detection Limits for Chemical Tests**

Rev. 3, 5/99
Supersedes: Revision 2

Policy #: QA-005

OBJECTIVE:

To describe policies and procedures relative to the determination and use of method detection limits (MDLs) for chemical tests. It is the empirically determined MDLs that provide the basis to establish STL reporting limits (RLs). This process is further delineated in the STL Policy No. QA-009.

SCOPE:

To be followed throughout the company.

POLICY:

1. MDLs must be determined annually, for aqueous and solid matrices, for primary tests performed by each STL laboratory. (See definition: MDL Annual Requirement.) This shall include all individual analytes that can be spiked except multi-analyte parameters which are mixtures of the same isomers (e.g., Aroclors) in which case representative MDLs may be

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determined. (MDLs for these multi-analyte parameters need only be determined every two years.)

2. The MDL is determined for the most commonly performed preparative method for a particular analyte and determinative method.

3. The following procedures must be used to determine the MDLs for all tests performed at STL laboratories with the following exceptions. This procedure does not apply to radiochemical methods. Methods described in the USEPA SOWs for CLP do not require MDLs. Other documented deviations from this policy (including use of alternate procedures), based on specific regulatory, method or client requirements may be made as approved by the STL Quality Assurance Director (or designee).

4. The QA Manager and senior technical staff at the facility must be consulted if there are questions regarding the procedure or data interpretation. If resolution cannot be achieved at this level, the Corporate Director of QA or Corporate Technical Director must be consulted.

5. This policy meets the requirements of NELAC Quality Systems Standard approved July 1998.

DEFINITIONS:

1. The Method Detection Limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from replicate analyses of low-level standards in a typical representative matrix (i.e., soils and waters).

2. STL Reporting Limit (RL) is the lowest level at which measurements become quantitatively meaningful. An RL is normally greater than the statistically determined MDLs. In some limited situations, RLs may be established based on maximum contaminant levels (MCLs), applicable or relevant and appropriate requirements (ARARs), or project-specific data quality objectives (DQOs).

3. Method Detection Limit Study (MDL Study) is defined as the procedures performed by the laboratory to determine the detection limit associated with the laboratory's analytical practices for a method in accordance with requirements set forth in 40CFR Part 136, Appendix B.

4. MDL Annual Requirement is that MDLs are useable from the date of analysis through the end of the following year, in which the MDLs should be either rerun or confirmed.

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5. MDL Check Sample is a clean matrix spike at a known concentration at approximately 2-3 times the MDL used to confirm the MDL through detection of the analyte using a criteria of detection as a signal 3X noise or a response distinguishable from the blank. The MDL Check Sample may be used to extend the use period of the MDL or validate an MDL after a significant process change.

PROCEDURES:

1. MDLs are determined annually, as defined above, for the primary methods in use at the laboratory for aqueous and solid matrices using the method described in 40 CFR Part 136, Appendix B. The statistical method described in Appendix B is also applied to solid samples using the appropriate preparation techniques.

2. MDLs are required for any analyte reported (that can be spiked). The only exception is multi-component analytes which have similar isomers that can be measured using a representative analyte (e.g., a mixture of Aroclor 1016 and Aroclor 1260 for all Aroclors).

3. For all aqueous tests, reagent water is to be used as the control matrix. The control matrix for solid tests will be dependent upon the test. For organic tests, Ottawa sand or sodium sulfate may be used as the control matrix for determining solid MDLs. For metals, due to the inherent problems in finding an appropriate matrix, MDL studies for the determination of metals in soil do not need to be performed. An appropriate soil MDL may be computed from the experimentally determined MDL for metals in aqueous solution. For other inorganic parameters, Ottawa sand or other inert material shall be used unless it is established that there is an interference. For any test, if an interference occurs and no suitable substitute matrix is available, no solid control matrix shall be used in completing the MDL Study.

4. If MDLs are processed independently of client samples, a method blank must be processed together with the spiked aliquots for the MDL determination and meet acceptance criteria of Policy QA-003. Note that if an analyte is detected in the blank, the blank level is not subtracted from the spiked sample results. A Laboratory Control Sample is not required when only processing spiked aliquots for the MDL determination.

5. MDLs are representative of the performance of the method in the lab and are independent of instrument (assuming the same configuration is used) and analyst. Therefore only one MDL per matrix per method needs to be determined. In cases where a client requests instrument-specific MDLs to prove that we are able to meet our MDLs on all instruments, an acceptable approach is to use historical response factors to identify the overall least sensitive instrument that meets method criteria and run MDLs on that unit. This approach will assure clients that our MDLs can be achieved by all instruments. (See STL report entitled “Routine QC Standards Used as a Guide to Conducting MDL Studies” by Larry Penfold.) Another

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approach for confirming MDLs on multiple instruments or confirmation columns is the use of the MDL Check Sample. (See Definitions: MDL Check Sample.)

6. Appendix B of 40 CFR Part 136 requires the use of seven replicates (after any outliers are removed). More than 7 replicates may be used in calculating the MDL. In this case, the appropriate student's t-value (n-1 degrees of freedom, 99% confidence level) must also be used in the calculation of the MDL. (See 40 CFR Part 136, Appendix B). The seven replicates may be analyzed on the same or different days.

7. The reasons for rejecting ANY data must be clearly documented and understood. It is not acceptable to reject points in order to generate a lower MDL.

8. Spike concentrations for the determination of MDLs are to be selected based on prior experience and knowledge of the method and the instrument. When possible, spiking at the RL is recommended. If an MDL is being determined for the first time, the concentration of the spike should be at or slightly below the lowest reporting limit anticipated for the method. Typically, the spiking levels to be used are recommended to be 1-5 times the estimated detection limit, but analyte concentrations up to 10 times the estimated detection limit may be used.

9. The analytical procedure must not be altered during the process of determining the MDL. If an analytical procedure is subsequently altered, a new MDL must be established.

10. If there are separate SOPs for performance of similar methods or multiple options within a given SOP, an MDL must only be determined for the variations of the method routinely utilized. Variations apply to differences in method due to matrix, extraction procedure (e.g., separatory funnel extraction, sonication, soxhlet, etc.) and analysis procedure (e.g., GFAA vs. ICP, etc.). The specific procedures used must be clearly documented in the MDL file. Optional cleanup steps are to be validated independently (for example use of a MDL Check Sample) and are not required to be incorporated in the MDL determination. If a cleanup is ALWAYS used, it should be incorporated in the MDL determination.

11. MDL records shall be retained by the laboratory's QA files as part of the laboratory's Quality Records. MDL records, including all raw data, are to be retained for the same period as analytical data. Current MDL summaries shall be available to the analysts. The MDL summary, for example, includes, for each analyte: the spike level, each replicate result, the mean, the standard deviation, the estimated reporting limit, date of determination, instrument ID, analyst name, and the calculated MDL.

12. MDL data must be reviewed by the QA staff or designee in accordance with this policy, before data are released for use in reporting data.

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DATA EVALUATION:

- The calculated MDL shall be evaluated to determine if a "valid MDL" was obtained. In order to be valid the MDL must be below the lowest reporting limit typically used for the method. If this relationship is not achieved, the study for the “failed” analytes should be repeated, possibly at a different spike concentration. If it is not possible to achieve an MDL below the reporting limit, the reporting limit must be elevated.

- In addition, if the analyte level in the MDL standard is less than the calculated MDL or greater than 10 times the MDL, the MDL may not truly reflect method variance at lower analyte concentrations. If this is the case, the following should be considered: (1) if this is an initial study, the MDL value should be compared to the lowest calibration standard concentration or evaluated based on response. If, for example, the MDL value is less than one-tenth the lowest calibration standard or the response is low, corrective action may consist of conducting additional MDL measurements at a different concentration. (2) If the new MDL is inconsistent with previous studies, the 40 CFR 136 protocol allows the new data to be pooled with the old data; or (3) another concern is that situation where an unrealistically low MDL concentration may not allow qualitative identification (see Section 13), then an acceptable approach is to increase the MDL to ten times less than the spiking level and flag the result on the MDL spreadsheet.

<u>Example:</u>

Spike concentration 10 µg/L

MDL - 1.3 ==> Valid
MDL - 11 ==> Invalid
MDL - 0.8 ==> Change the reported MDL to 1.0 and flag the MDL spreadsheet as “The calculated MDL was more than ten times less than the spiking level and may not be accurate. The reported MDL has been increased to exactly 10 times less than the spiking level.”

- The data should be reviewed for accuracy in terms of percent analyte recovery. Performance data from the reference method used in the determination of the MDL should be used to evaluate accuracy. Most, but not necessarily all of the analytes, should fall within these ranges. Low or high recoveries of the analyte are probably indicative of poor method performance, and the resulting calculated MDL may not be realistic. Investigation of blanks, calibrations, or preparation anomalies should

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occur to identify the problem. It may be necessary to repeat the MDL study after corrective actions are taken or with a spike at an appropriately higher concentration.

1. A calculated MDL may be at a level that does not permit qualitative identification. If this occurs, the procedure in 40 CFR Part 136, Appendix B, suggests that the MDL may be reported at a concentration that permits qualitative identification. If this is necessary, appropriate documentation (explaining in detail what was done) must be provided in the MDL file to explain how the reported MDL was obtained.

2. If the MDL is greater than the STL RL, the data must be evaluated to determine if the study is valid. If no problems can be identified (including preparation and instrument problems), a request to change the RL shall be submitted to the QA Manager.

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QA-008

Data Recording Requirements

APPROVAL:

Director, Quality Assurance

Vice President - Operations Services

STL Incorporated **POLICY NAME**

COMPANY WIDE **Data Recording Requirements**

Rev. 2, 10/5/98 Policy #: QA-008
Supersedes: Rev. 1, 10/1/96

OBJECTIVE:

This document identifies the requirements for proper documentation of data and records to ensure data completeness and integrity.

SCOPE:

To be enforced and followed throughout the company.

POLICY:

Bound logbooks (i.e., permanent, spiral or three-ring) must be used for documenting analytical instrument operations (e.g., injection/analysis/run, maintenance). All pages in permanent and spiral logs must be prenumbered. Pages inserted into three-ring notebooks must be sequentially numbered as they are added to the notebook.

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1. Preprinted, LIMS-generated forms (individual sheets that are not bound) or electronic forms may be used in place of bound logbooks for documenting sample processing operations (e.g., extraction, digestion, distillation); wet chemical tests; routine monitoring activities for reagent water system, balances, refrigerators, freezers and data review processes. Such preprinted forms must be described in an appropriate SOP.

2. Any form (used either in a bound logbook or as a loose form) used for monitoring purposes must include the acceptance range for that monitoring. If the form must be modified, it must be done through a revision approved by Quality Assurance and the Supervisor or Manager responsible for this activity and include a revision date. (Revision of Corporate SOP forms must be approved by Corporate QA and Technology.) Preprinted forms must include company name and laboratory location. For forms which may be utilized by more than one SOP, there must be a space to record or mark the actual SOP used to complete the procedure. The SOP should direct how these forms are to be used and where filed.

3. All recording of data shall be done directly on the described forms or logbooks designed for the record keeping purpose at the time of data generation. It is ***not*** acceptable to record data on loose papers, scraps of papers, or "Post-It" notes. Personal notes from training sessions and meetings may be kept in personal logs. These personal logs are exempt from this policy. Personal logs shall not be used for data recording purposes.

4. All data entries must be signed by the individual recording the data with their own signature or initials and date. If data are recorded on a single form by more than one individual, each individual must document that data which they entered with their initials and date. If one individual completes the record, only one signature is required at the time of data recording. If that same individual adds data at a later date, a second signature to document the addition is required.

5. All blank fields in logbooks or forms must be completed. If an entry is not appropriate for the particular data recording event, that blank space must be marked with a dash or "NA" (not applicable). If extra lines at the end of the data recording event are blank, and will not be used for the next set of data to be recorded, the page must be marked through with a diagonal "\" or "Z" line out to prevent addition of data at a later date. Such a mark must be dated and initialed by the person placing the mark. Sequential data recorded in tabular form should be entered in the next available line or on the next page if the previous page is Z'd out (provided the log is not closed, see item 13).

6. Computer printouts, standards certification information, or other printed record may be inserted into the logbooks, provided that no other data are covered and the information is

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properly taped into the logbook. To properly tape the article into the logbook, the analyst shall sign over the article being inserted, the tape and the logbook page so that it can be determined if something has been removed. "Post-It" notes are ***not*** an acceptable form to use to affix information to a logbook.

7. All manually recorded data entries and corrections in laboratory logbooks, data recording forms (i.e., worksheets, benchsheets), and any other analytical data-related documentation (e.g., computer printout) shall be recorded in permanent ink. Black ink is preferred, but blue or red ink may be used so long as copy quality can be assured. Each entry must be ***legible***, dark and clear enough for photocopying.

8. All data corrections to written or printed records, must be made using a single line cross-out of the error, made in such a manner that the original entry may still be read. Each correction must be dated and initialed by the person making the change. Liquid correction fluid, other correction tape, or other blocking material or obliterating techniques must ***never*** be used on any original laboratory data records. (Note: It may be necessary for such an obliteration technique to be used to protect client confidentiality information on copies of laboratory records.) All additions or notations made to written or printed data must be legibly signed (or initialed) and dated by the person making the change. For records where multiple edits are necessary (e.g., GC quantitation reports), an initial and date on the page where edits are made are sufficient.

9. Original records, additions, notations, or corrections made via computer must be clearly documented with the analyst's initials or name as part of the record. The computer record, so marked, is adequate without a physical signature provided the computer system has a security system with access controlled by password and has an audit trail, which documents any changes to that record (e.g., QuantIMS). The audit trail must be retrievable for the life of the record. If the computer system does not have such controlled access and audit trail, the record must be printed and signed (or initialed) and dated by the person generating the record. If this record is an integral part of a data package, the analyst's signature on the Level 1 data review checklist serves as the signature documentation of such a record that the same analyst generates.

10. Data entry personnel shall not edit or change any data provided to them for the purpose of report production or at the *verbal* direction of any associate. Any questions concerning the data at data entry shall be directed to the last reviewer of that data or the supervisor or group leader for the area in which the data were generated. This individual is responsible for having any necessary corrections made and documented as required.

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11. When a logbook is no longer used, but unused pages remain, a notation such as the following must be made on the first blank page after the last entries: "**LOG NO LONGER IN USE -- CLOSED ON [***date***]**". This entry must be signed and dated by the person recording it and the remainder of the page Z'd out. It is not necessary to Z out all remaining blank pages. A retired log must be removed from the area where work is actively performed. It may be used in the desk area of the laboratory if it is still needed for reference.

    All logbooks and records of routine monitoring (whether bound or on loose sheets) must be reviewed at least monthly to ensure accuracy, consistency and compliance with its SOP and this policy. This review must be performed by a supervisor, team leader, group leader or designee. At a minimum, five percent of completed pages of each logbook (i.e., injection/run/analysis logs, maintenance logs, standard preparation, balance records, temperature records, reagent water records, etc.) must be reviewed. Review is documented by signature or initials and date of the reviewer. The signature may be on every page or the reviewer can sign a single page and document the specific pages reviewed. Logbook review may be part of normal data review processes and documented on a copy of the appropriate logbook pages maintained in the laboratory records.

12. A record of each associate's signature and initials alongside their printed or typed name must be kept in the training or QA files.

13. Completed logbooks and forms must not be removed from the laboratory facilities, except for off-site archiving and except in circumstances deemed to require otherwise by current business requirements, as determined by STL facility management.

14. Record keeping and data recording practices for manual integrations are described in STL Policy QA-011.

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QA-009

Reporting Limits

APPROVAL:

Director, Quality Assurance

Vice President, Operations Services

STL Incorporated

POLICY NAME

COMPANY WIDE

Reporting Limits

Rev. 3, 01/01/99
Supersedes: Rev. 2, 03/10/97

Policy #: QA-009

OBJECTIVE:

This document describes STL policy for establishing, modifying, or updating reporting limits (RLs).

SCOPE:

To be enforced and followed throughout the company unless specific program, contract, or other approved document describes a suitable alternative practice to meet the program or client-specific RL requirements. This policy supplements the information described in the STL QAMP that describes the STL-wide policy for establishing RLs and the reporting of analytical results. At STL, the term RL is used synonymously with the term practical quantiation limit (PQL) which may be preferred by particular client programs.

Two types of analyses are not covered by this policy. Radiochemistry analyses have reporting limits based upon the Minimum Detectable Amount, described in STL Policy No. QA-007 or other specified criteria. Dioxin/furan reporting limits are described in the method SOPs.

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POLICY:

1. Establishing Reporting Limits (RLs)

Establishing an RL is part of the analytical method implementation process. STL must establish RLs for each analyte tested by a given method as described in a laboratory standard operating procedure (SOP). Significant changes to analytical processes documented in a lab SOP may require re-evaluation of the RLs.

Basis of RLs:

- RLs must be greater than the statistically based MDLs (see STL Policy QA-005 for details on MDLs). RLs are typically two to ten times the analyte MDL.
- In some situations, higher RLs may be established based on project objectives, such as maximum contaminant levels (MCLs) or applicable or relevant and appropriate requirements (ARARs), or other program objectives.
- Other technical information may be used when approved by the STL Director of Quality Assurance or designee (e.g., use of a detection limit from a published method or a regulatory level).

To the extent possible, RLs are further supported by the routine analysis of a standard at a concentration equal to or less than the RL concentration.

2. Reporting Limits in Final Analytical Reports

RLs presented in final analytical reports are adjusted based on other factors including but not limited to:

a. Dilutions
Dilutions of samples are required due to high concentrations of analytes or interferents, in which case the RL is adjusted proportionally. RLs cannot be adjusted down in order to maintain a given reporting limit for a diluted sample. If different dilutions are used, different RLs are reported.

$$\textit{Adjusted RL} = \textit{RL} \times \textit{Dilution Factor}$$

Co-elution or matrix interferences may also cause raised RLs even for undiluted samples.

b. Moisture Content of Solid Samples

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If dry weight results are requested, the reported RL will also be adjusted for each sample based on water content, as well as dilution factors. The following equation describes how these corrections are made:

$$Adjusted\ RL = \frac{RL\ x\ Dilution\ Factor}{(\%\ Solids\ /100)}$$

c. Sample Volume or Mass
In the case of insufficient sample volume or mass, the standard reporting limit may be used as an acceptable default as long as the sample volume or mass used for preparation exceeds 80% of the amount specified in the laboratory SOP. If the sample amount is less the 80% of the required amount, the RL must be adjusted for the actual sample amount used.

$$Adjusted\ RL = \frac{RL\ x\ Amount\ of\ Sample\ Used}{Required\ Sample\ Amount}$$

d. Other adjustments to the reporting limits may be required on a project-specific basis and must be approved prior to reporting by the laboratory QA Manager.

3. Project-Specific Reporting Limits (PSRLs)
Clients may request PSRLs that are different than the STL RL. These may be used provided the following requirements are met. PSRLs can be adjusted based on moisture content as described above. Adjustments for dilutions or sample amounts include consideration of the standard RL.

a. PSRL Greater Than STL RL

Adjusted PSRL = standard RL x Dilution Factor
or
Adjusted PSRL = PSRL

whichever is higher

For example, if:

Standard RL	=	10 µg/L	
PSRL	=	100 µg/L	
Dilution Factor	=	10,	then
Adjusted PSRL	=	100 µg/L	

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But if:

Standard RL	=	10 µg/L	
PSRL	=	100 µg/L	
Dilution Factor	=	20,	then
Adjusted PSRL	=	200 µg/L	

b. PSRL Less Than STL RL
The PSRL cannot be lower than the standard MDL (the EPA CLP program is the one possible exception). The client must be informed in writing (e.g., confirmation of communication, letter of agreement, QAPjP, or report narrative) of the possibility of false positive/false negative results, less accurate quantitation, and potential misidentification at the lower concentrations. The client should also be informed that some QC criteria are based on the standard reporting limits and may not be met, nor adjusted based on the lower PSRL requirement. Further, the client should be informed that second-column confirmation of results is not required for analyte levels less than the RL. If the PSRL is less than the STL RL and the sample is diluted, the adjusted PSRL equals

Adjusted PSRL = PSRL x Dilution Factor

DEFINITIONS:

1. **STL Reporting Limit (RL)** is the lowest level at which measurements become quantitatively meaningful. An RL is greater than the statistically determined MDLs. An RL is typically 2-10 times the MDL value. In some limited situations, higher RLs may be established based on maximum contaminant level (MCLs), applicable or relevant and appropriate requirements (ARARs), or project-specific data quality objectives (DQOs).

2. **Project-Specific Reporting Limit (PSRL):** PSRLs are used when project data quality objectives require an RL other than the STL RL. PSRLs tailor STL product to meet customer requirements. PSRLs may not be less than the current MDL.

PROCEDURES:

1. Each year, the laboratory Operations Staff and the Quality Assurance Staff are responsible for reviewing current MDLs relative to STL RLs to ensure the laboratory can consistently achieve established RLs. When changes are made to the RL, the Quality Assurance Manager will distribute these changes to the appropriate Operations Staff for review to ensure the laboratory can meet the new RL. Laboratory groups must ensure that all "other" supporting data systems, i.e., Target, must have the latest published STL RLs.

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2. In the event that an analyte does not have an MDL (or other technical documentation) that supports the RL or PSRL this must be reported to the Laboratory Manager and the Laboratory QA Manager.

3. The Laboratory Manager is responsible for ensuring that MDLs are performed as scheduled in accordance with STL Policy No. QA-005.

4. Project Managers must communicate with appropriate Operations Staff to ensure that when PSRLs below the RL are requested, or additional or unique compounds are requested for which there is no RL, that the requested PSRLs are supportable with a valid MDL (or other approved technical information).

5. At the initiation of a project, PMs are responsible for reviewing contractual documents or QAPjPs to ensure that RLs required can be met by the laboratory-established RLs. If discrepancies occur, the PM must negotiate the best approach for reporting data within the guidelines of this policy. Project Managers must also ensure that clients are informed of the possibility of false positives and misidentifications when reported PSRLs are below the RL (but above the MDL).

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QA-011

Acceptable Manual Integration Practices

APPROVAL:

Director, Quality Assurance | Vice President, Operations Services

STL Incorporated

POLICY NAME

COMPANY-WIDE

Acceptable Manual Integration Practices

Rev. 2, 07/15/98
Supersedes: Rev 1, 08/15/96

Policy #: QA-011

OBJECTIVE:

This document describes STL-wide policy for proper manual peak integrations and requirements for documentation and review of manual peak integrations performed during the course of analyses.

SCOPE:

This policy shall be enforced and followed throughout the company. It applies to any analytical procedure involving identification or quantitation based on peak analysis (e.g., GC, GC/MS, HPLC, IC).

POLICY:

1. Analysts and data reviewers using peak integration techniques must have completed an internal training course covering acceptable peak integration techniques. This is to ensure that integration parameters are used in a manner that minimizes the need for manual integrations, and

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that circumstances requiring manual integrations are performed in accordance with acceptable practices.

2. In some situations manual integrations are necessary to produce good chromatography, but manual integration must be performed ONLY when necessary. Manual integrations shall not be used to manipulate analytical results (commonly known as peak shaving or peak clipping) in order to meet method- or project-specific quality control (QC) acceptance criteria. Willful failure to follow this policy shall result in disciplinary action, up to and including termination (see STL Policy LEG-001). If manual integration is the only initial procedure for determining peak area (i.e. some dioxin analyses) each project shall be reviewed for proper manual integration and the approval documented by the second level reviewer on the checklist, in place of the requirements outlined in sections 4, 5 and 6.

3. The same manual integration technique must be applied **consistently** to any sample, i.e., field samples, calibration standards, calibration verification standards, and other applicable QC, etc., within the same analytical batch affected by the manual integration.

4. Any manual integration or other manipulations of a chromatographic peak or group of peaks must be documented. Documentation of the change will be done by a printout of the before* chromatogram and the after newly integrated chromatographic peak or group of peaks, including baseline if the data system can provide it. This must be documented by an initialed and dated, discernible, graphical display of the new integration, accompanied by the technical reason for the reintegration.

5. Analysts are responsible for completing the documentation before submitting the data package for second level data review. The documents shall be kept as an integral part of the raw analytical data.

6. Data reviewers shall confirm that documentation of manual integrations is complete and appropriate when it is obvious that manual integrations have been performed. This inspection shall be documented on a data review checklist used for all raw data packages. At a minimum, the following information must be reviewed:

- Manual integrations indicated on expanded scale “after” chromatograms.
- Before* chromatograms provided.
- Reintegration technique marked if available on the data system
- Technical justification for manual integration.
- Analyst’s initials and date.

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*Note: Before chromatograms for some GC/MS data systems, i.e., Target® may not require documentation if approved by QA Manager.

7. If integration indicates problems with analytical instrumentation, investigate the problem and take action to correct it.

8. Any deficiencies must be resolved with the analyst or their supervisor before the results are approved and released to the Project Managers. Any questions arising from review of the documentation must be investigated in the electronic record, when available, prior to data acceptance. Any failures to complete these requirements shall be described in a Nonconformance Memo.

9. Any concerns about violations of this policy must be reported to the facility QA Manager, the Assistant Director of QA, the Corporate Director of QA, or Corporate Counsel.

DEFINITIONS:

Integration is the determination of the area under a curve (peak).

Manual integrations include any adjustments to measurements of analytical peaks not applied equally to all applicable samples and QC parameters in an analytical batch by the data acquisition system. For the purpose of this policy, a manual integration has been performed if results for any of the analyses could not be duplicated by another analyst using the indicated calibration and standard peak integration protocol. Manual adjustments to peaks can include baseline changes, retention time window adjustments, changes to peak identification in samples (calibration standards' changes as required are exempt), manual peak height measurements, or changes to the formula used to model analytical peak areas or changes to background subtraction algorithims for GC/MS tuning. Although latest analytical instruments are equipped to perform automatic integrations, manual integrations are sometimes necessary to accurately analyze samples if peaks are poorly resolved, exhibit tailing, the baseline drifts or is noisy, or other similar situations.

Chromatograms in the context of this policy are not necessarily limited to the output of chromatography instruments or automated data systems. They can include strip charts, integrator printouts, computer screen dumps, or any graphic display of a continuous signal from an analytical detector.

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QA-014

Determination of IDL

APPROVAL:

Director, Quality Assurance

Vice President, Operations Services

STL Incorporated

POLICY NAME

COMPANY WIDE

Determination of Instrument Detection Limits

Rev. 1, 12/99
Supersedes: Rev. 0

Policy #: QA-014

OBJECTIVE:

To describe policies and procedures relative to the determination and use of instrument detection limits (IDLs) for metals, cyanide, and organics (under the NYS DEC ASP CLP protocol) tests.

SCOPE:

To be followed throughout the company, where appropriate.

POLICY:

1. IDLs are required to be performed quarterly for metals constituents and cyanide when analyses are performed in support of CERCLA (Superfund) activities or when the U.S. EPA CLP Statement of Work (SOW) protocol or NYS DEC ASP CLP are required. IDLs for organic constituents analyses are only required when analyses are performed under NYS

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DEC ASP CLP protocol. The frequency of IDLs for organics under the NYS DEC ASP CLP protocol is semiannually.

2. IDL protocol does not include sample preparation procedures and therefore an IDL is a more direct indication of instrument sensitivity. The primary distinction between an IDL and a MDL is that the IDL estimates the detection limit of the instrument, whereas the MDL estimates the detection limit for the entire analytical method by subjecting a known concentration of analyte in a suitable matrix to all method-specified processes. IDLs are not required by the SW-846 methods, except for method 6020. When required, IDLs will be performed in accordance with the procedures defined in the applicable U.S. EPA SOW, ILMO4.0 or subsequent versions and in this policy.

3. If the instrument is adjusted in anyway that may affect the IDL, a new IDL for that instrument must be determined and the results submitted for use as the established IDL for that instrument.

4. Since the MDL and the IDL are both statistically derived values using different approaches, there is no relationship of the values. The IDL may be less than, greater than, or equal to the MDL.

5. Prior to acceptance and use for reporting purposes, all data from detection limit studies and reporting limits must undergo technical review and approval by the laboratory management and QA staff.

DEFINITIONS:

1. The Instrument Detection Limit (IDL) IDL is a calculated estimate of instrument detectability defined by the USEPA Contract Laboratory Program (CLP).

2. NYS DEC ASP CLP is New York State Department of Environmental Conservation Analytical Services Protocol Contract Laboratory Program. This protocol is used under contract with NYS DEC or when work is performed for New York State under this protocol.

PROCEDURES:

1. **Requirements for Metals and Cyanide**: Before any field samples are analyzed and reported, the IDL must be determined for each instrument used for CLP work, and

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quarterly thereafter. Prepare the standard (containing each analyte in reagent water) at the required concentration, three to five times the previous instrument detection limit or the manufacturer's suggested IDL. The IDLs can be analyzed in conjunction with samples.

2. Analyze the standard with seven consecutive measurements per day on three nonconsecutive days. Each measurement must be performed as though it were a separate analytical sample. IDLs must be determined and reported for each wavelength used in the analysis of the sample.

3. For typical CLP work: The IDL is calculated by multiplying by 3, the average of the standard deviations obtained on three nonconsecutive days.

   IDL = (3) (s), where s = standard deviation

4. For NYS DEC ASP CLP: The IDL is determined by multiplying by the Students t-Test value (for n = 7) the standard deviation obtained for the analysis of a standard solution at a concentration three to five times the estimated IDL on three nonconsecutive days with a minimum of seven measurements per day. The IDL frequency is quarterly.

5. **Requirements for Organics According to NYS DEC ASP CLP**: IDLs for organic analyses are required by NYS DEC ASP CLP protocol. The seven replicates can be run on one or multiple days like the MDL. The IDL is determined by multiplying by the Students t-Test value the standard deviation obtained for minimum of seven replicate analyses of a standard solution at a concentration of three to five times the estimated IDL. The standard deviation is calculated with n-1 degrees of freedom. The IDL is calculated as follows:

   IDL = (t_{n-1}) (s), where t_{n-1} is the students t-Test value for a 99% confidence level at n-1 and n is the number of replicates. For seven replicates the t_{n-1}= 3.143 and s = standard deviation.

6. IDLs are required to be determined semiannually for organics by NYS DEC ASP CLP protocol.

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PITT-QA-0003

Glassware Prep

Controlled Copy
Copy No.: _____

OPERATION-SPECIFIC STANDARD OPERATING PROCEDURE

Title: Glassware Clean-Up for Organic/Inorganic Procedures

(SUPERSEDES: None)

Prepared by: _____

Reviewed by: _____
Technical Specialist

Approved by: _____
Quality Assurance Manager

Approved by: _____
Environmental, Health and Safety Coordinator

Approved by: _____
Laboratory Director

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1. SCOPE AND APPLICATION

1.1 The following procedures must be followed to ensure all glassware being cleaned is free of contamination. Laboratory coat, safety glasses and gloves must be worn at all times when cleaning glassware.

2. SUMMARY OF METHOD

2.1 This procedure describes the glassware cleaning practices at the Quanterra Pittsburgh laboratory.

3. DEFINITIONS

3.1 Not applicable.

4. INTERFERENCES

4.1 Not applicable.

5. SAFETY

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

5.2 Eye protection that satisfies ANSI Z87.1 (as per the Chemical Hygiene Plan), laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have become contaminated will be removed and discarded, other gloves will be cleaned immediately.

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

5.3.1 Chemicals that have been classified as **carcinogens**, or **potential carcinogens**, under OSHA include: Refer to method SOPs associated with the glassware being washed.

5.3.2 Chemicals known to be **flammable** are: Refer to method SOPs associated with the glassware being washed.

5.3.3 The following materials are known to be corrosive: Sodium Hydroxide (NaOH), Sulfuric Acid (H_2SO_4)

5.4 Exposure to chemicals must be maintained **as low as reasonably achievably**, therefore, unless they are known to be non-hazardous, all samples must be opened, transferred, and prepared in a fume hood or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

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

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

6. EQUIPMENT AND SUPPLIES

6.1 Autoclave.

6.2 Muffle oven.

6.3 180 ° C oven

6.4 Dessicator

7. REAGENTS AND STANDARDS

7.1 Soap.

7.2 DI water.

7.3 Super-Q water.

7.4 Chromic acid, it is received in a safe plastic container.

7.5 Nitric acid diluted (1: 5).

7.6 Sulfuric acid (1:4).

7.7 Aluminum foil.

8. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 Not applicable.

9. QUALITY CONTROL

9.1 Any blank contamination due to unclean glassware is subject to repreparation and reanalysis of samples.

9.2 Nonconformance & Corrective Action

9.2.1 Any deviation from this SOP is considered a nonconformance and will be documented by a Nonconformance Memo.

10. CALIBRATION AND STANDARDIZATION

10.1 Not applicable

11. PROCEDURE

12. DATA ANALYSIS AND CALCULATIONS

12.1 **Metals and Inorganic prep:**

12.1.1 Wash with soap and water.

12.1.2 Rinse with tap water.

12.1.3 Glassware must be rinsed once with DI water and once with 20 percent nitric acid (HNO_3) before the final DI rinse.

12.1.4 Rinse with DI water three times.

12.2 **General Chemistry:**

12.2.1 **Evaporating Dishes (TDS, TS):**

12.2.1.1 Scour out residue with soap and water.

12.2.1.2 Soak in chromic acid or 1:1 HCL for one hour, if needed.

12.2.1.3 Rinse three times with tap water.

12.2.1.4 Rinse three times with DI water.

12.2.1.5 Dry upside down in 180°C oven, overnight.

12.2.1.6 Remove from oven and store in dessicator.

12.2.2 Boiling Flasks (125 mL w/round glass top):

12.2.2.1 Proceed as in 12.2.1.1 - 12.2.1.4.

12.2.2.2 Place flask in muffle oven ~ 550 °C for 2 hours

12.2.2.3 Store in dessicator

12.2.3 B.O.D. bottles (300 mL round glass top):

12.2.3.1 Rinse once with tap water.

12.2.3.2 Rinse with 1:1 HCL or Chromic Acid.

12.2.3.3 Rinse with tap water three times.

12.2.3.4 Rinse with DI water three times.

12.2.3.5 Bottles may be placed in 180°C oven overnight to dry.

12.2.4 Phosphate: C.O.D. FLASKS (125 mL Erlenmeyer w/round glass top):

12.2.4.1 Rinse once with tap water.

12.2.4.2 Soak for two hours in 1:1 HCL or chromic acid.

12.2.4.3 Rinse three times with tap water.

12.2.4.4 Rinse three times with DI water.

12.2.4.5 Cover tops with aluminum foil.

12.2.4.6 Phosphate glassware is stored separately.

12.2.5 Surfactant glassware (125, 250, 500 mL separatory funnels):

12.2.5.1 Do not use any detergent !!

12.2.5.2 Rinse with 1:1 HCL or Chromic Acid

12.2.5.3 Rinse three times with tap water.

12.2.5.4 Rinse three times with DI water.

12.2.6 Phenol flasks, 1000 mL separatory funnels, Cyanide flasks:

12.2.6.1 Wash with soap and water (if needed).

12.2.6.2 Rinse with 1:1 HCL or chromic acid.

12.2.6.3 Rinse three times with tap water.

12.2.6.4 Rinse three times with DI water.

12.3 Mercury BOD bottles:

12.3.1 Same procedure as Metals glassware.

12.3.2 Do not autoclave.

12.4 **Organic Glassware Cleanup**: (for base neutrals/acids, herbicides, pesticides & PCBs) (LAB COATS, SAFETY GLASSES AND GLOVES MUST BE WORN).

12.4.1 Rinse with last solvent used (must be done by technician or chemist after use).

12.4.2 Wash with soap and water.

12.4.3 Rinse with tap water.

12.4.4 Rinse three times with DI water.

12.4.5 Let dry.

12.4.6 All glassware in baked in a muffle furnace at 400 °C for two hours before use.

12.5 VOA glassware cleaning procedure:

12.5.1 Tubes: Tubes are cleaned using dishwashing detergent and rinsed with tap water. Then they are baked in oven (180°C) for at least 1 hour before being used again.

12.5.2 Volumetrics: Volumetrics are cleaned by rinsing with tap water after use and put in oven (180°C) for at least 1 hour before being used again.

12.5.3 Pipettes: Pipettes are placed in oven (180°C) after each use. They remain in oven for at least 1 hour before being used again.

12.5.4 Syringes: Syringes for samples (5 mL and 25 mL) are cleaned before each use by rinsing at least 3 times with Super-Q water. Other syringes (1000 Tl, 500 Tl, 25 Tl, and 10 Tl) are cleaned by rinsing with methanol before each use.

13. METHOD PERFORMANCE

14. POLLUTION PREVENTION

15. WASTE MANAGEMENT

16. REFERENCES

16.1 Quanterra Pittsburgh, Laboratory Specific Attachment, Quality Assurance Manual, Current Revision.

17. MISCELLANEOUS (TABLES, APPENDICES, ETC.)

17.1 Training Qualifications

17.1.1 The group/team leader has the responsibility to ensure that this procedure is performed by an analyst who has been properly trained in its use and has the required experience. The group/team leader must document the training and submit to the QA/QC Coordinator for inclusion in associate training files.

17.2 Records Management/Documentation

17.2.1 All records will be managed and kept in accordance with Quanterra policy QA-008.

Organics Bench Sheet
Refer to SOP for additional details

Organic Glassware Cleanup: (for base neutrals/acids, herbicides, and pesticides) (LAB COATS, SAFETY GLASSES AND GLOVES MUST BE WORN).

1. Rinse with last solvent used (must be done by technician or chemist after use).
2. Wash with soap and water.
3. Rinse with tap water.
4. Rinse three times with DI water.
5. Let dry.
6. All glassware in baked in a muffle furnace at 400 °C for two hours before use.

VOA glassware cleaning procedure:

1. Tubes: Tubes are cleaned using dishwashing detergent and rinsed with tap water. Then they are baked in oven (180°C) for at least 1 hour before being used again.
2. Volumetrics: Volumetrics are cleaned by rinsing with tap water after use and put in oven (180°C) for at least 1 hour before being used again.
3. Pipettes: Pipettes are placed in oven (180°C) after each use. They remain in oven for at least 1 hour before being used again.
4. Syringes: Syringes for samples (5 mL and 25 mL) are cleaned before each use by rinsing at least 3 times with Super-Q water. Other syringes (1000 Tl, 500 Tl, 25 Tl, and 10 Tl) are cleaned by rinsing with methanol before each use.

(bench sheet may be posted in laboratory by the group leader. the location of the posted copies must be recorded below by the group leader. Posted copy must be initialed and dated by the group leader)

Location	Posted by	Date

Metals Glassware Cleaning Bench Sheet
Refer to SOP for additional details
(bench sheet may be posted in laboratory by the group leader)

Metals and Inorganic prep:

1. Wash with soap and water.
2. Rinse with tap water.
3. Glassware must be rinsed once with DI water and once with 20 percent nitric acid (HNO_3) before the final DI rinse.
4. Rinse with DI water three times.

Mercury BOD bottles:

1. Wash with soap and water.
2. Rinse with tap water.
3. Glassware must be rinsed once with DI water and once with 20 percent nitric acid (HNO_3) before the final DI rinse.
4. Rinse with DI water three times.

(bench sheet may be posted in laboratory by the group leader. the location of the posted copies must be recorded below by the group leader. Posted copy must be initialed and dated by the group leader)

Location	Posted by	Date

Inorganic Glassware Cleaning Bench Sheet page one of two
Refer to SOP for additional details
(bench sheet may be posted in laboratory by the group leader)

General Chemistry:

Evaporating Dishes (TDS, TS):

1. Scour out residue with soap and water.
2. Soak in chromic acid or 1:1 HCL for one hour, if needed.
3. Rinse three times with tap water.
4. Rinse three times with DI water.
5. Dry upside down in 180°C oven, overnight.
6. Remove from oven and store in dessicator.

Boiling Flasks (125 mL w/round glass top):

1. Proceed as in 12.2.1.1 - 12.2.1.4.
2. Place flask in muffle oven ~ 550 °C for 2 hours
3. Store in dessicator

B.O.D. bottles (300 mL round glass top):

1. Rinse once with tap water.
2. Rinse with 1:1 HCL or Chromic Acid.
3. Rinse with tap water three times.
4. Rinse with DI water three times.
5. Bottles may be placed in 180°C oven overnight to dry.

Phosphate: C.O.D. FLASKS (125 mL Erlenmeyer w/round glass top):

1. Rinse once with tap water.
2. Soak for two hours in 1:1 HCL or chromic acid.
3. Rinse three times with tap water.
4. Rinse three times with DI water.
5. Cover tops with aluminum foil.
6. Phosphate glassware is stored separately.

Inorganic Glassware Cleaning Bench Sheet page two of two
Refer to SOP for additional details
(bench sheet may be posted in laboratory by the group leader)

Surfactant glassware (125, 250, 500 mL separatory funnels):

1. *Do not use any detergent !!*
2. Rinse with 1:1 HCL or Chromic Acid
3. Rinse three times with tap water.
4. Rinse three times with DI water.

Phenol flasks, 1000 mL separatory funnels, Cyanide flasks:

1. Wash with soap and water (if needed).
2. Rinse with 1:1 HCL or chromic acid.
3. Rinse three times with tap water.
4. Rinse three times with DI water.

(bench sheet may be posted in laboratory by the group leader. the location of the posted copies must be recorded below by the group leader. Posted copy must be initialed and dated by the group leader)

Location	Posted by	Date

NC-QA-0018

Statistical Evaluation of Data and Development of Control Charts

STL STANDARD OPERATING PROCEDURE

TITLE: STATISTICAL EVALUATION OF DATA AND DEVELOPMENT OF CONTROL CHARTS

(SUPERSEDES: REVISION 4, DATED 06/19/00

Reviewed by:		5/3/01 Date
Reviewed by:	Technology Specialist	6/7/01 Date
Approved by:	Quality Assurance Manager	5/3/01 Date
Approved by:	Environmental Health and Safety Coordinator	6-7-01 Date
Approved by:	Laboratory Director	6-7-01 Date

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STL STANDARD OPERATING PROCEDURE

TITLE: STATISTICAL EVALUATION OF DATA AND DEVELOPMENT OF CONTROL CHARTS

(SUPERSEDES: REVISION 4, DATED 06/19/00

Intranet Controlled

Reviewed by: _____
Date

Reviewed by: _____
Technology Specialist Date

Approved by: _____
Quality Assurance Manager Date

Approved by: _____
Environmental Health and Safety Coordinator Date

Approved by: _____
Laboratory Director Date

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1. PURPOSE

1.1. The purpose of this SOP is to describe the requirements for: (1) statistically establishing QC acceptance criteria and (2) long-term trend analysis of QC data using control charts at the STL-North Canton Laboratory.

1.2. The control chart is an effective tool for long-term trending because it records in real time the accuracy (bias) and precision of the appropriate parts of the measurement process. The control chart provides the means to demonstrate statistical control.

1.3. This document accurately reflects current standard operating procedures (SOP) as of the date above. All facility SOPs are maintained and updated as necessary by the laboratory QA department.

2. RESPONSIBILITIES

2.1. Analyst

2.1.1. All non-CLP QC data is entered into the Laboratory Information Management System (LIMS) for statistical evaluation for the generation of control charts. (Data entry may be automated or may be completed from the report generation software as part of the report or review group activities.)

2.1.2. Monitor method performance using established limits and identify any out-of-control situation. Respond to out-of-control conditions. QC Data results are considered out of control when recoveries exceed established control limits.

2.2. Group Leader/Supervisor

2.2.1. Respond to out-of-control conditions.

2.3. QA Department Staff

2.3.1. For analytical methods, coordinate updating of control limits annually. During this process, review control charts to detect any trends in routine analytical procedures.

2.3.2. Archive control charts and statistically derived QC acceptance data.

2.3.3. Each year at a minimum, publish statistically derived QC acceptance criteria.

2.3.4. Provide guidance in the development of control charts and in the application of QC samples and acceptance data.

2.3.5. With the Laboratory Director, ensure that Operations staff conforms to the requirements provided in this SOP.

2.4. Project Manager

2.4.1. Incorporate updated limits into project-specific QAPPs.

2.4.2. Submit project-specific control charts to the requesting client.

3. SAFETY

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

3.2. Normal office dependent safety precautions must be taken in performing this SOP. If personnel are required to perform any portion of the procedure in the laboratory area, appropriate personal protective equipment and precautions must be utilized.

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

4. PROCEDURE

4.1. Empirical Establishment of QC Acceptance Limits

4.1.1. The assessment of QC sample data shall be performed by comparing precision and accuracy results against control limits. As defined in the following subsections, the control limits used for this comparison shall be either in-house (statistically generated using historical data) control limits or published limits from methods, contracts, or project QA plans.

4.1.2. In-house limits for all QC data must be determined and compared to those limits published in the methods for applicable matrices. Method limits will be employed until sufficient QC data are acquired. A minimum of 20 to 30 of the most recent data points should be used to establish in-house limits based on historical performance data for each major method. Periodically, QC data may need to be reviewed and house limits reestablished whenever a <u>significant</u> <u>change</u> in an analytical process occurs.

4.1.3. Control limits shall be generated for each matrix (i.e., aqueous and soil) for each preparative method using data from at least 20-30 of the most recent data points.

4.1.4. In-house control limits shall be established for the following samples:

4.1.4.1. Laboratory control sample (LCS) spike recoveries for method required analytes list.

4.1.4.2. Matrix Spike and Matrix Spike Duplicate (MS/MSD) spike recoveries for method required analytes list.

4.1.4.3. Surrogate spike recoveries in LCSs for organic analyses only.

4.1.5. Control limits shall be established for all methods except for CLP. For CLP-related projects, the acceptance criteria specified in the most current SOW shall be followed in evaluating data quality. CLP SOWs do not specify the generation of control charts.

4.1.6. The calculations used to generate the control limits for accuracy (%R) are described in the following subsections.

4.1.6.1. The %R is defined as the observed concentration in LCS divided by the theoretical concentration of the spike or LCS, times 100:

$$\%R = \frac{Found}{True} \times 100$$

4.1.6.2. The mean percent recovery and standard deviation is calculated using the following formulas:

$$\overline{\%R} = \frac{\sum_{i=1}^{n} \%R_i}{n}$$

$$S = \sqrt{\frac{\sum_{i=1}^{n}\left(\%R_i - \overline{\%R}\right)^2}{n-1}}$$

where:

%R = the mean percent recovery

$\%R_i$ = the percent recovery of an LCS

n = the number of data points

S = the standard deviation of the data set of percent recoveries

4.1.6.3. The warning (95% or 2-sigma) and control limits (99% or 3-sigma) are then calculated from the following equations:

Upper Control Limit = $\overline{\%R}$ + 3 s

Lower Control Limit = $\overline{\%R}$ - 3 s

Upper Warning Limit = $\overline{\%R}$ + 2 s

Lower Warning Limit = $\overline{\%R}$ - 2 s

where:

$\overline{\%R}$ = the mean percent recovery

S = the standard deviation of the data set

4.1.7. Control limits will be recalculated after excluding the following points from the calculations:

4.1.7.1. Samples with values outside control limits due to assignable cause.

4.1.7.2. True outliers as defined in the Grubbs test.

4.1.7.3. The LIMS is equipped to perform a Grubbs outlier test used to generate the control charts.

4.2. Monthly Trend Control Charts (Navy Only)

4.2.1. Control charts are required for LCSs only.

4.2.2. Control charts will be generated and reviewed on a monthly basis to keep current assessment of laboratory performance. Charts generated on a monthly basis will include a subset of parameters spiked as indicated in Table 4-1.

Table 4-1

Analyte	Analytical Method	Analyte	Analytical Method
Cyanide	Manual distillation/ automated analysis	Aluminum and Cadmium	Total Prep/ Inductively Coupled Plasma
Thallium	Total Prep, Graphite Furnace Atomic Absorption	Mercury	Manual digestion/ automated CVAA
Trichloroethene	Purge & Trap/ GC Volatile Hall	Toluene	Purge & Trap/ GC Volatile - PID
1,1-Dichloroethene, Benzene	Purge & Trap, GC Mass Spec Volatiles	1,2,4-Trichlorobenzene, 4-Nitrophenol	Liq/Liq, GC Mass Spec Semivolatile
Aldrin, Endrin	Liq/Liq, GC ECD	Aroclor 1016, Aroclor 1260	Liq/Liq, GC ECD
TCMX	Liq/Liq, GC ECD		

4.2.3. A control chart (X chart) is generated using the LIMS or a commercially available software to monitor accuracy and precision by plotting the LCS %R data in a graphical format as follows:

4.2.3.1. The average of the %R determinations for the original data set is established as the midpoint on the Y axis of the graph.

4.2.3.2. The upper and lower warning and control limits are plotted as solid horizontal lines across the graph at their respective points on the Y axis.

4.2.3.3. The calculated %R of each spiked sample is plotted chronologically on the graph to determine whether the recovery is within the warning and control limits of the control chart.

4.2.4. Control charts can be generated from any networked system (see network administrator) as follows:

4.2.4.1. From the Desktop, TraQAr double click the “Control limit ” icon button.

4.2.4.2. Select “On-line Control Charts”

4.2.4.3. Select “QC Type”

4.2.4.4. Select “QuantIMS Method”

4.2.4.5. Select “QC Program” and write down spike list number

4.2.4.6. Select “Close Form”

4.2.4.7. Select QA Access button to create control charts and limits.

4.2.4.8. Select “location” (North Canton), “QC Type” (LCS/DCS, MS/MSD, LCS/DCS Surrogates, MS/MSD Surrogates, All Surrogates), “Start and End Date”, “spike form” and then spike number.

4.2.4.9. Select “Collect Data” this screen will run and then the Control Limits Review screen comes up.

4.2.5. Control Limits Review screen

4.2.5.1. A “Grubbs test complete” sign comes up, select OK

4.2.5.2. A minimum of 20 - 30 points are required. If points are below 20 - 30 select close form and increase the start and end date to no more than one year.

4.2.5.3. If points are at least 30, select individual matrix.

4.2.5.4. Select "Grubbs Test"

4.2.5.5. A "Grubbs test complete" sign comes up, select OK

4.2.5.6. Select "Control Limits Rpt". Right click on report and select print.

4.2.5.7. Select "Control Charts Rpt". Right click on report and select print.

4.2.5.8. Close form and repeat 4.2.5.3. through 4.2.5.7.

4.2.5.9. This procedure can be used to demonstrate both "before" and "after" data sets used for control charts generation. An evaluation of the data excluded by a student-t test is useful to reveal existing problems (high volume of unused analyses, etc.).

4.2.6. The following information must be present on the control charts or in an associated table:

4.2.6.1. Parameter, Analytical Method and preparation procedure

4.2.6.2. LCS Batch ID allowing cross-reference to LIMS containing all analytical information.

4.2.6.3. Matrix

4.2.6.4. Number of points used

4.2.6.5. Mean

4.2.6.6. Standard Deviation

4.2.6.7. Percent recoveries

4.2.6.8. Upper and Lower warning and Control limits

4.2.6.9. Chart generation date.

4.2.6.10. An example of the Excel workbook output is provided in **Appendix A**.

4.3. Evaluation of Control Charts

4.3.1. When method, contract, or project plan requirements stipulate control limits which are more stringent than the laboratory generated limits, the more stringent limits shall be used to evaluate the quality control sample data.

4.3.2. If the laboratory-generated limits are more stringent than the method, contract, or project specific limits, the laboratory-generated limits shall be used to evaluate QC samples.

4.3.3. Criteria for an Out-of-Control Conditions

4.3.3.1. The causes for a shift or a trend in control charts could result from (1) incorrect preparation of a standard or a reagent, (2) sample contamination, (3) improper storage or preservation, (4) incorrect instrument calibration, (5) poor analytical technique, and (6) deviation from the analytical method. A measurement process for a particular analyte will be considered out-of-statistical-control when one of the following conditions occur:

4.3.3.1.1. A single point outside 3-sigma control limits

4.3.3.1.2. A series of eight consecutive points on the same side of the central line.

4.3.3.1.3. A series of three consecutive points between the warning limits and control limits.

4.3.3.1.4. A series of six consecutively increasing or decreasing points on the same side of the centerline.

4.3.3.1.5. A cyclic pattern of control values.

4.3.3.1.6. These conditions may indicate that the measurement system is out of statistical control. When this situation occurs, the data must be evaluated thoroughly to identify the most appropriate corrective action to be implemented. The problem and its solution may be documented through a Nonconformance Memo as appropriate. Exceeding warning limits will only require a close observation of the measurement system. In reviewing control charts, any significant changes in key analysts, instrumentation, standard

reference materials, or processes must be kept in mind to explain potential out-of-control situations. After thorough evaluation of the data and documentation of corrective actions taken, the QA Department must determine if the defensiveness of analytical results generated during the out of control situation has been jeopardized. If it is determined that data defensiveness has been compromised, the client will be notified of the out of control situation.

4.4. Setting Control Limits

4.4.1. The working control limits to be used by the laboratory are based on evaluation of the calculated laboratory statistical performance and available interlaboratory limits provided in the reference methods. Note that some SW-846 methods only supply single-operator or single-laboratory method performance data, which may not be appropriate. Some method define what the control limits must be. The laboratory may still generated internally derived limits; however, the method limits will remain in affect (e.g. Wisconsin DRO/GRO, HEM-1664, etc.)

Accuracy Evaluation

Lower Limit Evaluation	**Upper Limit Evaluation**	**Accuracy Decision**
Laboratory-generated Lower Limit > Guidance Limit	Laboratory-generated Upper Limit > Guidance Limit	Use laboratory-gen. Lower Limit & Guidance Upper Limit
Laboratory-generated Lower Limit > Guidance Limit	Laboratory-generated Upper Limit < Guidance Limit	Use laboratory-gen. Lower Limit & laboratory-generated Upper Limit
Laboratory-generated Lower Limit < Guidance Limit	Laboratory-generated Upper Limit > Guidance limit	Use guidance Lower Limit & guidance Upper Limit
Laboratory-generated Lower Limit < Guidance Limit	Laboratory-generated Upper Limit < Guidance limit	Use guidance Lower Limit & laboratory-generated Upper Limit

Precision Evaluation

Range Evaluation	**Precision Decision**
Laboratory-generated precision value > Guidance	Use guidance precision

precision	
Laboratory-generated precision < Guidance precision	Use laboratory-generated precision

Notes: If the decision is to use guidance limits from the method, the laboratory should investigate procedural improvements leading to better performance.

The following outlines other criteria:

Min/Max	Limit	Percentage	Inorganics	Organics
Minimum	**LCL**	**10%**	√	√
Maximum	**LCL**	**90%**	√	√
Minimum	**UCL**	**110%**	√	√
Maximum	**UCL**	**200%**	√	√
Minimum	**RPD**	**20%**	√	√
Maximum	**RPD**	**99%**	√	√

NOTE: Best Practice limits may be utilized for a particular method/parameter based on laboratory and client approval. Best Practice limits combines the data from a group of laboratories (Knoxville, North Canton and Pittsburgh) to generate limits that are used between the laboratories. This allows for the ease in transfer of work between the laboratories including sharing large projects.

5. DEFINITIONS

5.1. Control Chart - A graphical QC tool to monitor method performance over time and to establish acceptance limits.

5.2. Relative Percent Difference (RPD) - a measure of intra-lab precision based on a duplicate sample analyses.

5.3. Grubbs Test – extension of sample sizes and percentage points for significant tests of outlying observations - a statistical outlier test.

5.4. Percent Recovery (%R) or Recovery - a measure of the accuracy (bias) of the measurement process based on a comparison of a measured value for a fortified (spiked) QC sample against the known spiked values.

5.5. Precision - a measure of mutual agreement (or variability) among individual measurements of the same property, usually under prescribed similar conditions.

5.6. Accuracy - the degree of agreement of a measurement (or an average of measurements of the same thing) with an accepted reference or true value. Accuracy is the measure of bias inherent in the system.

5.7. Bias - a systematic (consistent) error in test results. The difference between the population mean and the true or reference value, or as estimated from sample statistics; the difference between the sample average and the reference value.

5.8. X-chart - a control chart that plots a single measurement of a property (e.g., percent recovery) of quality control samples over time. The chart consists of a single line that is the mean of the statistic, warning limits at ± two standard deviations, and control limits at ± 3 sigma.

5.9. Assignable cause - a known reason for an outlying result (e.g., no spike added).

5.10. Duplicate: A second aliquot of a sample that is treated the same as the original sample in order to determine the precision of the method.

5.11. Laboratory Control Sample (LCS):

5.11.1. Organics: A LCS is a volume of deionized laboratory water (for water samples) or a suitable solid material (e.g., clean sand) (for soil/sediment samples) which is spiked with compounds of interest and subjected to the entire analytical procedure in order to estimate the accuracy of the method via percent spike recovery.

5.11.2. Inorganics: A well characterized liquid or solid sample which is prepared, digested or extracted along with each analytical batch of samples.

6. REFERENCES

6.1. .

6.1.1. HAZWRAP Requirements for Quality Control of Analytical Data DOE/HWP-65/R1, July, 1990 or current revision.

6.1.2. Navy Installation Restoration Laboratory Quality Assurance Guide (Interim Guidance Document), February 1996.

6.1.3. Handbook for Analytical Quality Control in Water and Wastewater Laboratories, EMSL, US EPA, March 1977.

6.1.4. Test Methods for Evaluating Solid Waste, Third Edition, SW-846, US EPA, Final Update III, September 1994.

6.1.5. Corporate Quality Management Plan (QMP), current version.

6.1.6. STL Laboratory Quality Manual (LQM), current version.

6.2. Associated SOPs and Policies, latest version

6.2.1. QA Policy, QA-003

6.2.2. Control Chart Generation SOP, NC-QA-0024

6.2.3. Navy/Army SOP, NC-QA-0016

APPENDIX A

(Examples of Control Charts)

Calculated Control Limits

SEVERN TRENT SERVICES

North Canton
Spike List: 928: NC: 8082 Best Practice -LCS

QC Type: LCS/DCS
Analysis Dates: 05/25/2000 - 06/07/2000

Associated SACs:

QC	*Method*	*Prep*
01	MY	1U
01	MY	2W
01	MY	57
01	MY	60
01	MY	61
01	MY	63
01	MY	71
01	QH	
2U	MY	61
50	QH	
72	QH	

Aqueous

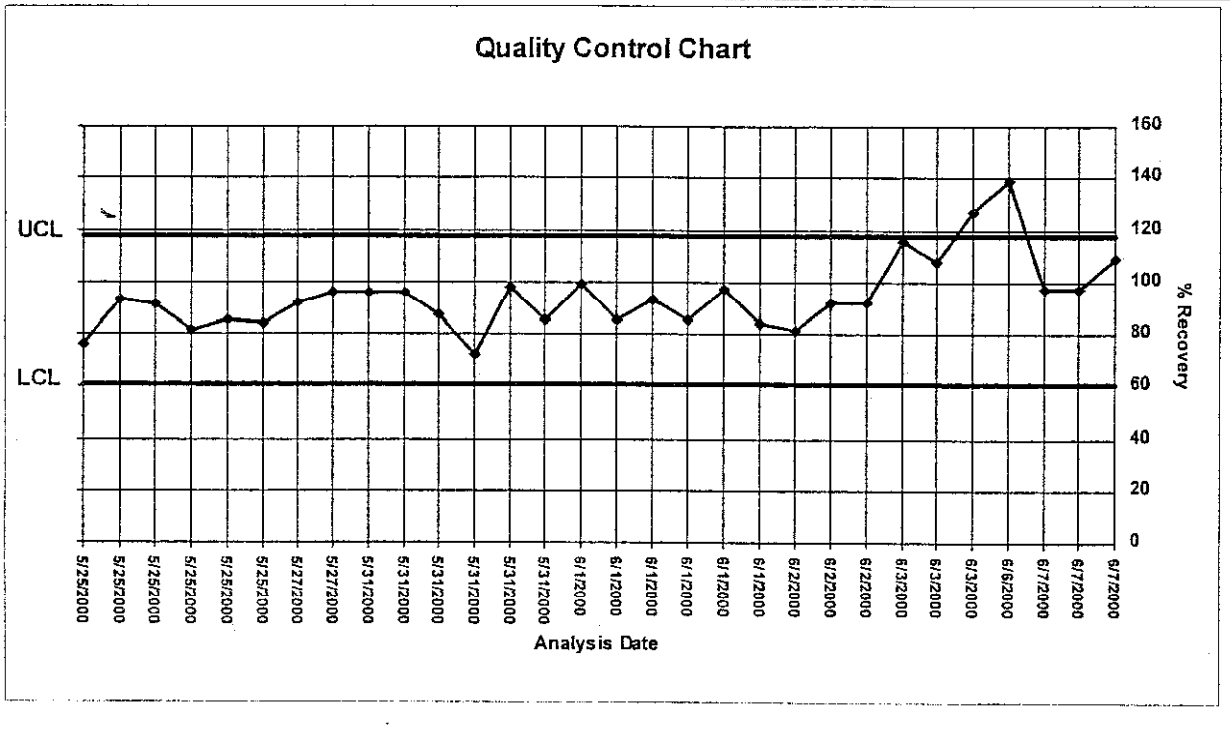
Constituent	*Spike Level*	*Units*	*N*	*Mean*	*Std. Dev.*	*QuantIMS LCL*	*QuantIMS UCL*	*QuantIMS RPD*	*Calculated LCL*	*Calculated UCL*	*Calculated RPD*
PCB-1016	10	ug/L	29	92.90	11.62	61	118	20	58	128	33
PCB-1260	10	ug/L	30	91.20	17.69	61	124	27	38	144	53

PCB-1016 — Laboratory Control Sample — Aqueous

QuantIMS Spike List: 928 (NC: 8082 Best Practice -LCS)

Analysis Dates: 05/25/2000 - 06/07/2000

Method	Method Description	Extraction
8081	Pesticides/PCBs (8081)	EXTRACTION, SOLID/SOLVENT (Auto shaker) w/ACID STRIP (P
8081	Pesticides/PCBs (8081)	LIQ/LIQ, ACCEL ONE STEP w/ACID STRIP (PCB) - Nominal
8081	Pesticides/PCBs (8081)	LIQ/LIQ, CONT w/ACID STRIP (PCB) - Nominal
8081	Pesticides/PCBs (8081)	LIQ/LIQ, SEP FUNNEL w/ACID STRIP (PCB) - Nominal
8081	Pesticides/PCBs (8081)	SONICATION w/ACID STRIP (PCB)
8081	Pesticides/PCBs (8081)	SOXHLET (Na2SO4) w/ACID STRIP (PCB)
8081	Pesticides/PCBs (8081)	WASTE DILUTION w/ACID STRIP (PCB)
8082	PCBs (8082)	Not specified



Statistical Calculations

N	29
Mean %R:	92.897
Std. Dev.:	11.620
Spike Level:	10
Spike Units:	ug/L
QIMS LCL	61
QIMS UCL	118
CALC LWL	70
CALC UWL	116
CALC LCL	58
CALC UCL	128
N RPD	11
QIMS RPD	20
Calc RPD	33.310

Rejected data points are charted

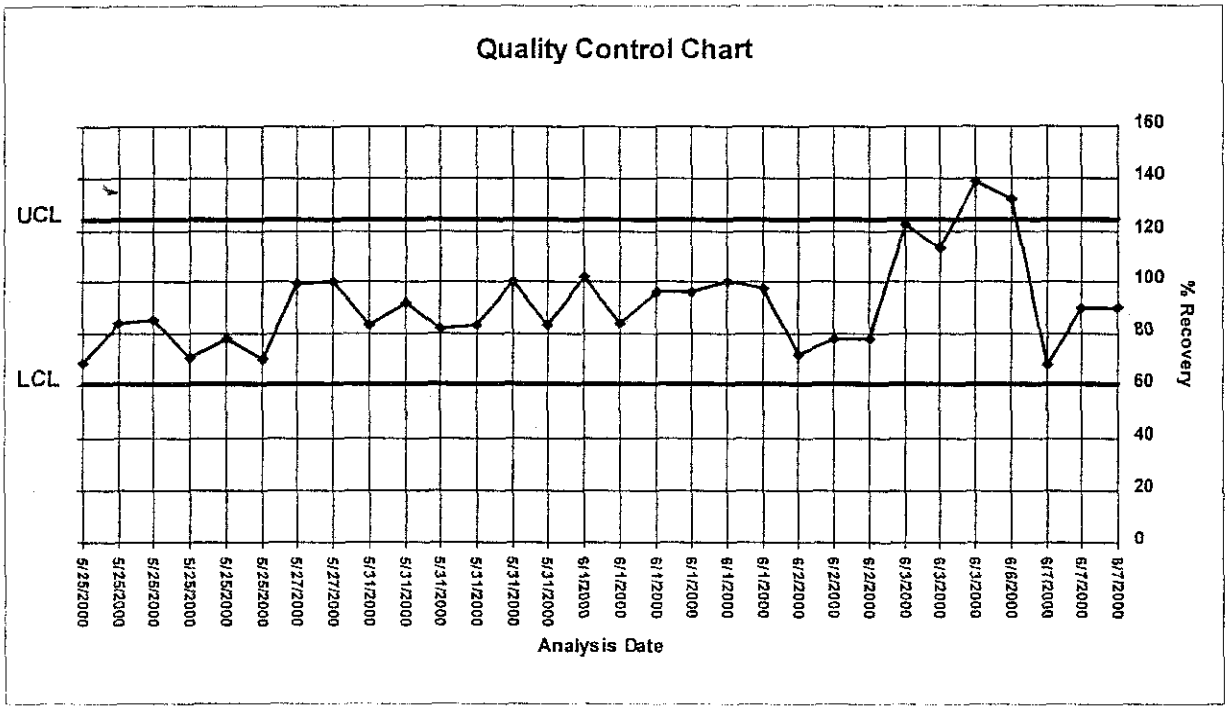
Generated: 6/19/2000

PCB-1260 — Laboratory Control Sample — Aqueous

QuantIMS Spike List: 928 (NC: 8082 Best Practice -LCS)

Analysis Dates: 05/25/2000 - 06/07/2000

Method	Method Description	Extraction
8081	Pesticides/PCBs (8081)	EXTRACTION, SOLID/SOLVENT (Auto shaker) w/ACID STRIP (P
8081	Pesticides/PCBs (8081)	LIQ/LIQ, ACCEL ONE STEP w/ACID STRIP (PCB) - Nominal
8081	Pesticides/PCBs (8081)	LIQ/LIQ, CONT w/ACID STRIP (PCB) - Nominal
8081	Pesticides/PCBs (8081)	LIQ/LIQ, SEP FUNNEL w/ACID STRIP (PCB) - Nominal
8081	Pesticides/PCBs (8081)	SONICATION w/ACID STRIP (PCB)
8081	Pesticides/PCBs (8081)	SOXHLET (Na2SO4) w/ACID STRIP (PCB)
8081	Pesticides/PCBs (8081)	WASTE DILUTION w/ACID STRIP (PCB)
8082	PCBs (8082)	Not specified



Statistical Calculations

N	30
Mean %R:	91.2
Std. Dev.:	17.69
Spike Level:	10
Spike Units:	ug/L
QIMS LCL	61
QIMS UCL	124
CALC LWL	56
CALC UWL	127
CALC LCL	38
CALC UCL	144
N RPD	12
QIMS RPD	27
Calc RPD	53.323

Rejected data points are charted

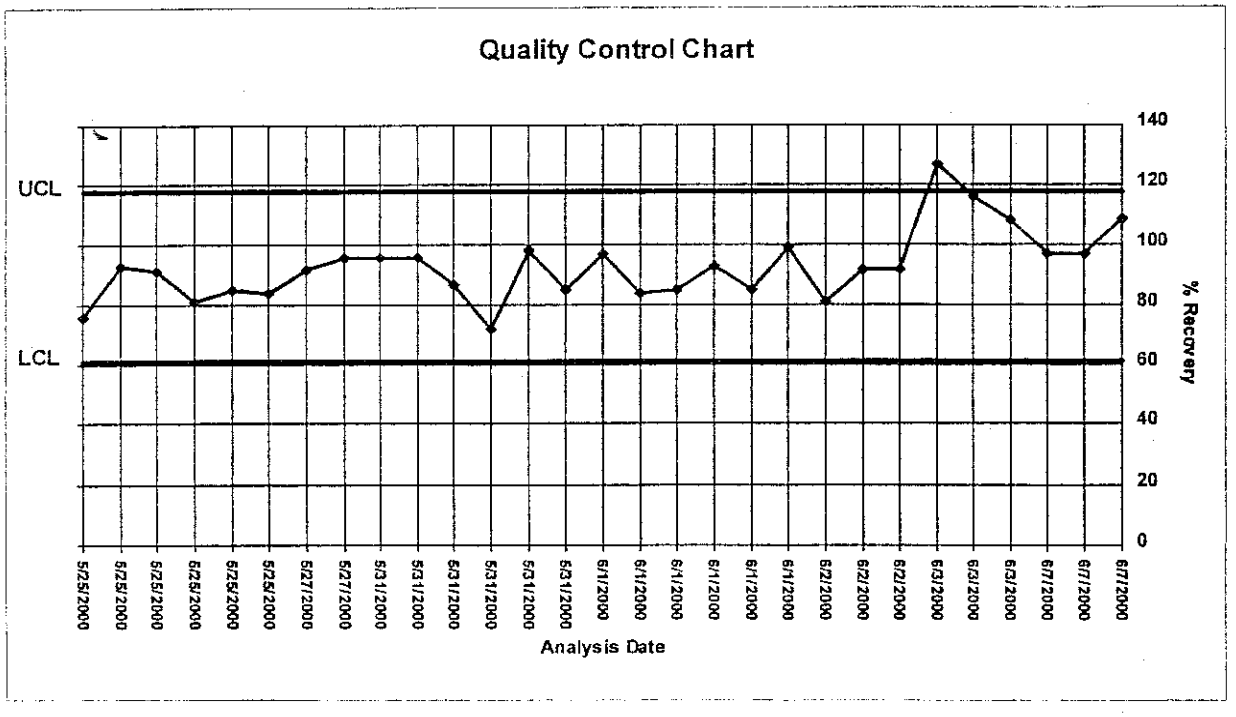
Generated: 6/19/2000

PCB-1016 — Laboratory Control Sample — Aqueous

QuantIMS Spike List: 928 (NC: 8082 Best Practice -LCS)

Analysis Dates: 05/25/2000 - 06/07/2000

Method	Method Description	Extraction
8081	Pesticides/PCBs (8081)	EXTRACTION, SOLID/SOLVENT (Auto shaker) w/ACID STRIP (P
8081	Pesticides/PCBs (8081)	LIQ/LIQ, ACCEL ONE STEP w/ACID STRIP (PCB) - Nominal
8081	Pesticides/PCBs (8081)	LIQ/LIQ, CONT w/ACID STRIP (PCB) - Nominal
8081	Pesticides/PCBs (8081)	LIQ/LIQ, SEP FUNNEL w/ACID STRIP (PCB) - Nominal
8081	Pesticides/PCBs (8081)	SONICATION w/ACID STRIP (PCB)
8081	Pesticides/PCBs (8081)	SOXHLET (Na2SO4) w/ACID STRIP (PCB)
8081	Pesticides/PCBs (8081)	WASTE DILUTION w/ACID STRIP (PCB)
8082	PCBs (8082)	Not specified



Statistical Calculations

N	29
Mean %R:	92.897
Std. Dev.:	11.620
Spike Level:	10
Spike Units:	ug/L
QIMS LCL	61
QIMS UCL	118
CALC LWL	70
CALC UWL	116
CALC LCL	58
CALC UCL	128
N RPD	11
QIMS RPD	20
Calc RPD	33.310

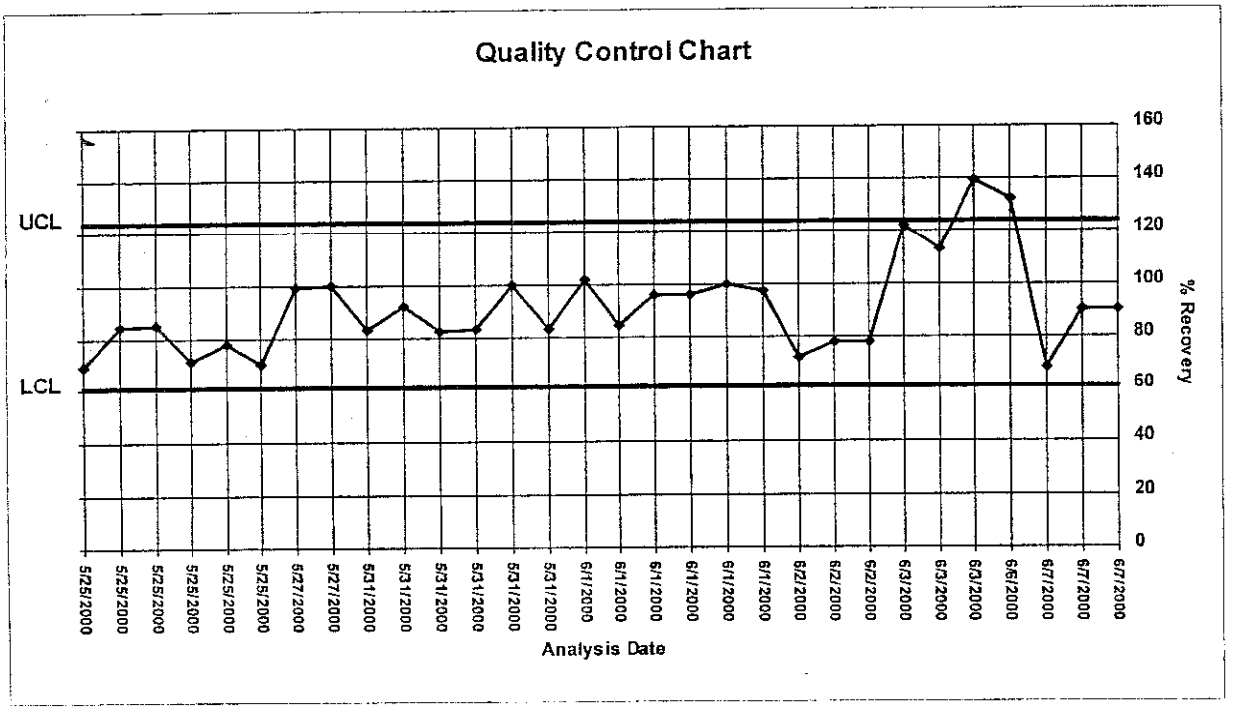
Rejected data points are not charted

PCB-1260 — Laboratory Control Sample — Aqueous

QuantIMS Spike List: 928 (NC: 8082 Best Practice -LCS)

Analysis Dates: 05/25/2000 - 06/07/2000

Method	Method Description	Extraction
8081	Pesticides/PCBs (8081)	EXTRACTION, SOLID/SOLVENT (Auto shaker) w/ACID STRIP (P
8081	Pesticides/PCBs (8081)	LIQ/LIQ, ACCEL ONE STEP w/ACID STRIP (PCB) - Nominal
8081	Pesticides/PCBs (8081)	LIQ/LIQ, CONT w/ACID STRIP (PCB) - Nominal
8081	Pesticides/PCBs (8081)	LIQ/LIQ, SEP FUNNEL w/ACID STRIP (PCB) - Nominal
8081	Pesticides/PCBs (8081)	SONICATION w/ACID STRIP (PCB)
8081	Pesticides/PCBs (8081)	SOXHLET (Na2SO4) w/ACID STRIP (PCB)
8081	Pesticides/PCBs (8081)	WASTE DILUTION w/ACID STRIP (PCB)
8082	PCBs (8082)	Not specified



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Spike Level:	10
Spike Units:	ug/L
QIMS LCL	61
QIMS UCL	124
CALC LWL	56
CALC UWL	127
CALC LCL	38
CALC UCL	144
N RPD	12
QIMS RPD	27
Calc RPD	53.323

Rejected data points are not charted

PITT-QA-0051

Sample Receiving and Chain of Custody

OPERATION-SPECIFIC STANDARD OPERATING PROCEDURE

TITLE: SAMPLE RECEIVING AND CHAIN OF CUSTODY

(SUPERSEDES: SOP NO.: PITT-QA-0051 Rev. 4.2 2/25/00)

Prepared by: _____

Reviewed by: _____
Technical Specialist

Approved by: _____
Quality Assurance Manager

Approved by: _____
Environmental, Health and Safety Coordinator

Approved by: _____
Laboratory Director

Proprietary Information Statement:

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1. PURPOSE

1.1. This SOP details procedures for receiving samples into the laboratory and describes laboratory custody practices.

1.2. This protocol described here complies with accepted laboratory custody procedures and regulatory requirements, e.g. NYSDEC ASP.

2. RESPONSIBILITIES

2.1. It is the responsibility of the Sample Receiving Department to receive samples in full compliance with this SOP. Sample receiving duties of the sample custodian (and other designated individuals) are described in the "PROCEDURE" section. Following this SOP assures that all samples are properly received and will always be under the custody of a person or stored in a secure area while at the laboratory.

2.1.1. For the purpose of this SOP, a sample is under custody if:

2.1.1.1. It is in your possession, or

2.1.1.2. It is in your view after being in your possession, or

2.1.1.3. It was in your possession and you locked it up, or

2.1.1.4. It is in a designated secure area. (Secure areas shall be accessible only to authorized personnel.)

2.2. It is the responsibility of each analyst or any STL staff member to maintain sample custody for all entrusted samples as described herein in full compliance with this SOP.

2.3. It is the responsibility of the laboratory director, QA manager, and supervisors to assure that operations are conducted in full compliance with this SOP. It is also their responsibility to supply training, materials, and equipment so that the laboratory staff can comply with all SOP requirements.

3. SAFETY

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

3.2. Eye protection that satisfies ANSI Z87.1 (as per the Chemical Hygiene Plan), laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents

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

3.3.1. The following materials are known to be corrosive: Sodium Hydroxide (NaOH), Sulfuric Acid (H_2SO_4), Hydrochloric Acid (HCl), and Nitric Acid (HNO_3)

3.4. Exposure to chemicals must be maintained **as low as reasonably achievable**, therefore, unless they are known to be non-hazardous, all samples must be opened, transferred, and prepared in a fume hood or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made. If waste is generated during operations, it will be segregated and disposed of according to the facility hazardous wastes procedures as appropriate. The Environmental Health and Safety Coordinator will be contacted if related information is required.

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

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

4. PROCEDURE

4.1. Samples will be received at the laboratory facility during normal working hours (8 a.m. to 5 p.m.). If sample receipt is anticipated outside normal working hours, the project manager must notify and coordinate sample receipt with the sample custodian, who in turn will designate personnel to receive the samples. The sample custodian examines the shipping container (cooler, box, or other shipping container) and completes the header information on a Cooler Receipt Form (see "APPENDICES," Section 6.2). Information recorded at this time will include: client name and project, quote number, STL lot number, the date the shipping container was received and temperature checked, and the date that the shipping container was unpacked.

4.1.1. The temperature of the cooler may be taken either by using an enclosed temperature blank, if supplied, or by inserting a thermometer between samples in the cooler (the thermometer must not come in contact with the ice). If the temperature of the cooler is not 4°C ±2°C, this must be noted on a Condition Upon Receipt Variance Report (see "APPENDICES," Section 6.3). The temperature will be recorded on the Cooler Receipt Form. The reading that is recorded will take into consideration the relevant thermometer correction factor.

4.1.2. Other information to be noted at this time is: presence/absence of custody seal(s) on the shipping container(s), and their condition.

4.2. The sample custodian opens the shipping container and removes the entire contents, assuring that all enclosed samples and documents are retained. After reviewing the entire contents of the shipping container and carefully checking sample integrity (intact, broken, leaking, etc.), labels, and shipment completeness, the remaining information is placed on the Cooler Receipt Form (see "APPENDICES," Section 6.2).

4.3. The sample custodian must compare the field chain(s) of custody, the sample labels, and airbills or bills of lading. If there are any inconsistencies between the forms, the discrepancies are documented on the Condition Upon Receipt Variance Report (see "APPENDICES," Section 6.3). If samples are received out of holding time, a Nonconformance Memo must be completed and the project manager notified. The project manager then notifies the client and a decision is made concerning whether to proceed with analysis.

4.4. The sample custodian measures the pH of preserved aqueous samples (with the exception of samples that have been submitted for the testing of volatile organic compounds). This is done by placing a few drops of the sample on *narrow*-range pH paper using *either a disposable cup (for DOD clients) or* a clean disposable Pasteur pipette. This measurement determines whether the sample has been properly preserved. (For Oil & Grease pour in cap and then pipette.) The used pipette is then discarded. **Note:** The pH of samples to be analyzed for VOAs will be measured by the volatiles analytical group after removing an aliquot for analysis.

4.5. For all potentially chlorinated samples the sample custodian checks for residual chlorine by testing the sample with KI-starch paper. If residual chlorine is present, the sample custodian must indicate so on the sample condition upon receipt form and issue a NCM. Also, the client, the PM, and the group responsible for analysis of the sample must be notified. Steps for removal of residual chlorine are included in the SOP for the method the sample is to be analyzed by.

4.6. An access-based program is utilized to determine samples ready for disposal. A report is generated listing samples to be disposed. Once sample disposal date has been entered into computer system (Quantims), a sample disposal report is generated and put into a disposal logbook. The disposal logbook is kept in sample receiving for reference.

4.7. If all samples recorded on the field chain(s) of custody were received by the laboratory and there are no problems observed with the sample shipment, the sample custodian signs the

field chain(s) of custody in the "Received for Laboratory by:" box on the document. Problems such as broken bottles and pH or temperature outside criteria are noted on the Condition Upon Receipt Variance Report (see "APPENDICES," Section 6.3). *Where approved by the project manager, unpreserved samples will be preserved by the sample custodian. This action will be documented on the Condition Upon Receipt Variance Report.. Whenever lab reagents are used to make a preservative adjustment, record the reagent, lot number and amount of reagent added.*

4.8. The project manager's Quote form (the LIMS description of the sampling program) is reviewed to assure that the field chain(s) of custody is in agreement. If the documents do not agree, the project manager is notified of the discrepancy. Samples are not logged in until all discrepancies are resolved.

4.9. If it has been necessary to complete a Condition Upon Receipt Variance Report, this will be forwarded to the project manager for review. The project manager will determine the action required and contact the client as necessary or otherwise agreed.

4.10. Once the project manager has resolved any discrepancies between the field chain(s) of custody and Quote and has taken the appropriate action for any Condition Upon Receipt Variance Report which has been generated, the samples are logged in using the Laboratory Information Management System (LIMS). A unique laboratory identification number is assigned to each sample (i.e., C6B060001-001: C denotes Pittsburgh; 6 references the year [1996]; B signifies the month [February]; 06 means the sixth day of the month; 0001 is the first lot logged in; and -001 is the first sample of that lot).

4.11. The Sample Control person will enter each sample into the laboratory computer (QuantIMS), where a unique lot number is assigned to each project received, and sequential sample numbers are designated for each client identification within the lot.

4.11.1. **Lot Numbers**: The lot number is nine characters in length and is based on the date of receipt. Lot number A5J010021 is described as follows:

A - STL location where the samples were received.
(A = North Canton, B = Tampa, C = Pittsburgh, etc.)
5 - Last digit of the year (i.e. 1995).
J - Month (i.e. A = January, B = February, J = October, etc.)
01 - The next 2 numeric characters identify the day of the month, in this case, the first day of the month.
0021 - The next 4 numeric characters are the sequential assignment of numbers specific to each lot received. Each day the first lot logged in receives the number "0001", the second lot receives the number "0002", etc..
For example:
If four bottles were submitted under Client ID numbers AB100-AB103 and the laboratory identification number generated by the computer is A2K100001, then the assigned laboratory number recorded on the Sample Log-In Sheet would be as follows:

Client ID Sample Number	Assigned Laboratory Number
AB 100	A2K100001-001
AB 101	A2K100001-002
AB 102	A2K100001-003
AB 103	A2K100001-004

4.11.2. **Sample Numbers**: The samples in each lot are assigned a sample number that is attached to the lot number and are reset at each new lot. For example: the first and second samples in the lot above are labeled A5J010121-001 and A5J010121-002.

4.11.3. **Sample Suffixes**: Each sample also has a 1 character field (which is not a required field for all samples) called the suffix which identifies the sample as specified below.

Client Sample	No. Suffix
Method Blank	B
Laboratory Control Sample	C
Laboratory Control Sample Duplicate	L
Matrix Spike	S
Matrix Spike Duplicate	D
Sample Duplicate	X
Serial Dilution	P
Sample Confirmation	Y
Post Digestion Spike	Z
Re-analysis	I

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

4.11.4. **Work Order Numbers**: Each test requested by the client for an individual sample receives an individual 8 digit work order number assigned by QuantIMS. Work order number A5WE1-2-1C is described as follows:

A5WE1 - In addition to the three digit sample (i.e. - 001 and - 002), the first 5 characters of the work order number also identifies each unique sample. This identification is generated in QuantIMS using a sequential logic.
2 - The "modifier" indicates the type of run. In this case this is the second time the sample had to be run. If it needs reprepared and run again, the number would indicate a "3". The original analysis work order number assigns "1" to the modifier position.
1C - The "suffix" is the identification of the specific test for that sample. The suffix in this case is not always sequential, but is unique to the test to be performed on the sample.

4.12. Worksheets and sample container labels are printed. The sample custodian will assure that each sample container is labeled with a unique laboratory identification number that cannot be accidentally removed in the laboratory.

4.12.1. The label will contain the following information:

4.12.1.1.The laboratory information management system unique Lab ID number.

4.12.1.2.Sampling date.

4.12.1.3.Client ID.

4.12.1.4.Storage location.

4.12.1.5.Client code.

4.12.1.6.Number and size of bottles received.

4.13. The sample custodian will put the samples into secure storage areas. Samples for tests other than volatile organics are placed on numbered shelves inside secure walk-in refrigerators. Samples received for volatile organics are placed in separate secure refrigeraters which have been designated for volatile sample storage only and are located within the volatiles lab area. From the time of log-in and refrigerator assignment by the sample receiving personnel, the volatiles personnel become the designated sample custodians for the volatile samples. As custodians they must document custody within their workgroup. In both cases temperature is maintained at 4°C ±2°C. The storage location for all received samples is entered in the laboratory information management system.

4.14. The sample custodian files the shipping documents, field chain(s) of custody, Quote, related correspondence, cooler receipt form, analytical summary, along with preliminary invoice. The summary and supporting documentation are reviewed for accuracy by the sample custodian and placed in a project folder before being submitted to Project Management. Laboratory information management system worksheets are generated by the sample custodian and distributed to the analytical group leaders.

4.15. Internal Chain of Custody

4.15.1. The sample custodian transfers the custody of requested raw samples to the analytical staff using a Sample Custodian Removal Request (see "APPENDICES," Section 6.4) which lists the laboratory identification number of the samples being transferred. The sample custodian checks that the sample labels and Sample Custodian Removal Request are in agreement, dates, records the time of transfer (using military time), and signs the Sample Custodian Removal Request as having relinquished the samples. The analyst will then sign the Sample Custodian Removal Request as having received the listed samples.

4.15.2. The Sample Custodian Removal Request form must accompany the raw samples while they are being analyzed. The analyst may transfer the samples to a second analyst using a second Sample Custodian Removal Request form which has been generated listing the samples and purpose of the transfer. All samples listed on the initial Sample Custodian Removal Request must be present and listed on the second Sample Custodian Removal Request. Transferring less than all of the samples listed on the initial Sample Custodian Removal Request is prohibited. If only several of the samples listed on the initial form are required, then all samples on the initial form will be returned to the laboratory sample custodian who will relinquish only those samples required, as described in the above section. The relinquishing analyst assures that all samples are present and correctly identified on the second Sample Custodian Removal Request before signing, dating, and recording the time of transfer (military time) on the second Sample Custodian Removal Request form. The second analyst signs the second Sample Custodian Removal Request form to accept the samples. The

original Sample Custodian Removal Request from the laboratory sample custodian must be relinquished to the second analyst and will remain with the samples.

4.15.3. Custody of raw samples may be maintained if the analyst receiving custody as described above places the samples in a secure storage area accessible only to authorized personnel for the purpose of analysis. Storage conditions must be such that the integrity of the sample will be maintained for the required analyses.

4.15.4. Raw samples (whether the containers have sample volume remaining or are empty) shall be returned to the sample custodian with the original Sample Custodian Removal Request and any additional Sample Custodian Removal Requests which were required to document subsequent transfers. The Sample Custodian Removal Request must be reconciled with the samples being returned before the sample custodian accepts receipt of the samples. (The sample custodian will not accept the samples unless <u>all</u> of the containers listed on the Sample Custodian Removal Request are present.) The analyst then signs as relinquishing the samples, and sample custodian accepts custody of returned raw samples by signing, dating, and recording the time of receipt (using military time) on the Sample Custodian Removal Request that documents the most recent transfer of the samples.

4.15.5. The sample custodian will record which samples have been completely expended in analyses by making an entry on the Sample Custodian Removal Request.

4.15.6. Custody information for extracts, distillates, and digestates prepared from raw samples shall be recorded on the sample preparation benchsheet used to document the preparation. (A Sample Custodian Removal Request will not be used for sample preparations.) The individual who has conducted the preparation is responsible for completing custody transfer information. The relinquishing analyst assures that all sample preparations are present and correctly identified before signing, dating, and recording the time of transfer (military time) on the benchsheet. Prepared samples are transferred to and kept in a secure area accessible only to authorized personnel for the purpose of analysis. If further custody transfers are necessary, these are recorded in a similar manner on the same benchsheet. The benchsheet with completed custody information must accompany the prepared samples whenever custody transfers are necessary.

4.16. Samples will be properly disposed of by the sample custodian thirty days after the final report unless the laboratory has been otherwise notified in writing. All samples in a single STL laboratory lot will be disposed of at the same time, and a record documenting the lot disposal will be kept in a logbook maintained by the sample custodian.

4.17. The temperature of each walk-in cooler is monitored daily Monday through Saturday using a calibrated mercury bulb thermometer. A seven day recording chart which monitors temperatures on a weekly basis is also in each cooler.

4.18. **Cooler Handling Procedure**: All coolers should be rinsed out after receipt and unloading. If a cooler smells or is visibly soiled it should be soaped and warm water rinsed. If a cooler cannot be cleaned up or remains odorous after cleaning, it should be discarded.

4.19. Any deviation from the conditions and handling described in the "PROCEDURES" section will be documented using a Nonconformance Memo (NCM) with distribution to the Project Manager and Quality Assurance Department. Corrective action must be fully explained in the Nonconformance.

5. DEFINITIONS

5.1. Custody: The definition of custody may be found in Section 2.1.1.

5.2. Internal Chain of Custody: Records generated by various departments internal to the laboratory and which document custody of samples or sample preparations for transfers within the laboratory.

5.3. LIMS: Laboratory Information Management System. The computer system used to track information about samples after being received by the laboratory.

6. APPENDICES

6.1. Disaster Recovery Plan Appendix

6.2. Cooler Receipt Form, Page 1 of 2 (example form).
Cooler Receipt Form, Page 2 of 2 (example form).

6.3. Condition Upon Receipt Variance Report (example form).

6.4. Sample Custodian Removal Request (example form).

6.5. Holding Time Tables 8.5-1 through 8.5-5, taken from the STL Quality Assurance Management Plan, Revision No. 3, Nov 2, 1998, pages 110-135 of 192. Please note, client specific or project specific holding times would supersede the holding times listed in these tables.

Disaster Recovery Plan Appendix

1. When sample location transfers are required due to cooler malfunction or power failure, all transfers must be properly documented as described in the above SOP sections. Sample security must be properly maintained with access to samples limited, controlled, and documented. Temperature of the relocated samples will be documented and controlled to 4°C ±2°C.

2. In the event of a power failure limiting available cold storage capacity to less than that required to adequately store all samples at the necessary temperature, backup refrigeration trucks will be called to give assistance on site to store samples and maintain proper temperature at 4°C ±2°C. Trucking companies that could be called are:
   Thermo King Transport Refrigeration
   Ryder Trucks
   Budget Trucks

3. If refrigeration trucks are not available during a power failure, dry ice will be used to maintain proper temperature.

4. When cooling units malfunction, a local heating, ventilation, and air conditioning contractor will immediately be called to correct the problem. Sample receiving will coordinate all service calls using a 24-hour servicing company to minimize impact on sample integrity.

Cooler Receipt Form

STL Pittsburgh

Client: _____ Project: _____ Quote: _____

Cooler Rec'd & Opened for Temp. Check on: _____

Coolers Opened and Unpacked on: _____ By: _____

(Signature)

STL Pittsburgh Lot Number: _____

		Yes	No
1.	Were custody seals on the outside of the cooler?	___	___
	If YES, how many and where? Quantity __ Location _____		
	Were signatures and date correct?	___	___
2.	Were custody papers included inside the cooler?	___	___
3.	Were custody papers properly filled out (ink, signed, match labels)?	___	___
4.	Did you sign the custody papers in the appropriate place?	___	___
5.	Was shippers packing slip attached to this form?	___	___
6.	Were packing materials used?	___	___
	If YES, what type? _____		
7.	Were the samples chilled? (Record temperatures on reverse side.)	___	___
8.	Were the samples appropriately preserved?	___	___
9.	Were all bottles sealed in separate plastic bags?	___	___
10.	Did all bottles arrive in good condition (unbroken)?	___	___
11.	Were all bottle labels complete (sample ID, preservatives, etc.)?	___	___
12.	Did all bottle labels and/or tags agree with custody papers?	___	___
13.	Were correct bottles used for tests indicated?	___	___
14.	Were all VOA vials checked for the presence of air bubbles?	___	___
15.	Was a sufficient amount of sample sent in each bottle?	___	___

16. Samples received by: FEDEX UPS CLIENT DROP-OFF OTHER AIRBORNE

Explain any discrepancies: _____

Level 2 Review _____

Was contacted on _____ by _____ to resolve discrepancies.

Cooler Receipt Form

STL Pittsburgh

P: Preserved

UP: Unpreserved

Sample ID	TMET PH<2	DMET PH<2	HG PH<2	NUT(1) PH<2	CN PH ≥12	OG TPHC PH<2	PHEN PH<2	SULF PH ≥12	TOC PH<2	TOX PH<2	VOA P/UP	hrdnss PH<2			

(1) "NUT" could include sample bottles for ammonia, chemical oxygen demand, nitrate/nitrite, TKN, or total phosphorus

Comments: _____

Cooler Number	Temperature

Bottle Type	Lot Number*

* Please use an asterisk if bottle lot number was covered by the label.

Condition Upon Receipt Variance Report
STL Pittsburgh Laboratory

Client: _____ Date: _____
Project No.: _____ Initiated by: _____
Analysis Requested: _____ RFA/COC: _____
Client Sample Numbers Affected: _____

Condition/Variance (Check all that apply):

1. ☐ Not enough sample received for proper analysis.
   Received approx. _____
2. ☐ Sample received broken/leaking.
3. ☐ Sample received without proper preservative.
   - ☐ Cooler temperature not within 4°C ± 2°C
     Record temperature: _____
   - ☐ pH _____
   - ☐ other: _____
4. ☐ Sample received in improper container.
5. ☐ Sample received without proper paperwork.
   _____
6. ☐ Paperwork received without sample.
7. ☐ No sample ID on sample container.
8. ☐ Custody tape disturbed/broken/missing.
9. ☐ Sample splits performed by lab.
10. ☐ Volatile sample received with approximately _____ mm headspace.
11. ☐ Sample ID on container does not match on paperwork.
    Explain:
    _____
    _____
12. ☐ All coolers on airbill not received with
13. ☐ Other (explain below):
    _____
    _____
    _____

Notes: _____
_____
_____

Corrective Action:

☐ Client's Name: _____ Informed verbally on: _____ By: _____

☐ Client's Name: _____ Informed in writing on: _____ By: _____

☐ Sample(s) processed "as is" _____

☐ Sample(s) on hold until: _____ If released: _____

Sample Control Supervisor Review: _____ Date: _____

Project Management Review: _____ Date: _____

SIGNED ORIGINAL MUST BE RETAINED IN THE PROJECT FILE

COC/Sample Request

STL Pittsburgh
450 William Pitt Way
Pittsburgh, Pennsylvania 15238
412/820/8380 FAX:412/820-2080

Project Name

Site

Lot Number/Sample Number	Analysis	Matrix

Raw Sample	Raw Relinquished by				Raw Received by			
	Date	Time	Analyst	Location	Date	Time	Analyst	Location

CORP-MT-0006

Preparation and Analysis of Mercury in Aqueous Samples by Cold Vapor Atomic Absorption, Method 245.1 CLP-M, SOW ILM03.0

Controlled Copy
Copy No._____

LABORATORY-SPECIFIC

STL STANDARD OPERATING PROCEDURE

TITLE: PREPARATION AND ANALYSIS OF MERCURY IN AQUEOUS SAMPLES BY COLD VAPOR ATOMIC ABSORPTION, METHOD 245.1 CLP-M, SOW ILM03.0

(SUPERSEDES: CORP-MT-0006, REVISION 0)

Prepared by: _____

Reviewed by: _____
Technical Specialist

Approved by: _____
Quality Assurance Manager

Approved by: _____
Environmental, Health and Safety Coordinator

Approved by: _____
Laboratory Director

Approved by: _____
Corporate Technology and/or Corporate Quality Assurance

Proprietary Information Statement:

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1. SCOPE AND APPLICATION

1.1. This procedure describes the preparation and analysis of mercury (Hg, CAS # 7439-97-6) by Cold Vapor Atomic Absorption Spectroscopy (CVAA) using Method 245.1 CLP-M as contained in CLP SOW ILMO3.0. In addition to SOW ILMO3.0, this SOP is also compliant with the requirements of CLP SOWs 7/88, 3/90, ILMO1.0 and ILMO2.1.

1.2. CVAA analysis provides for the determination of total mercury (organic and inorganic). The combination of the oxidants, potassium permanganate and potassium persulfate, has been found to give 100% recovery with both types of compounds. Detection limits, sensitivity and optimum concentration ranges for mercury analysis will vary with the matrices, instrumentation and volume of sample used.

1.3. Method 245.1 CLP-M is applicable to the determination of dissolved, suspended and total mercury in aqueous matrices. All matrices require sample preparation prior to analysis.

1.4. The STL reporting limit and CRDL for mercury in aqueous matrices is 0.2 ug/L.

2. SUMMARY OF METHOD

2.1. This SOP describes a technique for the determination of mercury in solution. The procedure is a physical method based on the absorption of radiation at 253.7 nm by mercury vapor. A representative portion of the sample is digested in sulfuric and nitric acids. Organic mercury compounds are oxidized with potassium permanganate and potassium persulfate and the mercury reduced to its elemental state with stannous chloride and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance is measured as a function of mercury concentration. Concentration of the analyte in the sample is determined by comparison of the sample absorbance to the calibration curve (absorbance vs. concentration).

3. DEFINITIONS

3.1. Dissolved Metals: Those elements which pass through a 0.45 um membrane. (Sample is acidified after filtration).

3.2. Suspended Metals: Those elements which are retained by a 0.45 um membrane.

3.3. Total Metals: The concentration determined on an unfiltered sample following digestion.

4. INTERFERENCES

Chemical and physical interferences may be encountered when analyzing samples using this method.

4.1. Potassium permanganate which is used to breakdown organic mercury compounds also eliminates possible interferences from sulfide. Concentrations as high as 20 mg/L of sulfide as sodium sulfide do not interfere with the recovery of inorganic mercury from reagent water.

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

4.3. Chlorides can cause a positive interference. Seawaters, brines and industrial effluents high in chlorides require additional permanganate (as much as 25 mL) because, during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation at 253.7 nm. Care must be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. This is accomplished by adding excess hydroxylamine reagent (25 mL) and purging the sample headspace before stannous chloride is added. Both inorganic and organic mercury spikes have been quantitatively recovered from seawater using this technique.

Note: Sufficient addition of permanganate is apparent when the purple color persists at least 15 minutes. Some samples may require dilution prior to digestion due to extremely high concentrations of chloride.

4.4. Interference from certain volatile organic materials that absorb at this wavelength may also occur. If suspected, a preliminary run without stannous chloride can determine if this type of interference is present. While the possibility of absorption from certain organic substances present in the sample does exist, this problem is not routinely encountered. This is mentioned only to caution the analyst of the possibility. If this condition is found to exist, the mercury concentration in the sample can be determined by subtracting the result of the sample run without the reducing reagent (stannous chloride) from that obtained with the reducing reagent.

4.5. Samples containing high concentrations of oxidizable organic materials, as evidenced by high COD levels, may not be completely oxidized by this procedure. When this occurs the recovery of mercury will be low. The problem can be eliminated by reducing the volume of original sample used.

4.6. The most common interference is laboratory contamination which may arise from impure reagents, dirty glassware, improper sample transfers, dirty work areas, etc. Be

aware of potential sources of contamination and take appropriate measures to minimize or avoid them.

5. SAFETY

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

5.2. Eye protection that satisfies ANSI Z87.1 (as per the Chemical Hygiene Plan), laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

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

5.3.1. The following materials are known to be **corrosive:**

hydrochloric acid, nitric acid and sulfuric acid.

5.3.2. The following materials are known to be **oxidizing agents**:

nitric acid, potassium permanganate, potassium persulfate and magnesium perchlorate.

5.3.3. Mercury is a highly toxic element that must be handled with care. The analyst must be aware of the handling and clean-up techniques before working with mercury. Since mercury vapor is toxic, precaution must be taken to avoid its inhalation, ingestion or absorption through skin. All lines should be checked for leakage and the mercury vapor must be vented into a hood or passed through a mercury absorbing media such as:

5.3.3.1. Equal volumes of 0.1 M $KMnO_4$ and 10% H_2SO_4, or

5.3.3.2. Iodine, 0.25%, in a 3% KI solution.

5.3.4. Magnesium sulfate is known to be a reproductive toxin (mutagen).

5.4. Exposure to chemicals must be maintained **as low as reasonably achievable.** Therefore, unless they are known to be non-hazardous, all samples should be opened, transferred

and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

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

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

5.7. Do not look directly into the beam of the Hg lamp. The UV light that these lamps radiate is harmful to the eyes.

5.8. Cylinders of compressed gas must be handled with caution, in accordance with local regulations. It is recommended that, wherever possible, cylinders be located outside the laboratory and the gas led to the instrument through approved lines.

5.9. The CVAA apparatus must be properly vented to remove potentially harmful fumes generated during sample analysis.

6. EQUIPMENT AND SUPPLIES

6.1. Temperature controlled water bath (capable of maintaining a temperature of 95 °C) or autoclave that is able to obtain conditions of 15 lbs., 120 °C for 15 minutes.

6.2. Atomic Absorption Spectrophotometer equipped with:

6.2.1. Absorption Cell with quartz end windows perpendicular to the longitudinal axis. Dimensions of the cell must result in sufficient sensitivity to meet the SOP defined reporting limit. The quartz windows must be maintained to provide accurate measurements. Any scratches or fingerprints can alter the absorption of UV radiation.

6.2.2. Mercury specific hollow cathode lamp (HCL) or electrodeless discharge lamp (EDL).

6.2.3. Peristaltic pump which can deliver 1 L/min air.

6.2.4. Flowmeter capable of measuring an airflow of 1 L/min.

6.2.5. Recorder or Printer.

6.2.6. Aeration Tubing: A straight glass frit having a course porosity and Tygon tubing is used for the transfer of mercury vapor from the sample bottle to the absorption cell and return.

6.2.7. Drying device (a drying tube containing magnesium perchlorate or magnesium sulfate and/or a lamp with a 60 W bulb) to prevent condensation in cell. The lamp is positioned to shine on the absorption cell maintaining the air temperature in the cell about 10 °C above room temperature. Other drying devices that achieve the same purpose are also acceptable (i.e., Gortex filter).

NOTE: Instruments designed specifically for the measurement of mercury using the cold vapor technique may be substituted for the atomic absorption spectrophotometer.

6.3. BOD bottles or equivalent.

6.4. Nitrogen or argon gas supply, welding grade or equivalent.

6.5. Calibrated automatic pipettes or Class A glass volumetric pipettes.

6.6. Class A volumetric flasks.

6.7. Thermometer (capable of accurate readings at 95 °C).

6.8. Disposable cups or tubes.

7. REAGENTS AND STANDARDS

7.1. Reagent water must be produced by a Millipore DI system or equivalent. Reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks.

7.2. Stock (1000 ppm) mercury standards (in 10% HNO_3) are purchased as custom STL solutions. All standards must be stored in FEP fluorocarbon or previously unused polyethylene or polypropylene bottles. Stock standard solutions must be replaced prior to the expiration date provided by the manufacturer. If no expiration date is provided, the stock solutions may be used for up to one year and must be replaced sooner if verification from an independent source indicates a problem.

7.3. Intermediate mercury standard (10 ppm): Take 1 mL of the stock mercury standard (7.2) and dilute to 100 mL with reagent water. The intermediate standard must be made monthly and must be prepared in a matrix of 2% HNO_3. This acid (2 mL of concentrated

HNO_3) must be added to the flask/bottle before the addition of the stock standard aliquot.

7.4. Working mercury standard (0.1 ppm): Take 1 mL of the intermediate mercury standard (7.3) and dilute to 100 mL with reagent water. The working mercury standard must be made daily and must be prepared in a matrix of 0.15% HNO_3. This acid (150 uL of concentrated HNO_3) must be added to the flask/bottle before the addition of the stock standard aliquot.

7.5. The calibration standards must be prepared fresh daily from the working standard (7.4) by transferring 0, 0.2, 0.5, 1.0, 2.0, 5.0 and 10.0 mL aliquots of the working mercury standard into 100 mL flasks and diluting to volume with reagent water.

Note: Alternate volumes of standards may be prepared as long as the accuracy and final standard concentrations as detailed in Table I are maintained.

7.6. The initial calibration verification standard must be made from a different stock than that of the calibration standard. For analyses performed under direct contract to the USEPA CLP, the EPA provided ICV solution must be used in place of the STL solution.

7.7. Refer to Table I (Appendix A) for details regarding the working standard concentrations for calibration, calibration verification and spiking solutions. All standards must be processed through the entire analytical procedure including sample preparation.

7.8. Nitric acid (HNO_3), concentrated, trace metal grade or better.

Note: If a high reagent blank is obtained, it may be necessary to distill the nitric acid.

7.9. Sulfuric acid (H_2SO_4), concentrated, trace metal grade or better.

7.9.1. Sulfuric acid, 0.5 N: Dilute 14.0 mL of concentrated H_2SO_4 to 1 liter with reagent water.

7.10. Stannous sulfate solution: Add 25 g of stannous sulfate to 250 mL of 0.5 N sulfuric acid. This mixture is a suspension and should appear cloudy. This solution should be made daily and should be stirred continuously during use.

Note: Stannous chloride may be used in place of stannous sulfate. Prepare the stannous chloride solution according to the recommendations provided by the instrument manufacturer.

7.11. Sodium chloride-hydroxylamine hydrochloride solution: Add 12 g of sodium chloride and 12 g of hydroxylamine hydrochloride to every 100 mL of reagent water.

Note: Hydroxylamine sulfate may be used in place of hydroxylamine hydrochloride.

7.12. Potassium permanganate, 5% solution (w/v): Dissolve 5 g of potassium permanganate for every 100 mL of reagent water.

7.13. Potassium persulfate, 5% solution (w/v): Dissolve 5 g of potassium persulfate for every 100 mL of reagent water.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Sample holding time for mercury is 26 days from time of receipt to the time of analysis.

8.2. Aqueous samples are preserved with nitric acid to a pH of <2 and may be stored in either plastic or glass. Refrigeration is not required. Preservation must be verified prior to analysis.

9. QUALITY CONTROL

The CLP SOW ILMO3.0 document provides further details of the QC and corrective action guidelines presented in this SOP. Refer to this document if additional guidance is required.

Table II (Appendix A) provides a summary of quality control requirements including type, frequency, acceptance criteria and corrective action.

9.1. Initial Demonstration of Capability

Prior to the analysis of any analyte using 245.1 CLP-M, the following requirements must be met.

9.1.1. Instrument Detection Limit (IDL) -The IDL for each analyte must be determined for each analyte wavelength used on each instrument. The IDL must be determined quarterly (every three months). If the instrument is adjusted in anyway that may affect the IDL, the IDL for that instrument must be redetermined. For example, the IDL must be redetermined after the instrument is moved or the internal optics cleaned. The IDL shall be determined by multiplying by 3, the average of the standard deviations obtained on three nonconsecutive days from the analysis of a standard solution (analyte in reagent water) at a concentration 3 - 5 times the previously determined IDL, with seven consecutive measurements per day. When initially determining the IDL for a new instrument, use the manufacturer's IDL as a reference point for making up the 3 - 5x IDL standard. Each measurement must be performed as though it were a separate analytical sample (i.e., each measurement must be followed by a rinse

and/or any other procedure performed between the analysis of separate samples). The result of the IDL determination must be below the CRDL.

- If the IDLs are not completed by the quarterly due date, no CLP analyses may be performed until the IDLs are completed (IDLs can not be retroactively applied).
- For reporting purposes, if multiple CVAA instruments are used for the analysis of an element in a SDG, the highest CVAA IDL must be used for reporting concentration values.
- Instrument specific IDLs must be used for all calculations.
- When calculating IDLs always round the IDL up and to the appropriate number of significant figures (one decimal place).

9.2. Sample Delivery Group (SDG)- An SDG is defined in the CLP SOW by the following, whichever is more frequent:

- each Case of field samples received, OR
- each 20 field samples within a Case, OR
- each 14 day calendar day period during which field samples in a Case are received.

For commercial clients, the SDG definition must be clarified with the client prior to the analysis of samples.

9.3. Analytical Sample - The CLP SOW defines the term “analytical sample” to include all field samples and all required QC samples (matrix spikes, duplicates, postdigestion spikes, serial dilutions, laboratory control samples, interference check samples, CRDL standards, preparation blanks and linear range analyses) except those directly related to instrument calibration or calibration verification (calibration standards, ICV/ICB and CCV/CCB).

9.4. Preparation Batch- The CLP SOW defines batch as “A group of samples prepared at the same time in the same location using the same method”.

9.5. Preparation Blank (PB) - One preparation blank (method blank) must be processed with each preparation batch (or with each SDG, whichever is more frequent for U.S.EPA CLP contract analyses). The preparation blank consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The preparation blank is used to identify any system

and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. The preparation blank should not contain any analyte of interest at or above the CRDL (exception: see below).

- If any analyte concentration in the blank is above the CRDL, the lowest concentration of that analyte in the associated samples must be 10X the blank concentration. Otherwise, all samples associated with the blank, with the analyte's concentration less than 10X the blank concentration and above the CRDL, must be redigested and reanalyzed for that analyte (except for identified aqueous soil field blanks).

- If the concentration of the blank is below the negative CRDL, then all samples reported below 10X CRDL associated with the blank must be redigested and reanalyzed.

- If the above criteria are not met and reanalysis is not possible, then the sample data must be qualified. **This anomaly must be addressed in the project narrative and the client must be notified.**

9.6. Laboratory Control Sample (LCS)- An aqueous LCS is not required for CLP mercury determinations.

9.7. Matrix Spike (MS)- One matrix spike must be processed for each SDG or each group of samples of a similar matrix type, whichever is more frequent. A matrix spike is a field sample to which known concentrations of target analytes have been added prior to digestion. Samples identified as field blanks cannot be used for matrix spike analysis. The matrix spike results are used to determine the effect of a matrix on the accuracy of the analytical process. Spiking levels are provided in Table I.

- If any analyte recovery falls outside the control limits of 75-125%, the data of all samples associated with that spiked sample must be flagged appropriately. An exception to the rule is granted if the native analyte concentration in the MS exceeds 4x the spike level for that analyte. In such an event, the data shall be reported unflagged even if the recovery does not meet the criteria.

- If the MS recovery falls outside the control limits and the sample result does not exceed 4x the spike added, the data must be appropriately flagged.

- The average of the duplicate results cannot be used for the purpose of determining percent recovery.

9.8. Duplicate (DU)- One duplicate must be processed for each SDG or each group of samples of a similar matrix type, whichever is more frequent. Samples identified as field blanks cannot be used for duplicate sample analysis.

- If the sample results are greater than or equal to five times the CRDL, a control limit of ± 20 % RPD must be used.
- If either the sample or sample duplicate value is less than five times the CRDL, a control limit of ± the CRDL must be used.
- If both the sample and the sample duplicate are below the IDL, the RPD is not calculated and no control criteria apply.
- If the DU RPD is outside control limits, the data is flagged appropriately.

9.9. Initial Calibration Verification (ICV/ICB) - Calibration accuracy is verified by analyzing a second source standard (ICV) immediately after calibration. The ICV result must fall within 20% of the true value. An ICB is analyzed immediately following the ICV to monitor low level accuracy and system cleanliness. The ICB result must fall within +/- the CRDL from zero. If either the ICV or ICB fail to meet criteria, the analysis should be terminated, the problem corrected and the instrument recalibrated. (See Section 11.2.10 for required run sequence). If the cause of the ICV or ICB failure was not directly instrument related the corrective action will include repreparation of the associated samples.

9.10. CRDL Standard (CRA) - To verify linearity near the CRDL for CVAA analysis, a CRA standard is run at the beginning of each sample analysis run, but not before the ICV. The CRA standard must contain the analyte at the CRDL. (See Section 11.2.10 for required run sequence.)

9.11. Continuing Calibration Verification (CCV/CCB) - Calibration accuracy is monitored throughout the analytical run through the analysis of a known standard after every 10 samples or every 2 hours, whichever is more frequent. The CCV must be a mid-range standard at a concentration other than that of the ICV. The CCV result must fall within 20% of the true value for that solution. A CCB is analyzed immediately following each CCV. (See Section 11.2.10 for required run sequence.) The CCB result must fall within +/- CRDL from zero. If a mid-run CCV or CCB fails, the analysis must be terminated, the problem corrected, the instrument recalibrated, the calibration verified and the affected samples reanalyzed. If the cause of the CCV or CCB failure was not directly instrument related, the corrective action will include repreparation of the associated samples.

- Each CCV analyzed must reflect the conditions of analysis of all associated samples. The duration of analysis, rinses, and other operations that may affect the CCV result may not differ from those used for the associated samples. For example, the difference in time between a CCV analysis and the CCB immediately following it or the sample immediately preceding it may not exceed the smallest difference between any two consecutive samples associated with that CCV.

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

10. CALIBRATION AND STANDARDIZATION

10.1. Calibration standards must be processed through the preparation procedure as described in Section 11.1.

10.2. Due to the differences in preparation protocols separate calibration and calibration verification standards must be prepared for aqueous and solid matrices.

10.3. Calibration must be performed daily (every 24 hours) and each time the instrument is set up . The instrument calibration date and time must be included in the raw data.

10.4. Set up the instrument with the operating parameters recommended by the manufacturer. Allow the instrument to become thermally stable before beginning calibration (approximately 30 minutes of warm-up is required). Refer to the facility specific instrument SOP and CVAA instrument manual for detailed setup and operation protocols.

10.5. Calibrate the instrument according to instrument manufacturer's instructions, using a minimum of five standards and a blank. One standard must be at the CRDL. Analyze standards in ascending order beginning with the blank. Refer to Section 7.5 and Table I for additional information on preparing calibration standards and calibration levels.

10.6. The calibration curve must have a correlation coefficient of ≥0.995 or the instrument shall be stopped and recalibrated prior to running samples. Sample results can not be reported from a curve with an unacceptable correlation coefficient.

10.7. Refer to Section 9.0 for calibration verification procedures, acceptance criteria and corrective actions.

11. PROCEDURE

11.1. Sample Preparation:

11.1.1. All calibration and calibration verification standards (ICV, ICB, CCV, CCB, CRA) are processed through the digestion procedure as well as the field samples.

11.1.2. Transfer 100 mL of well mixed sample or standard to a clean sample digestion bottle.

11.1.3. Add 5 mL of concentrated H_2SO_4 and 2.5 mL of concentrated HNO_3 mixing after each addition.

Note: All spiking should be done after the initial addition of acids.

11.1.4. Add 15 mL of potassium permanganate solution. For samples high in organic materials or chlorides, additional permanganate may be added. Shake and add additional portions of permanganate solution until a purple color persists for at least 15 minutes. If after the addition of up to 25 mL additional permanganate the color does not persist, sample dilution prior to reanalysis may be required.

Note: If excess permanganate solution is added to a sample, the same volume of permanganate must be added to all associated samples, standards, *and QC samples (e.g. LCS and blank)* in the run.

11.1.5. Add 8 mL of potassium persulfate solution and heat for two hours in a water bath at 95 °C or autoclave samples at 120 °C (± 4 °C), 15 lbs., for 15 minutes.

11.1.6. Cool samples.

11.2. Sample Analysis:

11.2.1. Because of differences between various makes and models of CVAA instrumentation, no detailed operating instructions can be provided. Refer to the facility specific instrument operating SOP and the CVAA instrument manual for detailed setup and operation protocols.

11.2.2. All labs are required to detail the conditions/programs utilized for each instrument within the facility specific instrument operation SOP.

11.2.3. When ready to begin analysis, add 6 mL of sodium chloride-hydroxylamine hydrochloride solution to the samples to reduce the excess permanganate (the permanganate has been reduced when no purple color remains). Add this solution in 6 mL increments until the permanganate is completely reduced.

11.2.4. Manual determination:

11.2.4.1. Treating each sample individually, purge the head space of the sample bottle for at least one minute.

11.2.4.2. Add 5 mL of stannous chloride solution and immediately attach the bottle to the aeration apparatus.

11.2.4.3. Allow the sample to stand quietly without manual agitation while the sample is aerated (1 L/min flow). Monitor the sample absorbance during aeration. When the absorbance reaches a maximum and the signal levels off, open the bypass valve and continue aeration until the absorbance returns to its baseline level. Close the bypass valve and remove the aeration device.

11.2.4.4. Place the aeration device into 100 mLs of 1% HNO_3 and allow to bubble rinse until the next sample is analyzed.

11.2.5. Automated determination: Follow instructions provided by instrument manufacturer.

11.2.6. Perform a linear regression analysis of the calibration standards by plotting maximum response of the standards vs. concentration of mercury (ug/L) for automated determinations or total Hg (ug) for manual determinations. Determine the mercury concentration in the samples from the linear regression fit of the calibration curve. Calibration using computer or calculation based regression curve fitting techniques on concentration/response data is acceptable.

11.2.7. All measurements must fall within the defined calibration range to be valid. Dilute and reanalyze all samples for analytes that exceed the highest calibration standard.

11.2.8. The samples must be allowed to cool to room temperature prior to analysis or a decrease in the response signal can occur.

11.2.9. Baseline correction is acceptable as long as it is performed after every sample or after the CCV and CCB; resloping is acceptable as long as it is immediately preceded and followed by a compliant CCV and CCB.

11.2.10. The following run sequence is consistent with 254.1 CLP-M, SOW ILMO3.0 requirements:

Instrument Calibration
ICV
ICB
CRA
CCV
CCB
10 samples
CCV
CCB
Repeat sequence of 10 samples between CCV/CCB pairs as required to complete run.
CCV
CCB

11.3. To facilitate the early identification of QC failures and samples requiring rerun it is strongly recommended that sample data be reviewed periodically throughout the run.

11.4. Guidelines are provided in the appendices on procedures to minimize contamination of samples and standards, preventive maintenance and troubleshooting.

11.5. One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and is approved by a Technical Specialist and QA Manager. If contractually required, the client shall be notified. For U.S. EPA contract analyses the Technical Project Officer must be contacted in advance for approval. The Nonconformance Memo shall be filed in the project file.

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

12. DATA ANALYSIS AND CALCULATIONS

12.1. ICV percent recoveries are calculated according to the equation:

$$\%R = 100\left(\frac{Found(ICV)}{True(ICV)}\right)$$

12.2. CCV percent recoveries are calculated according to the equation:

$$\%R = 100\left(\frac{Found(CCV)}{True(CCV)}\right)$$

12.3. Matrix spike recoveries are calculated according to the following equation:

$$\%R = 100\left(\frac{SSR - SR}{SA}\right)$$

Where:
SSR = Spike Sample Result
SR = Sample Result
SA = Spike Added

12.4. The relative percent difference (RPD) of matrix spike/matrix spike duplicates or sample duplicates are calculated according to the following equations:

$$RPD = 100\left[\frac{|MSD - MS|}{\left(\frac{MSD + MS}{2}\right)}\right]$$

Where:
MS = determined spiked sample concentration
MSD = determined matrix spike duplicate concentration

$$RPD = 100\left[\frac{|DU1 - DU2|}{\left(\frac{DU1 + DU2}{2}\right)}\right]$$

Where:
DU1 = Sample result
DU2 = Sample duplicate result

12.5. Using the automated method, the final concentration for an aqueous sample is calculated as follows:

$$ug/L = C \times D$$

Where:

C = Concentration (ug/L) from instrument readout
D = Instrument dilution factor

12.6. Using the manual method, the final concentration for an aqueous sample is calculated as follows:

$$ug/L = C / V$$

Where:

C = ug Hg from linear regression
V = Volume of sample used for analysis

12.7. The LCS percent recovery is calculated according to the following equation:

$$\%R = 100\left(\frac{Found(LCS)}{True(LCS)}\right)$$

12.8. Sample results should be reported with up to three significant figures in accordance with the following:

Result	Significant Figures
< IDL	Report IDL u (2 sig figs)
> IDL and < 10.0 ug/L	Report 2 sig figs
≥ 10.0 ug/L	Report 3 sig figs

13. METHOD PERFORMANCE

13.1. Each laboratory must have initial demonstration of performance data on file for each analyte of interest as described in Section 9.0.

13.2. Method performance is determined by the analysis of preparation blanks, laboratory control samples, matrix spikes and matrix duplicate samples. The matrix spike recovery should fall within +/- 25 % and the matrix duplicates should compare within 20% RPD when sample results are greater than 5x the CRDL and ± the CRDL when sample results are < 5x the CRDL. Preparation blanks must meet the criteria in Section 9.5. Laboratory control samples should recover within 20% of the true value.

13.3. Training Qualification:

The group/team leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience.

14. POLLUTION PREVENTION

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

15. WASTE MANAGEMENT

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

16. REFERENCES

16.1. U.S.EPA Statement of Work for Inorganics Analysis, ILMO3.0.

17. MISCELLANEOUS (TABLES, APPENDICES, ETC. . .)

17.1. Modifications/Interpretations from reference method.

None

17.2. Modifications from previous SOP

17.2.1. CORP-MT-0006, rev0: Added text to Note in Section 11.1.4: “and QC samples (e.g. LCS and blank).”

17.3. Facility Specific SOPs

Each facility shall attach a list of facility specific SOPs or approved attachments (if applicable) which are required to implement this SOP or which are used in conjunction

with this SOP. If no facility specific SOPs or amendments are to be attached, a statement must be attached specifying that there are none. Refer to the Appendices for any facility specific information required to support this SOP.

17.4. Documentation and Record Management

The following documentation comprises a complete CVAA raw data package:

- Raw data (direct instrument printout)
- Run log printout from instrument software where this option is available or manually generated run log. (A bench sheet may be substituted for the run log as long as it contains an accurate representation of the analytical sequence and sufficient date and time information to verify that the QC time criteria were met).
- Data review checklist - See Appendix B
- Standards Documentation (source, lot, date).
- Copy of digestion log.
- Non-conformance summary (if applicable).

- **FIGURES**

Figure 1. Aqueous Sample Preparation - Mercury

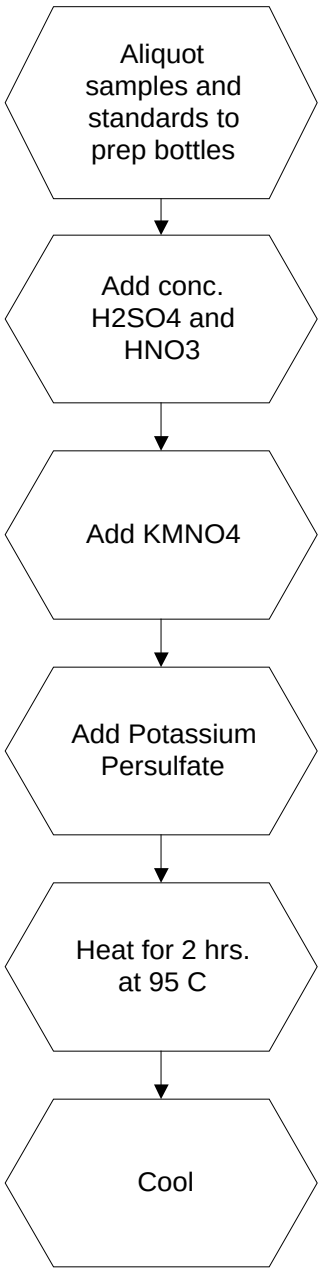
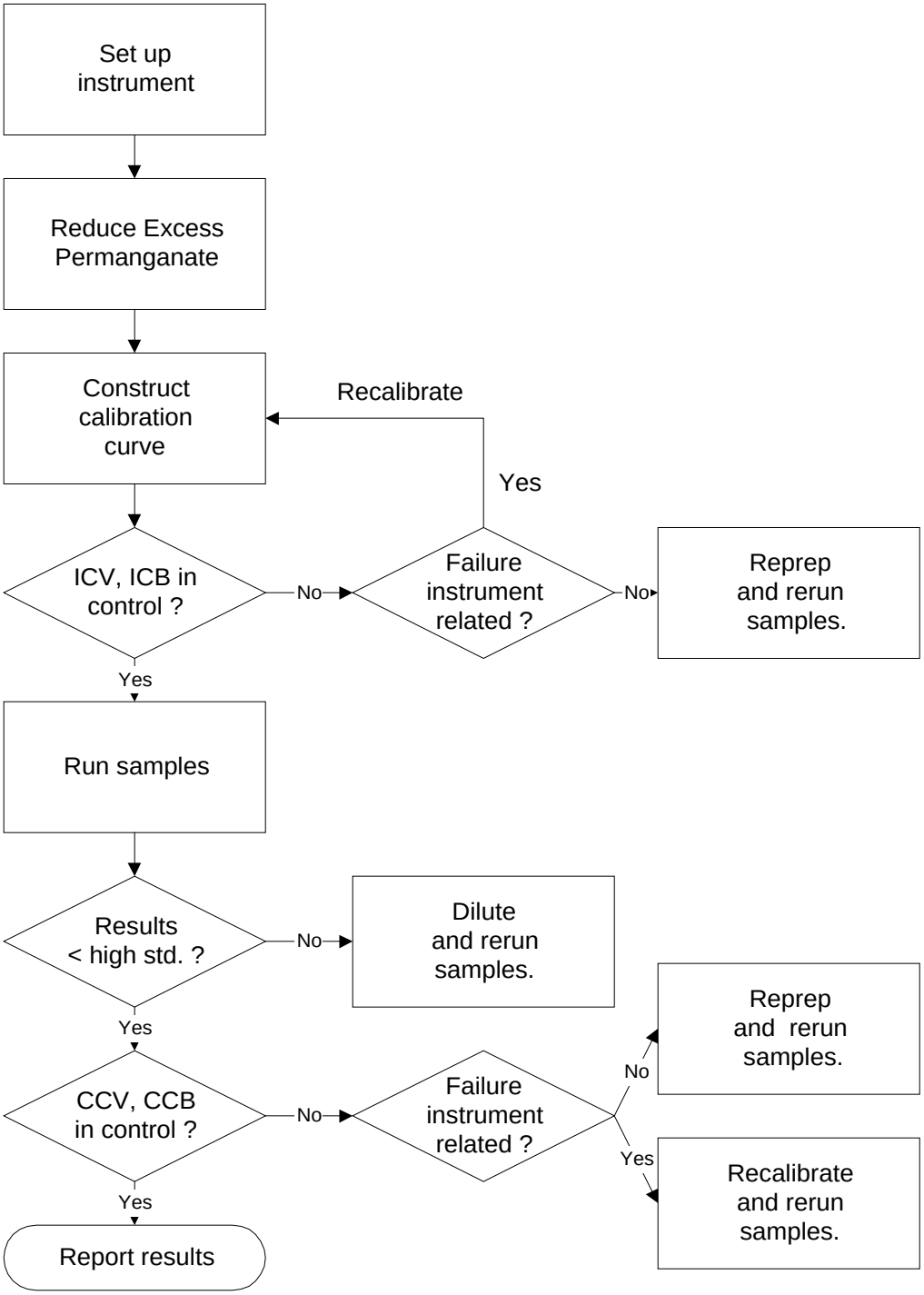


Figure 2. CVAA Mercury Analysis



APPENDIX A

TABLES

TABLE I . MERCURY REPORTING LIMITS, CALIBRATION STANDARD*, QC STANDARD AND SPIKING LEVELS (UG/L)

Aqueous CRDL	0.2
Std 0	0
Std 1	0.2
Std 2	0.5
Std 3	1.0
Std 4	2.0
Std 5	5.0
Std 6 **	10
ICV***	1.0 or 2.5 ***
LCS/CCV	2.5 or 5.0 ***
Aqueous MS	1.0

*** SOP specified calibration levels must be used unless prevented by the instrument configuration or client specific requirements. Deviations from specified calibration levels must be documented in the facility specific instrument operation SOP and must be approved by the facility technical manager and Quality Assurance Manager.**

**** Optional standard which may be used to extend the calibration range as allowed by the instrument configuration. If the instrument configuration prevents the use of 6 standards, the 2 ppb standard may be eliminated in favor of the 10 ppb standard.**

***** Concentration dependent on high calibration standard used. CCV must be 50% of the high standard concentration and ICV must be 20-25% of the high standard concentration (exception: For USEPA CLP contract analyses the EPA supplied ICV must be used).**

TABLE II. Summary Of Quality Control Requirements

QC PARAMETER	FREQUENCY *	ACCEPTANCE CRITERIA	CORRECTIVE ACTION
ICV	Beginning of every analytical run.	80 - 120 % recovery.	Terminate analysis; Correct the problem; Recalibrate or reprep batch (see Section 9.9).
ICB	Beginning of every analytical run, immediately following the ICV.	The result must be within +/- CRDL from zero.	Terminate analysis; Correct the problem; Recalibrate or reprep batch (see Section 9.9).
CCV	Beginning and end of run and every 10 samples or every 2 hours, whichever is more frequent.	80 - 120 % recovery.	Terminate analysis; Correct the problem; Recalibrate, reverify the calibration and rerun all samples since last acceptable CCV. Reprep of batch may be required (see Section 9.11).
CCB	Immediately following each CCV.	The result must be within +/- CRDL from zero.	Terminate analysis; Correct the problem; Recalibrate, reverify the calibration and rerun all samples since last acceptable CCB. Reprep of batch may be required (see Section 9.11)
Preparation Blank	One per sample preparation batch of up to 20 samples.	The result must be less than or equal to the CRDL. Sample results greater than 10x the blank concentration are acceptable. Samples for which the contaminant is < RL do not require redigestion (See Section 9.5).	Redigest and reanalyze samples. Note exceptions under criteria section. See Section 9.5 for additional requirements.

*See Section 11.2.10 for exact run sequence to be followed.

TABLE II. Summary of Quality Control Requirements (Continued)

QC PARAMETER	FREQUENCY*	ACCEPTANCE CRITERIA	CORRECTIVE ACTION
CRA	Beginning of each analytical run.	No criteria established by EPA at this time.	Not Applicable.
Laboratory Control Sample (LCS)	Not required for aqueous samples.	Not Applicable.	Not Applicable.
Matrix Spike	One per sample preparation batch of up to 20 samples.	75 - 125 % recovery.	Flag the data; no flag required if the sample level is > 4x the spike added. (see Section 9.7)
Sample Duplicate	One per sample preparation batch of up to 20 samples.	RPD ≤ 20% if results ≥ 5x CRDL or, ± CRDL if either result < 5x CRDL.	Flag the data. (see Section 9.8)

*See Section 11.2.10 for exact run sequence to be followed.

APPENDIX B

STL HG DATA REVIEW CHECKLIST

STL Hg Data Review Checklist

Run/Project Information

Run Date: _____ Analyst:_____ Instrument:_____
Prep Batches Run:_____

Circle Methods used: 7470A / 245.1 : CORP-MT-0005 Rev 0 7471 / 245.5 : CORP-MT-0007 Rev 0
CLP - AQ : CORP-MT-0006 Rev 0 CLP - SOL : CORP-MT-0008 Rev 0

Review Items

A. Calibration/Instrument Run QC	Yes	No	N/A	2nd Level
1. Instrument calibrated per manufacturer's instructions and at SOP specified levels ?				
2. ICV/CCV analyzed at appropriate frequency and within control limits?				
3. ICB/CCB analyzed at appropriate frequency and within +/- RL or +/- CRDL (CLP)?				
4. CRA run (CLP only)?				
B. Sample Results				
1. Were samples with concentrations > the high calibration standard diluted and reanalyzed?				
2. All reported results bracketed by in control QC ?				
3. Sample analyses done within holding time?				
C. Preparation/Matrix QC				
1. LCS done per prep batch and within QC limits ?				
2. Method blank done per prep batch and < RL or CRDL (CLP) ?				
3. MS run at required frequency and within limits ?				
4. MSD or DU run at required frequency and RPD within SOP limits?				
D. Other				
1. Are all nonconformances documented appropriately ?				
2. Current IDL/MDL data on file?				
3. Calculations and Transcriptions checked for error ?				
4. All client/ project specific requirements met?				
5. Date of analysis verified as correct ?				

Analyst: _____ Date:_____
Comments:
_____
_____

2nd Level Reviewer : _____ Date:_____
_____
_____

APPENDIX C

TROUBLESHOOTING GUIDE

APPENDIX C. TROUBLESHOOTING GUIDE

Problem	**Possible Cause**
Poor or No Absorbance or Sensitivity Check failed	Incorrect wavelength Dirty windows Window loose Etched or dirty optics Wrong lamp Bad lamp Not enough or no sample introduced Empty sample cup Incorrectly made standards Gas leak EDL power supply set on “Continuous”
Erratic Readings	Source lamp not aligned properly Lamp not prewarmed Injection tip partially clogged Contaminated reagents Contaminated glassware Drying tube saturated Bad lamp Injection tip hitting outside of tube Injection tip coated or not set properly Leak in sample tubing Power fluctuations Air bubbles in tubing
EDL Won’t Light	Lamp cable not plugged in Lamp power set at 0 Lamp is dead Power supply fuse is blown Short in cord
Standards reading twice or half normal absorbance or concentration	Incorrect standard used Incorrect dilution performed Dirty cell
Background Correction Light Blinking	Background screen or attenuator faulty

APPENDIX D

CONTAMINATION CONTROL GUIDELINES

APPENDIX D. CONTAMINATION CONTROL GUIDELINES

The following procedures are strongly recommended to prevent contamination:

All work areas used to prepare standards and spikes should be cleaned before and after each use.

All glassware should be washed with detergent and tap water and rinsed with 1:1 nitric acid followed by deionized water.

Proper laboratory housekeeping is essential in the reduction of contamination in the metals laboratory. All work areas must be kept scrupulously clean.

Powdered or Latex Gloves must not be used in the metals laboratory since the powder contains silica and zinc, as well as other metallic analytes. Only vinyl or nitrile gloves should be used in the metals laboratory.

Glassware should be periodically checked for cracks and etches and discarded if found. Etched glassware can cause cross contamination of any metallic analytes.

Autosampler trays should be covered to reduce the possibility of contamination. Trace levels of elements being analyzed in the samples can be easily contaminated by dust particles in the laboratory.

The following are helpful hints in the identification of the source of contaminants:

Reagents or standards can contain contaminants or be contaminated with the improper use of a pipette.

Improper cleaning of glassware can cause contamination.

Separate glassware if an unusually high sample is analyzed and soak with sulfuric acid prior to routine cleaning.

APPENDIX E

PREVENTIVE MAINTENANCE

APPENDIX E. PREVENTIVE MAINTENANCE

A maintenance log is used to record when maintenance is performed on instruments. When an instrument problem occurs indicate the date, time and instrument number, then identify the problem and corrective action in the maintenance log.

The following procedures are required to ensure that that the instrument is fully operational.

Cold Vapor Atomic Absorption (Leeman PS 200) (1)

Daily	Semi-annually	Annually
Clean lens.	Check Hg lamp intensity.	Change Hg lamp.
Check aperture.		Check liquid/gas separator.
Check argon flow.		
Check tubing.		
Check drain.		
Replace drying tube.		

Cold Vapor Atomic Absorption (PE 5000) (1)

Daily	Monthly
Clean aspirator by flushing with DI water.	Clean cell in aqua regia.
Check tubing and replace if needed.	Clean aspirator in aqua regia.
Clean windows with methanol.	
Change silica gel in drying tube.	
Check argon gas supply.	
Adjust lamp.	

CORP-MT-0008

Preparation and Analysis of Mercury in Solid Samples by Cold Vapor Atomic Absorption, Method 245.1 CLP-M, SOW ILM03.0

STL STANDARD OPERATING PROCEDURE

TITLE: PREPARATION AND ANALYSIS OF MERCURY IN SOLID SAMPLES BY COLD VAPOR ATOMIC ABSORPTION SPECTROSCOPY, METHOD 245.5 CLP-M, SOW ILMO3.0

(SUPERSEDES: REVISION 0)

Prepared by: Kurt Ill and Richard Burrows

Reviewed by: _____
Technical Specialist

Approved by: _____
Director, Quality Assurance

Approved by: _____
Director, Environmental Health and Safety

Approved by: _____
Management

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1. SCOPE AND APPLICATION

1.1. This procedure describes the preparation and analysis of mercury (Hg, CAS # 7439-97-6) by Cold Vapor Atomic Absorption Spectroscopy (CVAA) using Method 245.5 CLP-M as contained in CLP SOW ILMO3.0. In addition to SOW ILMO3.0, this SOP is also compliant with the requirements of CLP SOWs 7/88, 3/90, ILMO1.0 and ILMO2.1.

1.2. CVAA analysis provides for the determination of total mercury (organic and inorganic). The combination of the oxidants, potassium permanganate and potassium persulfate, has been found to give 100% recovery with both types of compounds. Detection limits, sensitivity and optimum concentration ranges for mercury analysis will vary with the matrices, instrumentation and volume of sample used.

1.3. Methods 245.5 CLP-M is applicable to the preparation and analysis of mercury in soils, sediments, bottom deposits and sludge-type materials. All matrices require sample preparation prior to analysis.

1.4. The CRDL for mercury in solid matrices is 0.1 mg/kg based a 0.2 g sample aliquot (wet weight).

2. SUMMARY OF METHOD

2.1. This SOP describes a technique for the determination of mercury in solution. The procedure is a physical method based on the absorption of radiation at 253.7 nm by mercury vapor. A representative portion of the sample is digested in sulfuric and nitric acids. Organic mercury compounds are oxidized with potassium permanganate and potassium persulfate and the mercury reduced to its elemental state with stannous chloride and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance is measured as a function of mercury concentration. Concentration of the analyte in the sample is determined by comparison of the sample absorbance to the calibration curve (absorbance vs. concentration).

3. DEFINITIONS

3.1. Total Metals: The concentration determined on an unfiltered sample following digestion.

4. INTERFERENCES

Chemical and physical interferences may be encountered when analyzing samples using this method.

4.1. Potassium permanganate which is used to breakdown organic mercury compounds also eliminates possible interferences from sulfide. Concentrations as high as 20 mg/L of sulfide as sodium sulfide do not interfere with the recovery of inorganic mercury from reagent water.

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

4.3. Chlorides can cause a positive interference. Samples high in chlorides require additional permanganate (as much as 25 mL) because, during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation at 253.7 nm. Care must be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. This is accomplished by adding excess hydroxylamine reagent (25 mL) and purging the sample headspace before stannous chloride is added. Both inorganic and organic mercury spikes have been quantitatively recovered from seawater using this technique.

Note: Sufficient addition of permanganate is apparent when the purple color persists at least 15 minutes. Some samples may require dilution prior to digestion due to extremely high concentrations of chloride.

4.4. Interference from certain volatile organic materials that absorb at this wavelength may also occur. If suspected, a preliminary run without stannous chloride can determine if this type of interference is present. While the possibility of absorption from certain organic substances present in the sample does exist, this problem is not routinely encountered. This is mentioned only to caution the analyst of the possibility. If this condition is found to exist, the mercury concentration in the sample can be determined by subtracting the result of the sample run without the reducing reagent (stannous chloride) from that obtained with the reducing reagent.

4.5. Samples containing high concentrations of oxidizable organic materials, as evidenced by high COD levels, may not be completely oxidized by this procedure. When this occurs the recovery of mercury will be low. The problem can be eliminated by reducing the volume of original sample used.

4.6. The most common interference is laboratory contamination which may arise from impure reagents, dirty glassware, improper sample transfers, dirty work areas, etc. Be

aware of potential sources of contamination and take appropriate measures to minimize or avoid them.

5. SAFETY

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

5.2. Eye protection that satisfies ANSI Z87.1 (as per the Chemical Hygiene Plan), laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

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

5.3.1. The following materials are known to be **corrosive:**

hydrochloric acid, nitric acid and sulfuric acid.

5.3.2. The following materials are known to be **oxidizing agents**:

nitric acid, potassium permanganate, potassium persulfate and magnesium perchlorate.

5.3.3. Mercury is a highly toxic element that must be handled with care. The analyst must be aware of the handling and clean-up techniques before working with mercury. Since mercury vapor is toxic, precaution must be taken to avoid its inhalation, ingestion or absorption through skin. All lines should be checked for leakage and the mercury vapor must be vented into a hood or passed through a mercury absorbing media such as:

5.3.3.1. Equal volumes of 0.1 M $KMnO_4$ and 10% H_2SO_4, or

5.3.3.2. Iodine, 0.25%, in a 3% KI solution.

5.3.4. Magnesium sulfate is known to be a reproductive toxin (mutagen).

5.4. Exposure to chemicals must be maintained **as low as reasonably achievable.** Therefore, unless they are known to be non-hazardous, all samples should be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

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

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

5.7. Do not look directly into the beam of the Hg lamp. The UV light that these lamps radiate is harmful to the eyes.

5.8. Cylinders of compressed gas must be handled with caution, in accordance with local regulations. It is recommended that, wherever possible, cylinders be located outside the laboratory and the gas led to the instrument through approved lines.

5.9. The CVAA apparatus must be properly vented to remove potentially harmful fumes generated during sample analysis.

6. EQUIPMENT AND SUPPLIES

6.1. Temperature controlled water bath (capable of maintaining a temperature of 90-95 °C) or autoclave capable of obtaining 15 lbs., 121 °C.

6.2. Atomic Absorption Spectrophotometer equipped with:

6.2.1. Absorption Cell with quartz end windows perpendicular to the longitudinal axis. Dimensions of the cell must result in sufficient sensitivity to meet the SOP defined reporting limit. The quartz windows must be maintained to provide accurate measurements. Any scratches or fingerprints can alter the absorption of UV radiation.

6.2.2. Mercury specific hollow cathode lamp (HCL) or electrodeless discharge lamp (EDL).

6.2.3. Peristaltic pump which can deliver 1 L/min air.

6.2.4. Flowmeter capable of measuring an airflow of 1 L/min.

6.2.5. Recorder or Printer.

6.2.6. Aeration Tubing: A straight glass frit having a course porosity and Tygon tubing is used for the transfer of mercury vapor from the sample bottle to the absorption cell and return.

6.2.7. Drying device (a drying tube containing magnesium perchlorate or magnesium sulfate and/or a lamp with a 60 W bulb) to prevent condensation in cell. The lamp is positioned to shine on the absorption cell maintaining the air temperature in the cell about 10 °C above room temperature. Other drying devices that achieve the same purpose are also acceptable (i.e., Gortex filter).

NOTE: Instruments designed specifically for the measurement of mercury using the cold vapor technique may be substituted for the atomic absorption spectrophotometer.

6.3. BOD bottles or equivalent.

6.4. Nitrogen or argon gas supply, welding grade or equivalent.

6.5. Calibrated automatic pipettes or Class A glass volumetric pipettes.

6.6. Class A volumetric flasks.

6.7. Top-loading balance, capable of reading up to two decimal places.

6.8. Thermometer (capable of accurate readings at 95 °C).

6.9. Disposable cups or tubes.

7. REAGENTS AND STANDARDS

7.1. Reagent water must be produced by a Millipore DI system or equivalent. Reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks.

7.2. Stock (1000 ppm) mercury standards are purchased as custom STL solutions. All standards must be stored in FEP fluorocarbon or previously unused polyethylene or polypropylene bottles. Stock standard solutions must be replaced prior to the expiration date provided by the manufacturer. If no expiration date is provided, the stock solutions may be used for up to one year and must be replaced sooner if verification from an independent source indicates a problem.

7.3. Intermediate mercury standard (10 ppm): Take 1 mL of the stock mercury standard (7.2) and dilute to 100 mL with reagent water. The intermediate standard must be made monthly and must be prepared in a matrix of 2% HNO_3 . This acid (2 mL of concentrated HNO_3) must be added to the flask/bottle before the addition of the stock standard aliquot.

7.4. Working mercury standard (0.1 ppm): Take 1 mL of the intermediate mercury standard (7.3) and dilute to 100 mL with reagent water. The working mercury standard must be made daily and must be prepared in a matrix of 0.15% HNO_3. This acid (150 uL of concentrated HNO_3) must be added to the flask/bottle before the addition of the stock standard aliquot.

7.5. The calibration standards must be prepared fresh daily from the working standard (7.4) by transferring 0, 0.2, 0.5, 1.0, 2.0, 5.0 and 10.0 mL aliquots of the working mercury standard into sample prep bottles and proceeding as specified in Section 11.1

Note: Alternate volumes of standard may be prepared as long as the accuracy and final standard concentrations as detailed in Table I are maintained.

7.6. The initial calibration verification standard must be made from a different stock solution than that of the calibration standards (see 7.8).

7.7. Solid reference material for use as soil LCS (see 7.8)

7.8. For analyses performed under direct contract to the USEPA CLP, the EPA provided ICV solution and solid LCS material must be used.

7.9. Refer to Table I (Appendix A) for details regarding the working standard concentrations for calibration, calibration verification and spiking solutions. All standards must be processed through the entire analytical procedure including sample preparation.

7.10. Nitric acid (HNO_3), concentrated, trace metal grade or better.

Note: If a high reagent blank is obtained, it may be necessary to distill the nitric acid.

7.11. Sulfuric acid (H_2SO_4), concentrated, trace metal grade or better.

7.12. Sulfuric acid, 0.5 N: Dilute 14.0 mL of concentrated H_2SO_4 to 1 liter with reagent water.

7.13. Stannous sulfate solution: Add 25 g of stannous sulfate to 250 mL of 0.5 N sulfuric acid. This mixture is a suspension and should appear cloudy. This solution should be made daily and should be stirred continuously during use.

Note: Stannous chloride may be used in place of stannous chloride. Prepare the stannous chloride solution according to the recommendations provided by the instrument manufacturer.

7.14. Sodium chloride-hydroxylamine hydrochloride solution: Add 12 g of sodium chloride and 12 g of hydroxylamine hydrochloride to every 100 mL of reagent water.

Note: Hydroxylamine sulfate may be used in place of hydroxylamine hydrochloride.

7.15. Potassium permanganate, 5% solution (w/v): Dissolve 5 g of potassium permanganate for every 100 mL of reagent water.

7.16. Potassium persulfate, 5% solution (w/v): Dissolve 5 g of potassium persulfate for every 100 mL of reagent water.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. The sample holding time for mercury is 26 days from time of receipt to the time of analysis.

8.2. Soil samples do not require preservation but must be stored at 4° C ± 2° C until the time of analysis.

9. QUALITY CONTROL

The CLP SOW ILMO3.0 document provides further details of the QC and corrective action guidelines presented in this SOP. Refer to this document if additional guidance is required

Table II (Appendix A) provides a summary of quality control requirements including type, frequency, acceptance criteria and corrective action.

9.1. Initial Demonstration of Capability

Prior to the analysis of any analyte using 245.5 CLP-M, the following requirements must be met.

9.1.1. Instrument Detection Limit (IDL) -The IDL for each analyte must be determined for each analyte wavelength used on each instrument. The IDL

must be determined quarterly (every three months). If the instrument is adjusted in anyway that may affect the IDL, the IDL for that instrument must be redetermined. For example, the IDL must be redetermined after the instrument is moved or the internal optics cleaned. The IDL shall be determined by multiplying by 3, the average of the standard deviations obtained on three nonconsecutive days from the analysis of a standard solution (analyte in reagent water) at a concentration 3 - 5 times the previously determined IDL, with seven consecutive measurements per day. When initially determining the IDL for a new instrument, use the manufacturer's IDL as a reference point for making up the 3 - 5x IDL standard. Each measurement must be performed as though it were a separate analytical sample (i.e., each measurement must be followed by a rinse and/or any other procedure performed between the analysis of separate samples). The result of the IDL determination must be below the CRDL.

- If the IDLs are not completed by the quarterly due date, no CLP analyses may be performed until the IDLs are completed (IDLs can not be retroactively applied).
- For reporting purposes, if multiple CVAA instruments are used for the analysis of an element in a SDG, the highest CVAA IDL must be used for reporting concentration values.
- Instrument specific IDLs must be used for all calculations.
- When calculating IDLs always round the IDL up and to the appropriate number of significant figures (one decimal place).

9.2. Sample Delivery Group (SDG)- An SDG is defined in the CLP SOW by the following, whichever is more frequent:

- each Case of field samples received, OR
- each 20 field samples within a Case, OR
- each 14 day calendar day period during which field samples in a Case are received.

For commercial clients, the SDG definition must be clarified with the client prior to the analysis of samples.

9.3. Analytical Sample - The CLP SOW defines the term "analytical sample" to include all field samples and all required QC samples (matrix spikes, duplicates, postdigestion

spikes, serial dilutions, laboratory control samples, interference check samples, CRDL standards, preparation blanks and linear range analyses) except those directly related to instrument calibration or calibration verification (calibration standards, ICV/ICB and CCV/CCB).

9.4. Preparation Batch- The CLP SOW defines batch as "A group of samples prepared at the same time in the same location using the same method".

9.5. Preparation Blank (PB) - One preparation blank (method blank) must be processed with each preparation batch (or with each SDG, whichever is more frequent for U.S.EPA CLP contract analyses). The preparation blank consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The preparation blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. The preparation blank should not contain any analyte of interest at or above the CRDL (exception: see below).

- If any analyte concentration in the blank is above the CRDL, the lowest concentration of that analyte in the associated samples must be 10X the blank concentration. Otherwise, all samples associated with the blank, with the analyte's concentration less than 10X the blank concentration and above the CRDL, must be redigested and reanalyzed for that analyte (except for identified aqueous soil field blanks).

- If the concentration of the blank is below the negative CRDL, then all samples reported below 10X CRDL associated with the blank must be redigested and reanalyzed.

- If the above criteria are not met and reanalysis is not possible, then the sample data must be qualified. **This anomaly must be addressed in the project narrative and the client must be notified.**

9.6. Laboratory Control Sample (LCS) - One solid LCS must be processed with each preparation batch (or with each SDG, whichever is more frequent for U.S.EPA CLP contract analyses). The LCS is used to monitor the accuracy of the analytical process. The solid LCS control limits shall be those established by the supplier of the solid LCS. Corrective action, when LCS results fail to meet control limits, will be repreparation and reanalysis of the batch.

9.7. Matrix Spike (MS)- One matrix spike must be processed for each SDG or each group of samples of a similar matrix type, whichever is more frequent. A matrix spike is a field sample to which known concentrations of target analytes have been added prior

to digestion. Samples identified as field blanks cannot be used for matrix spike analysis. The matrix spike results are used to determine the effect of a matrix on the accuracy of the analytical process. Spiking levels are provided in Table I.

- If any analyte recovery falls outside the control limits of 75-125%, the data of all samples associated with that spiked sample must be flagged appropriately. An exception to the rule is granted if the native analyte concentration in the MS exceeds 4x the spike level for that analyte. In such an event, the data shall be reported unflagged even if the recovery does not meet the criteria.

- If the MS recovery falls outside the control limits and the sample result does not exceed 4x the spike added, the data must be appropriately flagged.

- The average of the duplicate results cannot be used for the purpose of determining percent recovery.

9.8. Duplicate (DU)- One duplicate must be processed for each SDG or each group of samples of a similar matrix type, whichever is more frequent. Samples identified as field blanks cannot be used for duplicate sample analysis.

- If the sample results are greater than or equal to five times the CRDL, a control limit of ± 20 % RPD must be used.

- If either the sample or sample duplicate value is less than five times the CRDL, a control limit of ± the CRDL must be used.

- If both the sample and the sample duplicate are below the IDL, the RPD is not calculated and no control criteria apply.

- If the DU RPD is outside control limits, the data is flagged appropriately.

9.9. Initial Calibration Verification (ICV/ICB) - Calibration accuracy is verified by analyzing a second source standard (ICV) immediately after calibration. The ICV result must fall within 20% of the true value. An ICB is analyzed immediately following the ICV to monitor low level accuracy and system cleanliness. The ICB result must fall within +/- the CRDL from zero. If either the ICV or ICB fail to meet criteria, the analysis should be terminated, the problem corrected and the instrument recalibrated. (See Section 11.2.10 for required run sequence). If the cause of the ICV or ICB failure was not directly instrument related the corrective action will include repreparation of the associated samples.

9.10. CRDL Standard (CRA) - To verify linearity near the CRDL for CVAA analysis, a CRA standard is run at the beginning of each sample analysis run, but not before the

ICV. The CRA standard must contain the analyte at the CRDL. (See Section 11.2.10 for required run sequence.)

9.11. Continuing Calibration Verification (CCV/CCB) - Calibration accuracy is monitored throughout the analytical run through the analysis of a known standard after every 10 samples or every 2 hours, whichever is more frequent. The CCV must be a mid-range standard at a concentration other than that of the ICV. The CCV result must fall within 20% of the true value for that solution. A CCB is analyzed immediately following each CCV. (See Section 11.2.10 for required run sequence.) The CCB result must fall within +/- CRDL from zero. If a mid-run CCV or CCB fails, the analysis must be terminated, the problem corrected, the instrument recalibrated, the calibration verified and the affected samples reanalyzed. If the cause of the CCV or CCB failure was not directly instrument related, the corrective action will include repreparation of the associated samples.

- Each CCV analyzed must reflect the conditions of analysis of all associated samples. The duration of analysis, rinses, and other operations that may affect the CCV result may not differ from those used for the associated samples. For example, the difference in time between a CCV analysis and the CCB immediately following it or the sample immediately preceding it may not exceed the smallest difference between any two consecutive samples associated with that CCV.

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

10. CALIBRATION AND STANDARDIZATION

10.1. Calibration standards must be processed through the preparation procedure as described in Section 11.1.

10.2. Due to the differences in preparation protocols separate calibration and calibration verification standards must be prepared for aqueous and solid matrices.

10.3. Calibration must be performed daily (every 24 hours) and each time the instrument is set up. The instrument calibration date and time must be included in the raw data.

10.4. Set up the instrument with the operating parameters recommended by the manufacturer. Allow the instrument to become thermally stable before beginning calibration (approximately 30 minutes of warm-up is required). Refer to the facility specific instrument SOP and CVAA instrument manual for detailed setup and operation protocols.

10.5. Calibrate the instrument according to instrument manufacturer's instructions, using a minimum of five standards and a blank. One standard must be at the STL reporting limit. Analyze standards in ascending order beginning with the blank. Refer to Section 7.5 and Table I for additional information on preparing calibration standards and calibration levels.

10.6. The calibration curve must have a correlation coefficient of ≥0.995 or the instrument shall be stopped and recalibrated prior to running samples. Sample results can not be reported from a curve with an unacceptable correlation coefficient.

10.7. Refer to Section 9.0 for calibration verification procedures, acceptance criteria and corrective actions.

11. PROCEDURE

11.1. Standard and Sample Preparation:

11.1.1. All calibration and calibration verification standards (ICV, ICB, CCV, CCB) are processed through the digestion procedure as well as the field samples.

11.1.2. Transfer 0, 0.2, 0.5, 1.0, 5.0 and 10.0 mL aliquots of the working standard (7.5) into a series of sample digestion bottles.

Note: Alternate volumes of standard may be prepared as long as the accuracy and final standard concentrations as detailed in Table I are maintained.

11.1.3. Add reagent water to each standard bottle to make a total volume of 10 mL. Continue preparation as described under 11.1.5 or 11.1.6 below.

11.1.4. Transfer 0.2 g of well mixed sample to a clean sample digestion bottle. Continue preparation as described under 11.1.5 or 11.1.6 below.

11.1.5. Water Bath protocol:

11.1.5.1. Add 5 mL of concentrated H_2SO_4 and 2.5 mL concentrated HNO_3.

11.1.5.2. Heat for 2 minutes in a water bath at 95 ° C.

11.1.5.3. Cool.

11.1.5.4. Add 50 mL of distilled water.

11.1.5.5. Add 15 mL of potassium permanganate solution.

11.1.5.6. Add 8 mL of potassium persulfate solution, mix thoroughly

11.1.5.7. Heat for 30 minutes in the water bath at 95 °C.

11.1.5.8. Cool.

11.1.5.9. Add 6 mL of sodium chloride-hydroxylamine sulfate solution to reduce the excess permanganate.

11.1.5.10. To each **standard** bottle: Add 50 mL of reagent water. To each **sample** bottle: Add 60 mL of reagent water.

11.1.5.11. Continue as described under Section 11.2.

11.1.6. Autoclave protocol:

11.1.6.1. Add 5 mL concentrated of H_2SO_4 and 2 mL of concentrated HNO_3.

11.1.6.2. Add 5 mL of saturated potassium permanganate solution.

11.1.6.3. Add 8 mL of potassium persulfate solution.

11.1.6.4. Cover digestion bottle with aluminum foil or screw cap loosely applied.

11.1.6.5. Heat samples at 121 °C and 15 lbs. pressure for 15 minutes.

11.1.6.6. Cool.

11.1.6.7. Make up to volume of 100 mL with reagent water.

Note: Alternate final volumes may be used as long as the standards and samples are treated the same way.

11.1.6.8. Add 6 mL of sodium chloride-hydroxylamine sulfate solution to reduce excess permanganate.

11.1.6.9. Continue as described under Section 11.2.

11.2. Sample Analysis:

11.2.1. Because of differences between various makes and models of CVAA instrumentation, no detailed operating instructions can be provided. Refer to the facility specific instrument operating SOP and the CVAA instrument manual for detailed setup and operation protocols.

11.2.2. All labs are required to detail the conditions/programs utilized for each instrument within the facility specific instrument operation SOP.

11.2.3. Manual determination:

11.2.3.1. Treating each sample individually, purge the head space of the sample bottle for at least one minute.

11.2.3.2. Add 5 mL of stannous chloride solution and immediately attach the bottle to the aeration apparatus.

11.2.3.3. Allow the sample to stand quietly without manual agitation while the sample is aerated (1 L/min flow). Monitor the sample absorbance during aeration. When the absorbance reaches a maximum and the signal levels off, open the bypass valve and continue aeration until the absorbance returns to its baseline level. Close the bypass valve and remove the aeration device.

11.2.3.4. Place the aeration device into 100 mLs of 1% HNO_3 and allow to bubble rinse until the next sample is analyzed.

11.2.4. Automated determination: Follow instructions provided by instrument manufacturer.

11.2.5. Perform a linear regression analysis of the calibration standards by plotting maximum response of the standards vs. concentration of mercury. Determine the mercury concentration in the samples from the linear regression fit of the calibration curve. Calibration using computer or calculation based regression curve fitting techniques on concentration/response data is acceptable.

11.2.6. All measurements must fall within the defined calibration range to be valid. Dilute and reanalyze all samples for analytes that exceed the highest calibration standard.

11.2.7. If the sample results are negative and the absolute value of the negative result is greater than the reporting limit, the sample must be diluted and reanalyzed.

11.2.8. The samples must be allowed to cool to room temperature prior to analysis or a decrease in the response signal can occur.

11.2.9. Baseline correction is acceptable as long as it is performed after every sample or after the CCV and CCB; resloping is acceptable as long as it is immediately preceded and followed by a compliant CCV and CCB.

11.2.10. The following run sequence is consistent with 245.5 CLP-M, SOW ILMO3.0 requirements.

Instrument Calibration
ICV
ICB
CRA
CCV
CCB
10 samples
CCV
CCB
Repeat sequence of 10 samples between CCV/CCB pairs as required to complete run.
CCV
CCB

11.3. To facilitate the early identification of QC failures and samples requiring rerun it is strongly recommended that sample data be reviewed periodically throughout the run.

11.4. Guidelines are provided in the appendices on procedures to minimize contamination of samples and standards, preventive maintenance and troubleshooting.

11.5. One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure

shall be completely documented using a Nonconformance Memo and is approved by a Technical Specialist and QA Manager. If contractually required, the client shall be notified. For U.S. EPA contract analyses the Technical Project Officer must be contacted in advance for approval. The Nonconformance Memo shall be filed in the project file.

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

12. DATA ANALYSIS AND CALCULATIONS

12.1. ICV percent recoveries are calculated according to the equation:

$$\%R = 100\left(\frac{Found(ICV)}{True(ICV)}\right)$$

12.2. CCV percent recoveries are calculated according to the equation:

$$\%R = 100\left(\frac{Found(CCV)}{True(CCV)}\right)$$

12.3. Matrix spike recoveries are calculated according to the following equation:

$$\%R = 100\left(\frac{SSR - SR}{SA}\right)$$

Where:
SSR = Spike Sample Result
SR = Sample Result
SA = Spike Added

12.4. The relative percent difference (RPD) of sample duplicates are calculated according to the following equation :

$$RPD = 100\left[\frac{|DU1 - DU2|}{\left(\frac{DU1 + DU2}{2}\right)}\right]$$

Where:
DU1 = Sample result

DU2 = Sample duplicate result

12.5. For automated determinations, the final concentration determined in solid samples when reported on a dry weight basis is calculated as follows:

mg/kg, dry weight = (C x V x D)/(W x S)

Where:
C = Concentration (ug/L) from instrument readout
V = Volume of digestate (L)
D = Instrument dilution factor
W = Weight in g of wet sample digested
S = Percent solids/100

Note: A Percent Solids determination must be performed on a separate aliquot when dry weight concentrations are to be reported. If the results are to be reported on a wet weight basis, the "S" factor should be omitted from the above equation.

12.6. For manual (total) determinations, the final concentration determined in solid samples when reported on a dry weight basis is calculated as follows:

mg/kg, dry weight = (C)/(W x S)

Where:
C = Concentration (ug) from instrument readout
W = Weight in g of wet sample digested
S = Percent solids/100

Note: A Percent Solids determination must be performed on a separate aliquot when dry weight concentrations are to be reported. If the results are to be reported on a wet weight basis, the "S" factor should be omitted from the above equation.

12.7. The LCS percent recovery is calculated according to the following equation:

$$\%R = 100\left(\frac{Found(LCS)}{True(LCS)}\right)$$

12.8. Appropriate factors must be applied to sample values if dilutions are performed.

12.9. Sample results should be reported with up to three significant figures in accordance with the following:

Result	Significant Figures
< IDL mg/kg	Report IDL u (2 sig figs)
> IDL and < 10.0 mg/kg	Report 2 sig figs
≥ 10.0 mg/kg	Report 3 sig figs

13. METHOD PERFORMANCE

13.1. Each laboratory must have initial demonstration of performance data on file for each analyte of interest as described in Section 9.0.

13.2. Method performance is determined by the analysis of preparation blanks, laboratory control samples, matrix spikes and matrix duplicate samples. The matrix spike recovery should fall within +/- 25 % and the matrix spike duplicates should compare within 20% RPD. The preparation blank must meet the criteria specified in Section 9.5. The laboratory control sample should recover within the control limits established by the supplier.

13.3. Training Qualification:

The group/team leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience.

14. POLLUTION PREVENTION

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

15. WASTE MANAGEMENT

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

16. REFERENCES

16.1. U.S.EPA Statement of Work for Inorganics Analysis, ILMO3.0.

17. MISCELLANEOUS (TABLES, APPENDICES, ETC. . .)

17.1. Modifications/Interpretations from reference method.

17.1.1. Modifications from 245.5 CLP-M

17.1.1.1. The SOW specifies the use of reagent water with a purity equivalent to ASTM Type II water. This SOP specifies the use of a Millipore DI system or equivalent to produce reagent water. This SOP requires that reagent water must be free of the analytes of interest as demonstrated through the analysis of preparation blanks.

17.1.1.2. Section 11.1.5.10 requires that 60 mL of reagent water be added to each sample bottle versus the 55 mL indicated in 245.5 CLP-M. This modification corrects for an error contained in the reference method which would otherwise result in an unequal dilution of the samples relative to the calibration standards.

17.2. Modifications from previous SOP

None.

17.3. Facility Specific SOPs

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

17.4. Documentation and Record Management

The following documentation comprises a complete CVAA raw data package:

- Raw data (direct instrument printout)
- Run log printout from instrument software where this option is available or manually generated run log. (A bench sheet may be substituted for the run log as

long as it contains an accurate representation of the analytical sequence and sufficient date and time information to verify that the QC time criteria were met).

- Data review checklist - See Appendix B
- Standards Documentation (source, lot, date).
- Copy of digestion log.
- Non-conformance summary (if applicable).

Figure 1. Solid Sample Preparation for Mercury - Autoclave Procedure

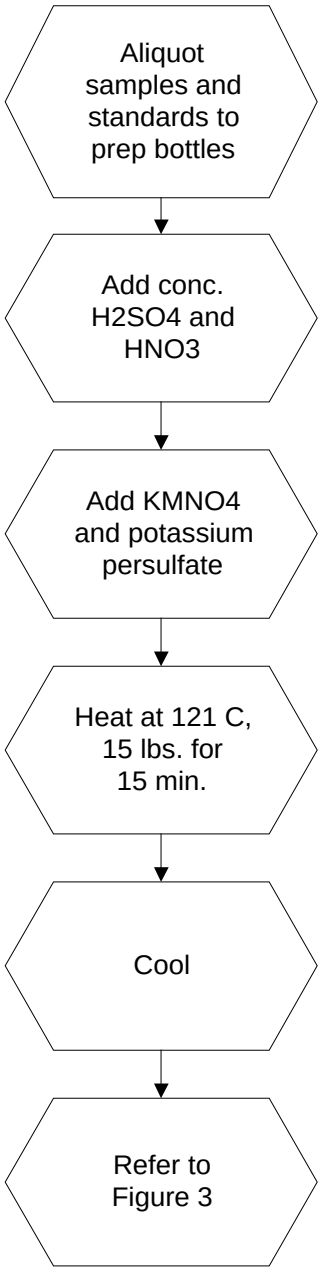


Figure 2. Solid Sample Preparation for Mercury - Water Bath Procedure

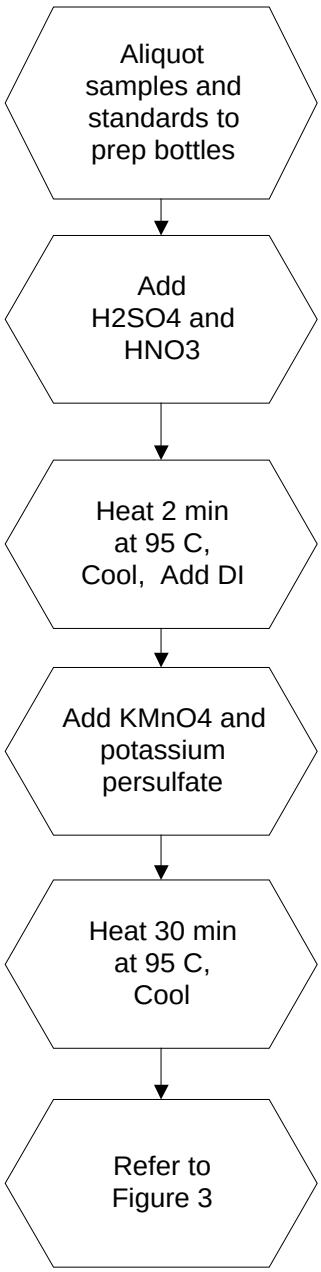
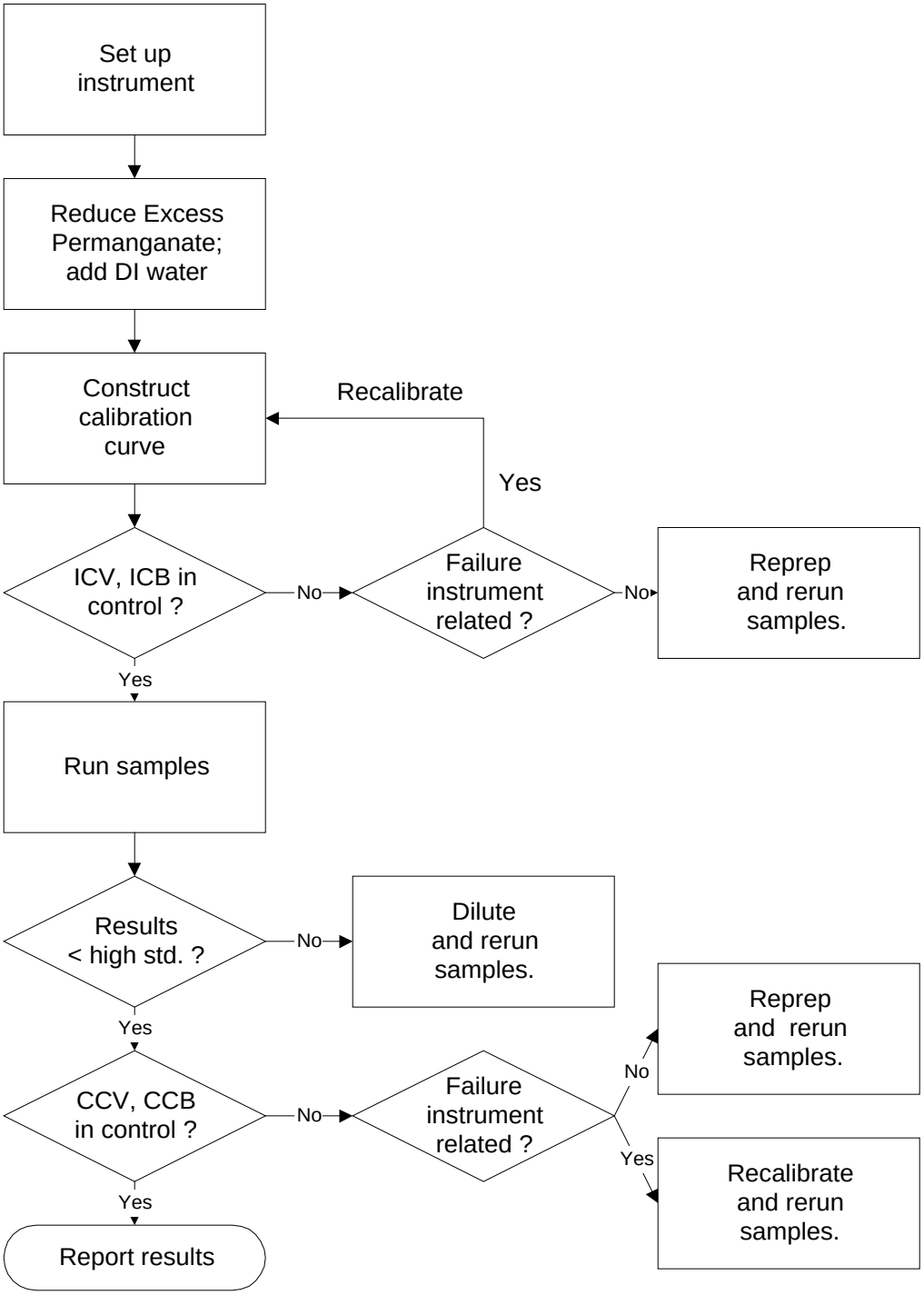


Figure 3. CVAA Mercury Analysis



APPENDIX A

TABLES

TABLE I . MERCURY REPORTING LIMITS, CALIBRATION STANDARD*, QC STANDARD AND SPIKING LEVELS

Soil RL (mg/kg)	0.1
Std 0 (ug/L)	0
Std 1 (ug/L)	0.2
Std 2 (ug/L)	0.5
Std 3 (ug/L)	1.0
Std 4 (ug/L)	2.0
Std 5 (ug/L)	5.0
Std 6 (ug/L) **	10
ICV (ug/L) ***	1.0 or 2.5 ***
CCV (ug/L)	2.5 or 5.0 ***
LCS (mg/kg) ***	Variable
MS (ug/L)	1.0

*** SOP specified calibration levels must be used unless prevented by the instrument configuration or client specific requirements. Deviations from specified calibration levels must be documented in the facility specific instrument operation SOP and must be approved by the facility technical manager and Quality Assurance Manager.**

**** Optional standard which may be used to extend the calibration range as allowed by the instrument configuration. If the instrument configuration prevents the use of 6 standards, the 2 ppb standard may be eliminated in favor of the 10 ppb standard.**

***** Concentration level dependent on high calibration standard used. CCV must be 50% of the high standard concentration and the ICV must be 20-25% of the high standard concentration.**

TABLE II. Summary Of Quality Control Requirements

QC PARAMETER	FREQUENCY *	ACCEPTANCE CRITERIA	CORRECTIVE ACTION
ICV	Beginning of every analytical run.	80 - 120 % recovery.	Terminate analysis; Correct the problem; Recalibrate or reprep batch (see Section 9.9).
ICB	Beginning of every analytical run, immediately following the ICV.	The result must be within +/- CRDL from zero.	Terminate analysis; Correct the problem; Recalibrate or reprep batch (see Section 9.9).
CCV	Beginning and end of run and every 10 samples or every 2 hours, whichever is more frequent.	80 - 120 % recovery.	Terminate analysis; Correct the problem; Recalibrate and rerun all samples not bracketed by acceptable CCV or reprep batch (see Section 9.11).
CCB	Immediately following each CCV.	The result must be within +/- CRDL from zero.	Terminate analysis; Correct the problem; Recalibrate and rerun all samples not bracketed by acceptable CCB or reprep batch (see Section 9.11).
Preparation Blank	One per sample preparation batch of up to 20 samples.	The result must be less than or equal to the CRDL. Sample results greater than 10x the blank concentration are acceptable. Samples for which the contaminant is < RL do not require redigestion (See Section 9.5).	Redigest and reanalyze samples. Note exceptions under criteria section. See Section 9.5 for additional requirements.

*See Section 11.2.10 for exact run sequence to be followed.

TABLE II. Summary of Quality Control Requirements (Continued)

QC PARAMETER	FREQUENCY	ACCEPTANCE CRITERIA	CORRECTIVE ACTION
CRA	Beginning of each analytical run.	No criteria established by EPA at this time.	Not Applicable.
Laboratory Control Sample (LCS)	One per sample preparation batch of up to 20 samples.	Soil LCS must be within limits established by supplier.	Terminate analysis; Correct the problem; Redigest and reanalyze all samples associated with the LCS (see Section 9.6).
Matrix Spike	One per SDG or each group of 20 samples of a similar matrix type.	75 - 125 % recovery .	Flag the data; no flag required if the sample level is > 4x the spike added. (see Section 9.7)
Matrix Duplicate	One per SDG or each group of 20 samples of a similar matrix type.	RPD ≤ 20% if results ≥ 5x CRDL or, ± CRDL if either result < 5x CRDL.	Flag the data. (see Section 9.8)

***** See Section 11.2.10 for exact run sequence.

APPENDIX B
STL Hg DATA REVIEW CHECKLIST

STL Hg Data Review Checklist

Run/Project Information

Run Date: _____ Analyst:_____ Instrument:_____
Prep Batches Run:_____

Circle Methods used: 7470A / 245.1 : CORP-MT-0005 Rev 0 7471 / 245.5 : CORP-MT-0007 Rev 0
CLP - AQ : CORP-MT-0006 Rev 0 CLP - SOL : CORP-MT-0008 Rev 0

Review Items

A. Calibration/Instrument Run QC	Yes	No	N/A	2nd Level
1. Instrument calibrated per manufacturer's instructions and at SOP specified levels ?				
2. ICV/CCV analyzed at appropriate frequency and within control limits?				
3. ICB/CCB analyzed at appropriate frequency and within +/- RL or +/- CRDL (CLP)?				
4. CRA run (CLP only)?				
B. Sample Results				
1. Were samples with concentrations > the high calibration standard diluted and reanalyzed?				
2. All reported results bracketed by in control QC ?				
3. Sample analyses done within holding time?				
C. Preparation/Matrix QC				
1. LCS done per prep batch and within QC limits ?				
2. Method blank done per prep batch and < RL or CRDL (CLP) ?				
3. MS run at required frequency and within limits ?				
4. MSD or DU run at required frequency and RPD within SOP limits?				
D. Other				
1. Are all nonconformances documented appropriately ?				
2. Current IDL/MDL data on file?				
3. Calculations and Transcriptions checked for error ?				
4. All client/ project specific requirements met?				
5. Date of analysis verified as correct ?				

Analyst: _____ Date:_____
Comments:
_____
_____

2nd Level Reviewer : _____ Date:_____
_____
_____

APPENDIX C

TROUBLESHOOTING GUIDE

APPENDIX C. TROUBLESHOOTING GUIDE

Problem	**Possible Cause**
Poor or No Absorbance or Sensitivity Check failed	Incorrect wavelength Dirty windows Window loose Etched or dirty optics Wrong lamp Bad lamp Not enough or no sample introduced Empty sample cup Incorrectly made standards Gas leak EDL power supply set on “Continuous”
Erratic Readings	Source lamp not aligned properly Lamp not prewarmed Injection tip partially clogged Contaminated reagents Contaminated glassware Drying tube saturated Bad lamp Injection tip hitting outside of tube Injection tip coated or not set properly Leak in sample tubing Power fluctuations Air bubbles in tubing
EDL Won’t Light	Lamp cable not plugged in Lamp power set at 0 Lamp is dead Power supply fuse is blown Short in cord
Standards reading twice or half normal absorbance or concentration	Incorrect standard used Incorrect dilution performed Dirty cell
Background Correction Light Blinking	Background screen or attenuator faulty

APPENDIX D

CONTAMINATION CONTROL GUIDELINES

APPENDIX D. CONTAMINATION CONTROL GUIDELINES

The following procedures are strongly recommended to prevent contamination:

All work areas used to prepare standards and spikes should be cleaned before and after each use.

All glassware should be washed with detergent and tap water and rinsed with 1:1 nitric acid followed by deionized water.

Proper laboratory housekeeping is essential in the reduction of contamination in the metals laboratory. All work areas must be kept scrupulously clean.

Powdered or Latex Gloves must not be used in the metals laboratory since the powder contains silica and zinc, as well as other metallic analytes. Only vinyl or nitrile gloves should be used in the metals laboratory.

Glassware should be periodically checked for cracks and etches and discarded if found. Etched glassware can cause cross contamination of any metallic analytes.

Autosampler trays should be covered to reduce the possibility of contamination. Trace levels of elements being analyzed in the samples can be easily contaminated by dust particles in the laboratory.

The following are helpful hints in the identification of the source of contaminants:

Reagents or standards can contain contaminants or be contaminated with the improper use of a pipette.

Improper cleaning of glassware can cause contamination.

Separate glassware if an unusually high sample is analyzed and soak with sulfuric acid prior to routine cleaning.

APPENDIX E

PREVENTIVE MAINTENANCE

APPENDIX E. PREVENTIVE MAINTENANCE

A maintenance log is used to record when maintenance is performed on instruments. When an instrument problem occurs indicate the date, time and instrument number, then identify the problem and corrective action in the maintenance log.

The following procedures are required to ensure that that the instrument is fully operational.

Cold Vapor Atomic Absorption (Leeman PS 200) (1)

Daily	Semi-annually	Annually
Clean lens.	Check Hg lamp intensity.	Change Hg lamp.
Check aperture.		Check liquid/gas separator.
Check argon flow.		
Check tubing.		
Check drain.		
Replace drying tube.		

Cold Vapor Atomic Absorption (PE 5000) (1)

Daily	Monthly
Clean aspirator by flushing with DI water.	Clean cell in aqua regia.
Check tubing and replace if needed.	Clean aspirator in aqua regia.
Clean windows with methanol.	
Change silica gel in drying tube.	
Check argon gas supply.	
Adjust lamp.	

CORP-MS-0002-PT

Determination of Volatile Organics by GC/MS Methods 8260B, 624 and 524.2

STL STANDARD OPERATING PROCEDURE

TITLE: DETERMINATION OF VOLATILE ORGANICS BY GC/MS BASED ON METHOD 8260B, 624 AND 524.2

(SUPERSEDES: REVISION 1)

Prepared by: Richard Burrows

Approved by: _____
Technology Specialist

Approved by: _____
Quality Assurance Manager

Approved by: _____
Environmental Health and Safety Coordinator

Approved by: _____
Laboratory Manager

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1. SCOPE AND APPLICATION

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

1.2. This SOP is applicable to method 8260B. At client request, it may also be used for analysis following method 8240B. Appendices A and B present modifications to the procedures in the main SOP that are necessary for analysis of drinking water by method 524.2 and wastewater by method 624.

1.3. This method can be used to quantify most volatile organic compounds that have boiling points below 200°C and are insoluble or slightly soluble in water. Volatile water soluble compounds can be included in this analytical technique; however, for more soluble compounds, quantitation limits are approximately ten times higher because of poor purging efficiency.

1.4. The method is based upon a purge and trap, gas chromatograph/mass spectrometric (GC/MS) procedure. The approximate working range is 5 to 200 µg/L for 5 mL waters, 1 to 60 µg/L for 25 mL purge waters, 5 to 200 µg/kg for low-level soils, and 250 to 25,000 µg/kg for medium-level soils. Reporting limits are listed in Tables 1, 3 and 14.

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

2. SUMMARY OF METHOD

2.1. Volatile compounds are introduced into the gas chromatograph by the purge and trap method. The components are separated via the chromatograph and detected using a mass spectrometer, which is used to provide both qualitative and quantitative information.

2.2. Aqueous samples are purged directly. Generally, soils are preserved by extracting the volatile analytes into methanol. If especially low detection limits are required, soil samples may be preserved with sodium bisulfate and purged directly.

2.3. In the purge and trap process, an inert gas is bubbled through the solution at ambient temperature or at 40°C (40°C required for low level soils) and the volatile components are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbant column where the volatile components are trapped. After purging is completed, the sorbant column (trap) is heated and backflushed with inert gas to desorb the components onto a gas chromatographic column. The gas chromatographic column is then heated to elute the components which are detected with a mass spectrometer.

2.4. Qualitative identifications are confirmed by analyzing standards under the same conditions used for samples and comparing the resultant mass spectra and GC retention times. Each identified component is quantified by relating the MS response for an appropriate selected ion produced by that compound to the MS response for another ion produced by an internal standard.

3. DEFINITIONS

3.1. Batch

The batch is a set of up to 20 samples of the same matrix processed using the same procedures and reagents within the same time period. Using this method, each BFB analysis will normally start a new batch. Batches for medium level soils are defined at the sample preparation stage and may be analyzed on multiple instruments over multiple days, although reasonable effort should be made to keep the samples together.

3.1.1. The Quality Control batch must contain a matrix spike/spike duplicate (MS/MSD), a Laboratory Control Sample (LCS), and a method blank. In some cases, at client request, the MS/MSD may be replaced with a matrix spike and sample duplicate. Refer to the STL QC Program document (QA-003) for further details of the batch definition.

3.2. Method Blank

A method blank consisting of all reagents added to the samples must be analyzed with each batch of samples. The method blank is used to identify any background interference or contamination of the analytical system which may lead to the reporting of elevated concentration levels or false positive data.

3.3. Laboratory Control Sample (LCS)

Laboratory Control Samples are well characterized, laboratory generated samples used to monitor the laboratory's day-to-day performance of routine analytical methods. The LCS, spiked with a group of target compounds representative of the method analytes, is used to monitor the accuracy of the analytical process, independent of matrix effects. Ongoing monitoring of the LCS results provides evidence that the laboratory is performing the method within accepted QC guidelines for accuracy and precision.

3.4. Surrogates

Surrogates are organic compounds which are similar to the target analyte(s) in chemical composition and behavior in the analytical process, but which are not normally found in environmental samples. Each sample, blank, LCS, and MS/MSD is spiked with surrogate

standards. Surrogate spike recoveries must be evaluated by determining whether the concentration (measured as percent recovery) falls within the required recovery limits.

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

A matrix spike is an environmental sample to which known concentrations of target analytes have been added. A matrix spike duplicate is a second aliquot of the same sample which is prepared and analyzed along with the sample and matrix spike. Matrix spikes and duplicates are used to evaluate accuracy and precision in the actual sample matrix.

3.6. Calibration Check Compound (CCC)

CCCs are a representative group of compounds which are used to evaluate initial calibrations and continuing calibrations. Relative percent difference for the initial calibration and % drift for the continuing calibration response factors are calculated and compared to the specified method criteria.

3.7. System Performance Check Compounds (SPCC)

SPCCs are compounds which are sensitive to system performance problems and are used to evaluate system performance and sensitivity. A response factor from the continuing calibration is calculated for the SPCC compounds and compared to the specified method criteria.

4. INTERFERENCES

4.1. Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus that lead to discrete artifacts. All of these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. The use of ultra high purity gases, pre-purged purified reagent water, and approved lots of purge and trap grade methanol will greatly reduce introduction of contaminants. In extreme cases the purging vessels may be pre-purged to isolate the instrument from laboratory air contaminated by solvents used in other parts of the laboratory.

4.2. Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride and fluorocarbons) into the sample through the septum seal during shipment and storage. A field blank prepared from reagent water and carried through the sampling and handling protocol can serve as a check on such contamination.

4.3. Matrix interferences may be caused by non-target contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from source to source depending upon the nature and diversity of the site being sampled.

4.4. Cross-contamination can occur whenever high-level and low-level samples are analyzed sequentially or in the same purge position on an autosampler. Whenever an unusually concentrated sample is analyzed, it should be followed by one or more blanks to check for cross-contamination. The purge and trap system may require extensive bake-out and cleaning after a high-level sample.

4.5. Some samples may foam when purged due to surfactants present in the sample. When this kind of sample is encountered an antifoaming agent (e.g., J.T. Baker's Antifoam B silicone emulsion) can be used. A blank spiked with this agent must be analyzed with the sample because of the non-target interferences associated with the agent.

5. SAFETY

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

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

5.3. Consult the STL Health and Safety Policies and Procedures Manual for information on Personal Protective Equipment. Eye protection that satisfies ANSI Z87.1 (as per the Chemical Hygiene Plan) and a laboratory coat must be worn in the lab. Appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately. Disposable gloves shall not be reused.

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

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

5.4.2. Chemicals known to be flammable are: Methanol.

5.5. Exposure to chemicals must be maintained **as low as reasonably achievable**, therefore, unless they are known to be non-hazardous, all samples should be opened, transferred, and

prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

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

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

5.8. Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices outlined in the STL Health and Safety Manual. These employees must have training on the hazardous waste disposal practices initially upon assignment of these tasks, followed by an annual refresher training.

6. EQUIPMENT AND SUPPLIES

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

6.2. Syringe: 5 or 25 mL glass with luerlok tip, if applicable to the purging device.

6.3. Balance: Analytical, capable of accurately weighing 0.0001 g, and a top-loading balance capable of weighing 0.1 g

6.4. Glassware:

6.4.1. Vials: 20 mL with screw caps and Teflon liners.

6.4.2. Volumetric flasks: 10 mL and 100 mL, class A with ground-glass stoppers.

6.5. Spatula: Stainless steel.

6.6. Disposable pipets: Pasteur.

6.7. pH paper: Wide range.

6.8. Gases:

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

6.8.2. Nitrogen: Ultra high purity, from cylinders of gas generators, may be used as an alternative to helium for purge gas.

6.8.3. Compressed air: Used for instrument pneumatics.

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

6.9. Purge and Trap Device: The purge and trap device consists of the sample purger, the trap, and the desorber.

6.9.1. Sample Purger: The recommended purging chamber is designed to accept 5 mL samples with a water column at least 3 cm deep. The purge gas must pass through the water column as finely divided bubbles, each with a diameter of less than 3 mm at the origin. The purge gas must be introduced no more than 5 mm from the base of the water column. Alternative sample purge devices may be used provided equivalent performance is demonstrated. Low level soils are purged directly from a VOA vial.

6.9.2. Trap: A variety of traps may be used, depending on the target analytes required. For most purposes the Vocarb 3000 trap is suitable. Other traps, such as Vocarb 4000, or Tenax / Silica gel / Charcoal may be used if the Quality Control criteria are met.

6.9.3. Desorber: The desorber should be capable of rapidly heating the trap to 180°C. Many such devices are commercially available.

6.9.4. Sample Heater: A heater capable of maintaining the purge device at 40°C is necessary for low level soil analysis.

6.10. Gas Chromatograph/Mass Spectrometer System:

1.1.1. Gas Chromatograph: The gas chromatograph (GC) system must be capable of temperature programming.

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

6.10.2.1.Column 1: 20m x 0.18 ID DB-624 with 1 µm film thickness.

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

6.10.2.3. Mass Spectrometer: The mass spectrometer must be capable of scanning 35-300 AMU every two seconds or less, using 70 volts electron energy in the electron impact mode and capable of producing a mass spectrum that meets the required criteria when 50 ng of 4-Bromofluorobenzene (BFB) are injected onto the gas chromatograph column inlet.

6.10.3. GC/MS interface: In general glass jet separators are used but any interface (including direct introduction to the mass spectrometer) that achieves all acceptance criteria may be used.

6.10.4. Data System: A computer system that allows the continuous acquisition and storage on machine readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that allows searching any GC/MS data file for ions of a specified mass and plotting such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundances in any EICP between the specified time or scan-number limits. Also, for the non-target compounds, software must be available that allows for the comparison of sample spectra against reference library spectra. The most recent release of the NIST/EPA mass spectral library should be used as the reference library. The computer system must also be capable of backing up data for long-term off-line storage.

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

7. REAGENTS AND STANDARDS

7.1. Reagents

7.1.1. Methanol: Purge and Trap Grade, High Purity

7.1.2. Reagent Water: High purity water that meets the requirements for a method blank when analyzed. (See section 9.4) Reagent water may be purchased as commercial distilled water and prepared by purging with an inert gas overnight. Other methods of preparing reagent water are acceptable.

7.2. Standards

7.2.1. Calibration Standard

7.2.1.1. Stock Solutions: Stock solutions may be purchased as certified solutions from commercial sources or prepared from pure standard materials as appropriate. These standards are prepared in methanol and stored in Teflon-sealed screw-cap bottles with minimal headspace at -10° to -20°C.

7.2.1.2. Working standards: A working solution containing the compounds of interest prepared from the stock solution(s) in methanol. These standards are stored in the freezer or as recommended by the manufacturer. Working standards are monitored by comparison to the initial calibration curve. If any of the calibration check compounds drift in response from the initial calibration by more than 20% then corrective action is necessary. This may include steps such as instrument maintenance, preparing a new calibration verification standard or tuning the instrument. If the corrective actions do not correct the problem then a new initial calibration must be performed.

7.2.1.3. Aqueous Calibration Standards are prepared in reagent water using the secondary dilution standards. These aqueous standards must be prepared daily.

7.2.1.4. If stock or secondary dilution standards are purchased in sealed ampoules they may be used up to the manufacturers expiration date.

7.2.2. Internal Standards: Internal standards are added to all samples, standards, and blank analyses. Refer to Table 7 for internal standard components.

7.2.3. Surrogate Standards: Refer to Table 8 for surrogate standard components and spiking levels.

7.2.4. Laboratory Control Sample Spiking Solutions: Refer to Table 9 for LCS components and spiking levels.

7.2.5. Matrix Spiking Solutions: The matrix spike contains the same components as the LCS. Refer to Table 9.

7.2.6. Tuning Standard: A standard is made up that will deliver 50 ng on column upon injection. A recommended concentration of 25 ng/µL of 4-Bromofluorobenzene in methanol is prepared as described in Sections 7.2.1.1 and 7.2.1.2.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Holding times for all volatile analysis are 14 days from sample collection.

8.2. Water samples are normally preserved at pH $\leq$ 2 with 1:1 hydrochloric acid. If residual chlorine is present, 2 drops of 10% sodium thiosulfate are added.

8.3. Solid samples are field preserved with sodium bisulfate solution for low level analysis, or with methanol for medium level analysis. Soil samples can also be taken using the EnCore™ sampler and preserved in the lab within 48 hours of sampling. At specific client request, unpreserved soil samples may be accepted.

8.4. There are several methods of sampling soil. The recommended method, which provides the minimum of field difficulties, is to take an EnCore sample. (The 5 g or 25 g sampler can be used, depending on client preference). Following shipment back to the lab the soil is preserved in methanol. This is the medium level procedure. If very low detection limits are needed (< 50 µg/kg for most analytes) then it will be necessary to use two additional 5 g EnCore samplers or to use field preservation.

8.5. Sample collection for medium level analysis using EnCore samplers.

8.5.1. Ship one 5 g (or 25 g) EnCore sampler per field sample position.

8.5.2. An additional bottle must be shipped for percent moisture determination.

8.5.3. When the samples are returned to the lab, extrude the (nominal) 5g (or 25 g) sample into a tared VOA vial containing 5 mL methanol (25 mL methanol for the 25 g sampler). Obtain the weight of the soil added to the vial and note on the label.

8.5.4. Add the correct amount of surrogate spiking mixture. (Add 50 uL of 1250 µg/mL solution for a nominal 25 g sample, 10µL for a nominal 5 g sample.)

8.5.5. Add the correct amount of matrix spiking solution to the matrix spike and matrix spike duplicate samples. (Add 50 uL of 1250 µg/mL solution for a nominal 25 g sample, 10µL for a nominal 5 g sample.) The addition of spike introduces a slight error (0.4%), which can be neglected, into the calculations.

8.5.6. Prepare an LCS for each batch by adding the correct amount of matrix spiking solution to clean methanol. (50 uL of spike to 25 mL methanol or 10 uL spike to 5 mL methanol).

8.5.7. Shake the samples for two minutes to distribute the methanol throughout the soil.

8.5.8. Allow to settle, then remove a portion of methanol and store in a clean Teflon capped vial at 4+2°C until analysis.

8.6. Sample collection for medium level analysis using field methanol preservation

8.6.1. Prepare a 2 oz sample container by adding 25 mL purge and trap grade methanol. (If a 5 g sample is to be used, add 5 mL methanol to a 2 oz container or VOA vial).

8.6.2. Seal the bottle and attach a label.

8.6.3. Weigh the bottle to the nearest 0.01g and note the weight on the label.

8.6.4. Ship with appropriate sampling instructions.

8.6.5. Each sample will require an additional bottle with no preservative for percent moisture determination.

8.6.6. At client request, the methanol addition and weighing may also be performed in the field.

8.6.7. When the samples are returned to the lab, obtain the weight of the soil added to the vial and note on the label.

8.6.8. Add the correct amount of surrogate spiking mixture. (Add 50 uL of 1250 µg/mL solution for a nominal 25 g sample, 10µL for a nominal 5 g sample.)

8.6.9. Add the correct amount of matrix spiking solution to the matrix spike and matrix spike duplicate samples. (Add 50 uL of 1250 µg/mL solution for a nominal 25 g sample, 10µL for a nominal 5 g sample.) The addition of spike introduces a slight error, (0.2%) which can be neglected, into the calculations.

8.6.10. Prepare an LCS for each batch by adding the correct amount of matrix spiking solution to clean methanol. (50 uL of spike to 25 mL methanol or 10 uL spike to 5 mL methanol).

8.6.11. Shake the samples for two minutes to distribute the methanol throughout the soil.

8.6.12. Allow to settle, then remove a portion of methanol and store in a clean Teflon capped vial at 4+2°C until analysis.

8.7. Low level procedure

8.7.1. If low detection limits are required (typically < 50 µg/kg) sodium bisulfate preservation must be used. However, it is also necessary to take a sample for the medium level (field methanol preserved or using the EnCore sampler) procedure, in case the concentration of analytes in the soil is above the calibration range of the low level procedure.

8.7.2. A purge and trap autosampler capable of sampling from a sealed vial is required for analysis of samples collected using this method. (Varian Archon or O.I. 4552).

8.7.3. The soil sample is taken using a 5g EnCore sampling device and returned to the lab. It is recommended that two EnCore samplers be used for each field sample position, to allow for any reruns than may be necessary. A separate sample for % moisture determination is also necessary.

8.7.4. Prepare VOA vials by adding a magnetic stir bar, approximately 1 g of sodium bisulfate and 5 mL of reagent water.

8.7.5. Seal and label the vial. It is strongly recommended that the vial is labeled with an indelible marker rather than a paper label, since paper labels may cause the autosampler to bind and malfunction. The label absolutely must not cover the neck of the vial or the autosampler will malfunction.

8.7.6. Weigh the vial to the nearest 0.1g and note the weight on the label.

8.7.7. Extrude the soil sample from the EnCore sampler into the prepared VOA vial. Reweigh the vial to obtain the weight of soil and note on the label.

8.7.8. **Note:** Soils containing carbonates may effervesce when added to the sodium bisulfate solution. If this is the case at a specific site, add 5 mL of water instead, and freeze at <10°C until analysis.

8.7.9. Alternatively the sodium bisulfate preservation may be performed in the field. This is not recommended because of the many problems that can occur in the field setting. Ship at least two vials per sample. The field samplers must determine the weight of soil sampled. Each sample will require an additional bottle with no preservative for percent moisture determination, and an additional bottle preserved with methanol for the medium level procedure. Depending on the type of soil it may also be necessary to ship vials with no or extra preservative.

8.8. Unpreserved soils

8.8.1. At specific client request unpreserved soils packed into glass jars or brass tubes may be accepted and subsampled in the lab. This is the old procedure based on method 5030A. It is no longer included and is likely to generate results that are biased low, possibly by more than an order of magnitude.

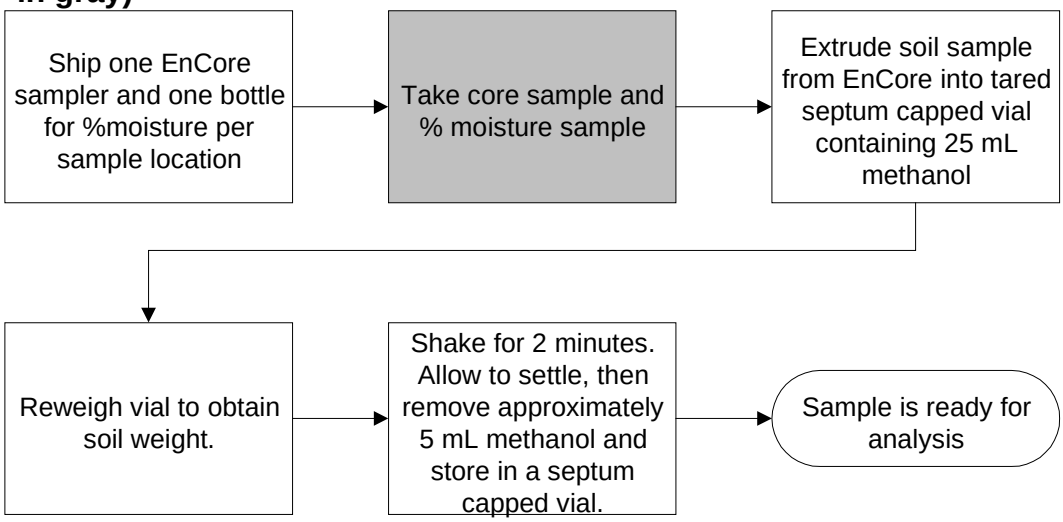
8.9. Aqueous samples are stored in glass containers with Teflon lined septa at 4°C +/- 2°C, with minimum headspace.

8.10. Medium level solid extracts are aliquoted into 2 - 5 mL glass vials with Teflon lined caps and stored at 4°C +/- 2°C. The extracts are stored with minimum headspace.

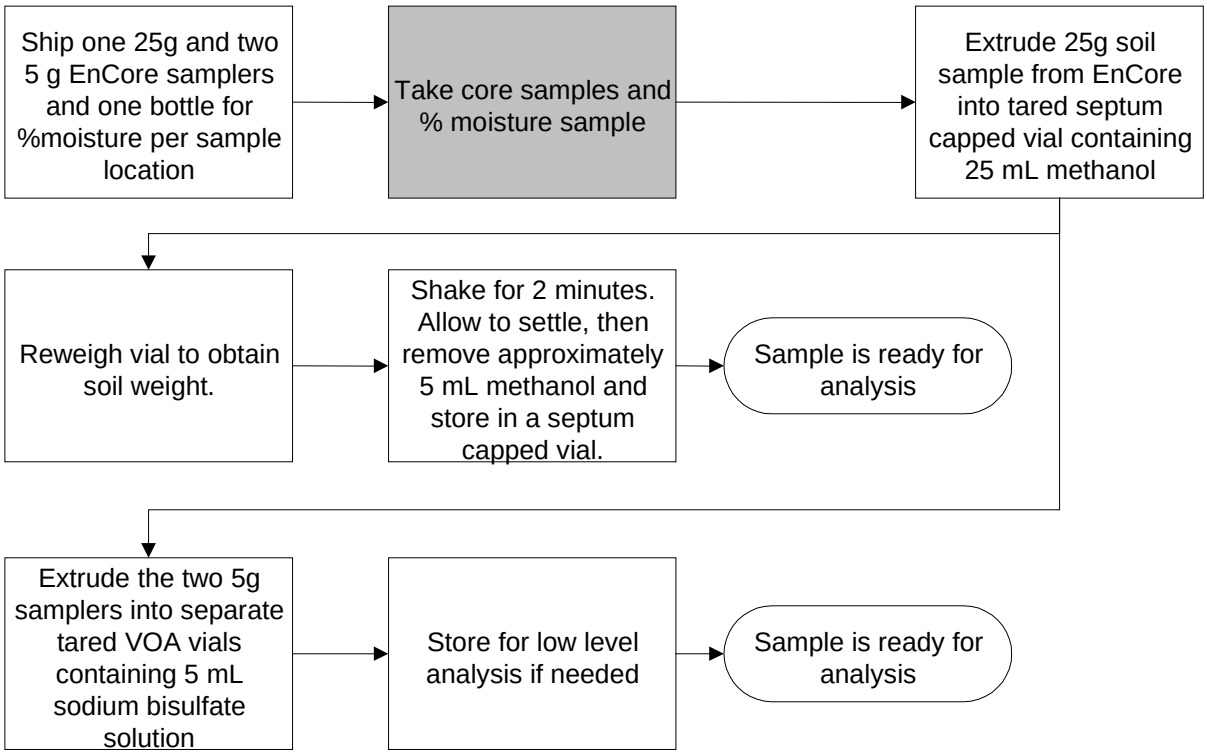
8.11. The maximum holding time is 14 days from sampling until the sample is analyzed. (Samples that are found to be unpreserved still have a 14 day holding time. However they should be analyzed as soon as possible. The lack of preservation should be addressed in the case narrative). Maximum holding time for the EnCore sampler (before the sample is added to methanol or sodium bisulfate) is 48 hours.

8.12. A holding blank is stored with the samples. This is analyzed and replaced if any of the trip blanks show any contamination. Otherwise it is replaced every 14 days.

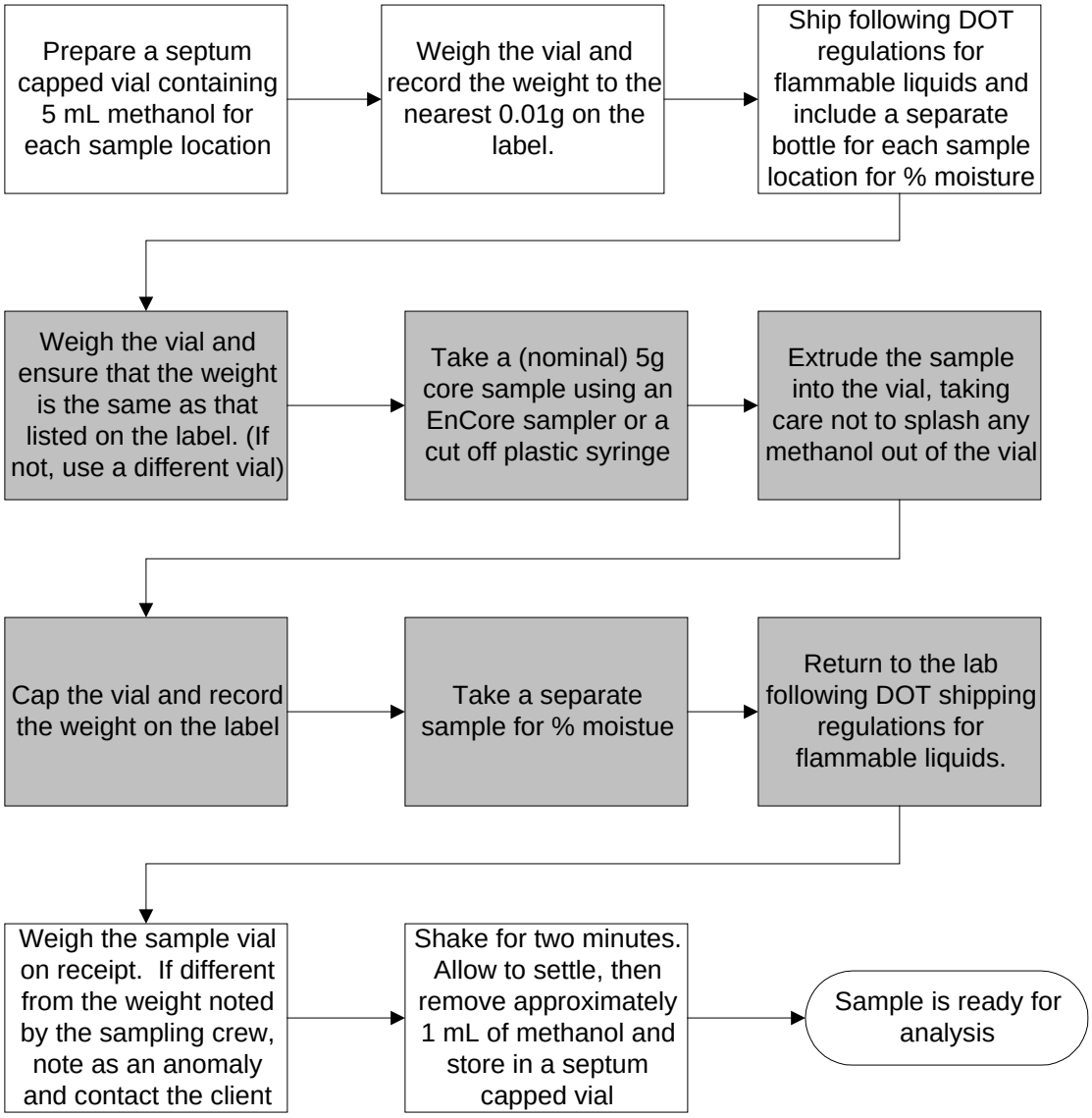
EnCore procedure when low level is not required (field steps in gray)



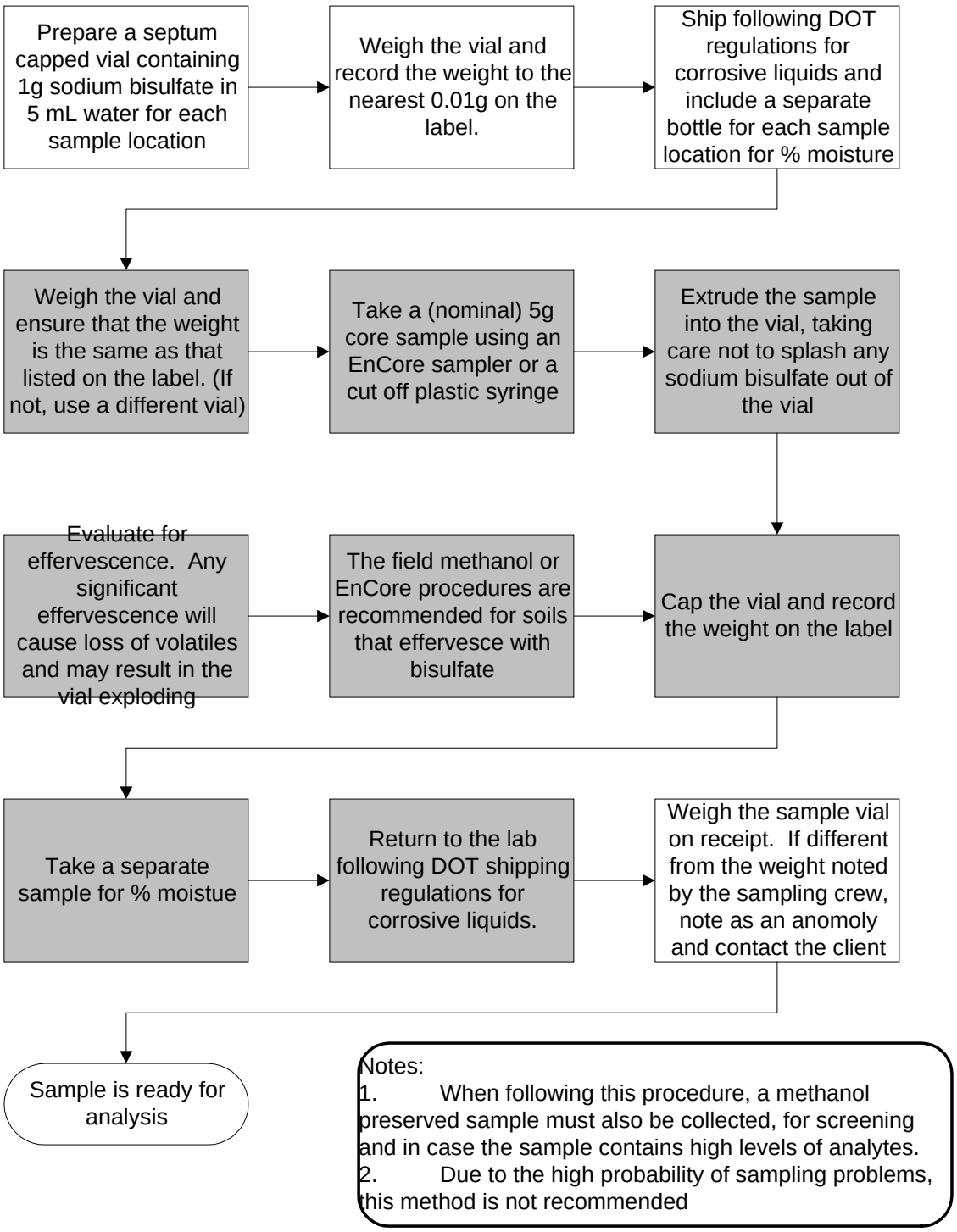
EnCore procedure when low level is required



Field methanol extraction procedure (field steps in gray)



Field bisulfate preservation procedure (field steps in gray)



9. QUALITY CONTROL

9.1. Initial Demonstration of Capability

9.1.1. For the standard analyte list, the initial demonstration described in Section 13 and method detection limit (MDL) studies must be acceptable before analysis of samples may begin. MDLs should be analyzed for low and medium soils and aqueous samples.

9.1.2. For non-standard analytes, a MDL study must be performed and calibration curve generated before analyzing any samples, unless lesser requirements are previously agreed to with the client. In any event, the minimum initial demonstration required is analysis of a standard at the reporting limit and a single point calibration.

9.2. Control Limits

In-house historical control limits must be determined for surrogates, matrix spikes, and laboratory control samples (LCS). These limits must be determined at least annually. The recovery limits are mean recovery +/- 3 standard deviations for surrogates, matrix spikes and LCS. Precision limits for matrix spikes / matrix spike duplicates are 0 to mean relative percent difference + 3 standard deviations.

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

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

9.3. Surrogates

Every sample, blank, and QC sample is spiked with surrogates. Surrogate recoveries in samples, blanks, and QC samples must be assessed to ensure that recoveries are within established limits. The compounds included in the surrogate spiking solutions are listed in Tables 8 and 16. If any surrogates are outside limits, the following corrective actions must take place (except for dilutions):

- Check all calculations for error.
- Ensure that instrument performance is acceptable.
- Recalculate the data and/or reanalyze if either of the above checks reveal a problem.

- Reprepare and reanalyze the sample or flag the data as "Estimated Concentration" if neither of the above resolves the problem.

The decision to reanalyze or flag the data should be made in consultation with the client. It is only necessary to reprepare/reanalyze a sample once to demonstrate that poor surrogate recovery is due to matrix effect, unless the analyst believes that the repeated out of control results are not due to matrix effect.

9.3.1. If the surrogates are out of control for the sample, matrix spike, and matrix spike duplicate, then matrix effect has been demonstrated for that sample and repreparation is not necessary. If the sample is out of control and the MS and/or MSD is in control, then reanalysis or flagging of the data is required.

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

9.4. Method Blanks

For each batch of samples, analyze a method blank. The method blank is analyzed after the calibration standards, normally before any samples. *If the first method blank does not meet criteria, a second blank may be put on. The method blank must meet criteria before proceeding.* For low-level volatiles, the method blank consists of reagent water. For medium-level volatiles, the method blank consists of 25.0 mL of methanol. Surrogates are added and the method blank is carried through the entire analytical procedure. The method blank must not contain any analyte of interest at or above the reporting limit (except common laboratory contaminants, see below) or at or above 5% of the measured concentration of that analyte in the associated samples, whichever is higher.

- If the analyte is a common laboratory contaminant (methylene chloride, acetone, 2-butanone) the data may be reported with qualifiers if the concentration of the analyte is less than five times the reporting limit. Such action must be taken in consultation with the client.

- Reanalysis of samples associated with an unacceptable method blank is required when reportable concentrations are determined in the samples.

- If there is no target analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. Such action should be done in consultation with the client.

9.4.1. The method blank must have acceptable surrogate recoveries. If surrogate recoveries are not acceptable, the data must be evaluated to determine if the method blank has served the purpose of demonstrating that the analysis is free of contamination. If

surrogate recoveries are low and there are reportable analytes in the associated samples re-extraction of the blank and affected samples will normally be required. Consultation with the client should take place.

9.4.2. If reanalysis of the batch is not possible due to limited sample volume or other constraints, the method blank is reported, all associated samples are flagged with a "B," and appropriate comments may be made in a narrative to provide further documentation.

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

9.5. Laboratory Control Samples (LCS)

For each batch of samples, analyze a LCS. The LCS is analyzed after the calibration standard, and normally before any samples. The LCS contains a representative subset of the analytes of interest (See Table 9), and must contain the same analytes as the matrix spike. If any analyte or surrogate is outside established control limits, the system is out of control and corrective action must occur. Corrective action will normally be repreparation and reanalysis of the batch.

- If the batch is not re-extracted and reanalyzed, the reasons for accepting the batch must be clearly presented in the project records and the report. (Examples of acceptable reasons for not reanalyzing might be that the matrix spike and matrix spike duplicate are acceptable, and sample surrogate recoveries are good, demonstrating that the problem was confined to the LCS.)

- If re-extraction and reanalysis of the batch is not possible due to limited sample volume or other constraints, the LCS is reported, all associated samples are flagged, and appropriate comments are made in a narrative to provide further documentation.

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

9.5.2. If full analyte spike lists are used at client request, it will be necessary to allow a percentage of the components to be outside control limits as this would be expected statistically. These requirements should be negotiated with the client. *Unless otherwise agreed only the control analytes (table 9) are used to evaluate analytical performance control.*

9.6. Matrix Spikes

For each QC batch, analyze a matrix spike and matrix spike duplicate. Spiking compounds and levels are given in Table 9. Compare the percent recovery and relative percent difference (RPD) to that in the laboratory specific historically generated limits.

- If any individual recovery or RPD falls outside the acceptable range, corrective action must occur. The initial corrective action will be to check the recovery of that analyte in the Laboratory Control Sample (LCS). Generally, if the recovery of the analyte in the LCS is within limits, then the laboratory operation is in control and analysis may proceed. The reasons for accepting the batch must be documented.

- If the recovery for any component is outside QC limits for both the matrix spike/ spike duplicate and the LCS, the laboratory is out of control and corrective action must be taken. Corrective action will normally include reanalysis of the batch.

- If a MS/MSD is not possible due to limited sample, then a LCS duplicate should be analyzed. RPD of the LCS and LCSD are compared to the matrix spike limits.

- The matrix spike/duplicate must be analyzed at the same dilution as the unspiked sample, even if the matrix spike compounds will be diluted out.

9.7. Nonconformance and Corrective Action

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

9.8. Quality Assurance Summaries

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

9.9. STL QC Program

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

10. CALIBRATION AND STANDARDIZATION

10.1. Summary

10.1.1. Prior to the analysis of samples and blanks, each GC/MS system must be tuned and calibrated. Hardware tuning is checked through the analysis of the 4-Bromofluoro-benzene (BFB) to establish that a given GC/MS system meets the standard mass spectral abundance criteria. The GC/MS system must be calibrated initially at a minimum of five concentrations (analyzed under the same BFB tune), to determine the linearity of the response utilizing target calibration standards. Once the system has been calibrated, the calibration must be verified each twelve hour time period for each

GC/MS system. The use of separate calibrations is required for water and low soil matrices.

10.2. Recommended Instrument Conditions

10.2.1. General

Electron Energy:	70 volts (nominal)
Mass Range:	35–300 AMU
Scan Time:	to give at least 5 scans/peak, but not to exceed 2 second/scan
Injector Temperature:	200–250°C
Source Temperature:	According to manufacturer's specifications
Transfer Line	Temperature: 250–300°C
Purge Flow:	40 mL/minute
Carrier Gas	Flow: 15 mL/minute
Make-up Gas Flow:	25–30 mL/minute

10.2.2. Gas chromatograph suggested temperature program

10.2.2.1.BFB Analysis

Isothermal:	170°C

10.2.2.2.Sample Analysis

Initial Temperature:	40°C
Initial Hold Time:	4 minutes
Temperature Program:	8°C/minute
Final Temperature:	184°C
Second Temperature	Program: 40°C/minute
Final Temperature:	240°C
Final Hold Time:	2.6 minutes

10.3. Instrument Tuning

1.1.1. Each GC/MS system must be hardware-tuned to meet the abundance criteria listed in Table 10 for a maximum of a 50 ng injection or purging of BFB. Analysis must not begin until these criteria are met. These criteria must be met for each twelve-hour time period. The twelve-hour time period begins at the moment of injection of BFB.

10.4. Initial Calibration

10.4.1. A series of five initial calibration standards is prepared and analyzed for the target compounds and each surrogate compound. *Typical calibration levels for a 5 mL purge are: 5, 20, 50, 100, and 200 µg/L. Certain analytes are prepared at higher concentrations due to poor purge performance. Typical calibration levels for a 25 mL purge are 1, 5, 10, 20, and 40 µg/L.* Again, some analytes are prepared at higher levels. Tables 2, 4, and 17 list the calibration levels for each analyte. Other calibration levels and purge volumes may be used depending on the capabilities of the specific instrument. However, the same purge volume must be used for calibration and sample analysis, and the low level standard must be at or below the reporting limit.

10.4.2. It may be necessary to analyze more than one set of calibration standards to encompass all of the analytes required for same tests. For example, the Appendix IX list requires the Primary standard (Table 5) and the Appendix IX standard (Table 6). If acceptable analytical performance can be obtained the primary and appendix IX standards may be analyzed together.

10.4.3. Internal standard calibration is used. The internal standards are listed in Table 7. Target compounds should reference the nearest internal standard. Each calibration standard is analyzed and the response factor (RF) for each compound is calculated using the area response of the characteristic ions against the concentration for each compound and internal standard. See equation 1, Section 12, for calculation of response factor.

10.4.4. The % RSD of the calibration check compounds (CCC) must be less than 30%. Refer to Table 12 for the CCCs.

10.4.4.1. If none of the CCCs are required analytes, project specific calibration specifications must be agreed with the client.

10.4.5. The average RF must be calculated for each compound. A system performance check is made prior to using the calibration curve. The five system performance check compounds (SPCC) are checked for a minimum average response factor. Refer to Table 11 for the SPCC compounds and required minimum response factors.

10.4.6. If the average of all the %RSDs in the calibration is $\leq$ 15%, then all analytes may use average response factor for calibration.

10.4.6.1. If the software in use is capable of routinely reporting curve coefficients for data validation purposes, and the necessary calibration reports can be generated, then the analyst should evaluate analytes with %RSD > 15% for calibration on a curve. If it appears that substantially better accuracy would be obtained using quantitation from a curve then the appropriate curve should be used for quantitation. If Relative Standard Error (RSE) is used to evaluate the

curve it must be better than 15%. Otherwise the correlation coefficient (coefficient of determination for non-linear curves) must be $\geq$ 0.990.

10.4.6.2. If the average of all the %RSDs in the calibration is > 15% then calibration on a curve must be used for all analytes with %RSD > 15%. The analyst should consider instrument maintenance to improve the linearity of response. If Relative Standard Error (RSE) is used to evaluate the curve it must be better than 15%. Otherwise the correlation coefficient, r (coefficient of determination, r^2 for non-linear curves) must be $\geq$ 0.990. If a client requests a non-standard target compound that is a poor performer (alcohols for example), the laboratory may not be able to assure linear performance. In this case, a best fit curve would be provided and an assessment of the quality of the data would be provided in the narrative. If in the judgement of the laboratory, data of usable quality cannot be generated, this will be reported to the client immediately.

10.4.7. Weighting of data points

In a linear or quadratic calibration fit, the points at the lower end of the calibration curve have less weight in determining the curve generated than points at the high concentration end of the curve. However, in environmental analysis, accuracy at the low end of the curve is very important. For this reason it is preferable to increase the weighting of the lower concentration points. $1/\text{Concentration}^2$ weighting (often called $1/X^2$ weighting) will improve accuracy at the low end of the curve and should be used if the data system has this capability.

10.4.8. If time remains in the 12-hour period initiated by the BFB injection before the initial calibration, samples may be analyzed. Otherwise, proceed to continuing calibration.

10.4.9. A separate five point calibration must be prepared for analysis of low level soils. Low level soils analysis requires the use of a closed vial autosampler such as the Varian Archon, O.I. 4552 or Tekmar Precept. Each standard is prepared by spiking the methanolic standard solution through the septum of a VOA vial containing 5 mL of water and 1 g sodium bisulfate. The standards are heated to 40°C for purging. All low-level soil samples, standards, and blanks must also be heated to 40°C for purging. Medium soil extracts should be analyzed using the water (unheated) calibration curve.

10.4.10. Non-standard analytes are sometimes requested. For these analytes, it is acceptable to analyze a single standard at the reporting limit with each continuing calibration rather than a five point initial calibration. If the analyte is detected in any of the samples, a five point initial calibration must be generated and the sample(s) reanalyzed for quantitation. However, if the analyte is not detected, the non-detect may be reported and no further action is necessary.

10.5. Continuing Calibration: The initial calibration must be verified every twelve hours.

10.5.1. Continuing calibration begins with analysis of BFB as described in Section 10.3. If the system tune is acceptable, the continuing calibration standard(s) are analyzed. The level 3 calibration standard is used as the continuing calibration.

10.5.2. The RF data from the standards are compared with the average RF from the initial five-point calibration to determine the percent drift of the CCC compounds. The calculation is given in equation 4, Section 12.3.4.

10.5.3. The % drift of the CCCs must be $\leq$ 20% for the continuing calibration to be valid. The SPCCs are also monitored. The SPCCs must meet the criteria described in Table 11. In addition, the % drift of all analytes must be $\leq$ 50% with allowance for up to six target analytes to have % drift > 50%.

10.5.3.1. If none of the CCCs are required analytes, project specific calibration specifications must be agreed with the client.

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

10.5.4. If the CCCs and or the SPCCs do not meet the criteria in Sections 10.5.3 and 10.5.4, the system must be evaluated and corrective action must be taken. The BFB tune and continuing calibration must be acceptable before analysis begins. Extensive corrective action such as a different type of column will require a new initial calibration.

10.5.5. Once the above criteria have been met, sample analysis may begin. **Initial calibration average RFs (or the calibration curve) will be used for sample quantitation, not the continuing calibration RFs.** Analysis may proceed until 12 hours from the injection of the BFB have passed. (A sample *desorbed* less than or equal to 12 hours after the BFB is acceptable.)

11. PROCEDURE

11.1. Procedural Variations

11.1.1. One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation shall be completely documented using a Nonconformance Memo and approved by a Supervisor or group leader and QA Manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file.

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

11.2. Preliminary Evaluation

11.2.1. Where possible, samples are screened by headspace or GC/MS off-tune analysis to determine the correct aliquot for analysis. Alternatively, an appropriate aliquot can be determined from sample histories.

11.2.2. Dilutions should be done just prior to the GC/MS analysis of the sample. Dilutions are made in volumetric flasks or in a Luerlok syringe. Calculate the volume of reagent water required for the dilution. Fill the syringe with reagent water, compress the water to vent any residual air and adjust the water volume to the desired amount. Adjust the plunger to the mark and inject the proper aliquot of sample into the syringe. If the dilution required would use less than 1 µL of sample then serial dilutions must be made in volumetric flasks.

11.2.2.1. The diluted concentration is to be estimated to be in the upper half of the calibration range.

11.3. Sample Analysis Procedure

11.3.1. All analysis conditions for samples must be the same as for the continuing calibration standards (including purge time and flow, desorb time and temperature, column temperatures, multiplier setting etc.).

11.3.2. All samples must be analyzed as part of a batch. The batch is a set of up to 20 samples of the same matrix processed using the same procedures and reagents within the same time period. The batch also must contain a MS/MSD, a LCS, and a method blank.

11.3.2.1. If there is insufficient time in the 12-hour tune period to analyze 20 samples, the batch may be continued into the next tune period. However, if any re-tuning of the instrument is necessary, or if a period of greater than 24 hours from the preceding BFB tune has passed, a new batch must be started. For medium level soils the batch is defined at the sample preparation stage.

11.3.2.2. Laboratory generated QC samples (Blank, LCS, MS/MSD) do not count towards the maximum 20 samples in a batch. Field QC samples are included in the batch count.

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

11.4. Water Samples

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

11.4.2. Fill a syringe with the sample. If a dilution is necessary it may be made in the syringe if the sample aliquot is $\geq$ 5 µL. Check and document the pH of the remaining sample.

11.4.3. Add 250 ng of each internal and surrogate standard (10 µL of a 25 µg/mL solution, refer to Tables 7, 8, 15 and 16). The internal standards and the surrogate standards may be mixed and added as one spiking solution (this results in a 50 µg/L solution for a 5 mL sample, and a 10 µg/L solution for a 25 mL sample). Inject the sample into the purging chamber.

11.4.3.1. For TCLP samples use 0.5 mL of TCLP leachate with 4.5 mL reagent water and spike with 10 µL of the 25 µg/mL TCLP spiking solution. (Note that TCLP reporting limits will be 10 times higher than the corresponding aqueous limits).

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

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

11.4.6. Desorb and bake time and temperature are optimized for the type of trap in use. The same conditions must be used for samples and standards.

11.5. Methanol Extract Soils

11.5.1. Rinse a gas-tight syringe with organic free water. Fill the syringe with the same volume of organic free water as used in the calibrations. Add no more than 2% (v/v) (100 µL for a 5 mL purge) methanolic extract (from Section 8.5 or 8.6) to the syringe. Add internal standard (if used). Load the sample onto the purge and trap device and analyze as for aqueous samples. If less than 5µL of methanolic extract is to be added to the water, dilute the methanolic extract such that a volume greater than 5µL will be added to the water in the syringe.

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

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

11.6.2. Quickly add 7 mL of methanol, then add 1 mL of surrogate spiking solution to bring the final volume to 10 mL. Cap the vial and shake for 2 minutes to mix thoroughly. For a

MS/MSD or LCS, 6 mL of methanol, 1 mL of surrogate solution, and 1 mL of matrix spike solution is used.

11.6.3. Rinse a gas-tight syringe with organic free water. Fill the syringe with the same volume of organic free water as used in the calibrations. Add no more than 2% (v/v) (100 µL for a 5 mL purge) methanolic extract (from Section 8.5 or 8.6) to the syringe. Add internal standard (if used). Load the sample onto the purge and trap device and analyze as for aqueous samples. If less than 5µL of methanolic extract is to be added to the water, dilute the methanolic extract such that a volume greater than 5µL will be added to the water in the syringe.

11.7. Aqueous and Low level Soil Sample Analysis (Purge and Trap units that sample directly from the VOA vial)

11.7.1. Units which sample from the VOA vial should be equipped with a module which automatically adds surrogate and internal standard solution to the sample prior to purging the sample.

11.7.2. If the autosampler uses automatic IS/SS injection, no further preparation of the VOA vial is needed. Otherwise the internal and surrogate standards must be added to the vial. *Note:* Aqueous samples with high amounts of sediment present in the vial may not be suitable for analysis on this instrumentation, or they may need to analyzed as soils.

11.7.3. Soil samples must be quantitated against a curve prepared with standards containing about the same amount of sodium bisulfate as the samples (1 g in 5 mL).

11.7.4. Sample remaining in the vial after sampling with one of these mechanisms is no longer valid for further analysis. A fresh VOA vial must be used for further sample analysis.

11.7.5. For aqueous samples, check the pH of the sample remaining in the VOA vial after analysis is completed.

11.8. Low-Level Solids Analysis using discrete autosamplers

Note: This technique may seriously underestimate analyte concentration and must not be used except at specific client request for the purpose of comparability with previous data. It is no longer part of SW-846.

This method is based on purging a heated sediment/soil sample mixed with sodium bisulfate solution containing the surrogate and, if applicable, internal and matrix spiking standards. Analyze all reagent blanks and standards under the same conditions as the samples (e.g., heated). The calibration curve is also heated during analysis. Purge temperature is 40°C.

11.8.1. Do not discard any supernatant liquids. Mix the contents of the container with a narrow metal spatula.

11.8.2. Weigh out 5 g (or other appropriate aliquot) of sample into a disposable culture tube or other purge vessel. Record the weight to the nearest 0.1 g. If method sensitivity is demonstrated, a smaller aliquot may be used. Do not use aliquots less than 1.0 g. If the sample is contaminated with analytes such that a purge amount less than 1.0 g is appropriate, use the medium level method described in section 11.7.

11.8.3. Connect the purge vessel to the purge and trap device.

11.8.4. Rinse a 5 mL gas-tight syringe with organic free water, and fill. Compress to 5 mL. Add surrogate/internal standard (and matrix spike solutions if required.). Add directly to the sample from 11.5.2.

11.8.5. The above steps should be performed rapidly and without interruption to avoid loss of volatile organics.

11.8.6. Add the heater jacket or other heating device and start the purge and trap unit.

11.8.7. Soil samples that have low IS recovery when analyzed (<50%) should be reanalyzed once to confirm matrix effect.

11.9. Initial review and corrective actions

11.9.1. If the retention time for any internal standard in the continuing calibration changes by more than 0.5 minutes from the mid-level initial calibration standard, the chromatographic system must be inspected for malfunctions and corrected. Reanalysis of samples analyzed while the system was malfunctioning is required.

11.9.2. If the internal standard response in the continuing calibration is more than 200% or less than 50% of the response in the mid-level of the initial calibration standard, the chromatographic system must be inspected for malfunctions and corrected. Reanalysis of samples analyzed while the system was malfunctioning is required.

11.9.2.1. Any samples that do not meet the internal standard criteria for the continuing calibration must be evaluated for validity. If the change in sensitivity is a matrix effect confined to an individual sample reanalysis is not necessary. If the change in sensitivity is due to instrumental problems all affected samples must be reanalyzed after the problem is corrected.

11.9.3. The surrogate standard recoveries are evaluated to ensure that they are within limits. Corrective action for surrogates out of control will normally be to reanalyze the affected samples. However, if the surrogate standard response is out high and there are no target

analytes or tentatively identified compounds, reanalysis may not be necessary. Out of control surrogate standard response may be a matrix effect. It is only necessary to reanalyze a sample once to demonstrate matrix effect, but reanalysis at a dilution should be considered.

11.10. Dilutions

If the response for any compound exceeds the working range of the GC/MS system, a dilution of the extract is prepared and analyzed. An appropriate dilution should be in the upper half of the calibration range. Samples may be screened to determine the appropriate dilution for the initial run. If the initial diluted run has no hits or hits below 20% of the calibration range and the matrix allows for analysis at a lesser dilution, then the sample must be reanalyzed at a dilution targeted to bring the largest hit above 50% of the calibration range.

11.10.1. Guidance for Dilutions Due to Matrix

If the sample is initially run at a dilution and the baseline rise is less than half the height of the internal standards, or if individual non target peaks are less than twice the height of the internal standards, then the sample should be reanalyzed at a more concentrated dilution. This requirement is approximate and subject to analyst judgement.

11.10.2. Reporting Dilutions

The most concentrated dilution with no target compounds above the calibration range will be reported. Other dilutions will only be reported at client request.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Qualitative identification

An analyte is identified by retention time and by comparison of the sample mass spectrum with the mass spectrum of a standard of the suspected compound (standard reference spectrum). Mass spectra for standard reference may be obtained on the user's GC/MS by analysis of the calibration standards or from the NIST Library. Two criteria must be satisfied to verify identification: (1) elution of sample component at the same GC retention time as the standard component; and (2) correspondence of the sample component and the standard component characteristic ions. (Note: Care must be taken to ensure that spectral distortion due to co-elution is evaluated.)

- The sample component retention time must compare to within ± 0.2 min. of the retention time of the standard component. For reference, the standard must be run within the same twelve hours as the sample.

- All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100%) should be present in the sample spectrum.

- The relative intensities of ions should agree to within ±30% between the standard and sample spectra. (Example: For an ion with an abundance of 50% in the standard spectra, the corresponding sample abundance must be between 20 and 80 percent.)

12.1.1. If a compound cannot be verified by all the above criteria, but in the technical judgment of the analyst, the identification is correct, then the analyst shall report that identification and proceed with quantitation.

12.2. Tentatively Identified Compounds (TICs)

12.2.1. If the client requests components not associated with the calibration standards, a search of the NIST library may be made for the purpose of tentative identification. Guidelines are:

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

12.2.1.2. The relative intensities of the major ions should agree to within 20%. (Example: If an ion shows an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30% and 70%).

12.2.1.3. Molecular ions present in the reference spectrum should be present in the sample spectrum.

12.2.1.4. Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.

12.2.1.5. Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the spectrum because of background contamination or coeluting peaks. (Data system reduction programs can sometimes create these discrepancies.)

12.2.1.6. Computer-generated library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other. Only after visual inspection of the sample with the nearest library searches should the analyst assign a tentative identification.

12.3. Calculations.

12.3.1. Response factor (RF):

Equation 1

$$RF = \frac{A_x C_{is}}{A_{is} C_x}$$

Where:

A_x = Area of the characteristic ion for the compound to be measured

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

C_{is} = Concentration of the specific internal standard, ng

C_x = Concentration of the compound being measured, ng

12.3.2. Standard deviation (SD):

Equation 2

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

X_i = Value of X at i through N

N = Number of points

X = Average value of X_i

12.3.3. Percent relative standard deviation (%RSD):

Equation 3

$$\%RSD = \frac{\text{Standard Deviation}}{\overline{RF_i}} \times 100$$

$\overline{RF_i}$ = Mean of RF values in the curve

12.3.4. Percent drift between the initial calibration and the continuing calibration:

Equation 4

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

Where

$C_{expected}$ = Known concentration in standard

C_{found} = Measured concentration using selected quantitation method

12.3.5. Target compound and surrogate concentrations:

Concentrations in the sample may be determined from linear or second order (quadratic) curve fitted to the initial calibration points, or from the average response factor of the initial calibration points. Average response factor may only be used when the % RSD of the response factors in the initial calibration is $\leq$ 15%.

12.3.5.1. Calculation of concentration using Average Response Factors

Equation 5

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

12.3.5.2. Calculation of concentration using Linear fit

Equation 6

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

12.3.5.3. Calculation of concentration using Quadratic fit

Equation 7

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

x is defined in equations 8, 9 and 10

A is a constant defined by the intercept

B is the slope of the curve

C is the curvature

12.3.5.4. Calculation of ***x*** for Water and water-miscible waste:

Equation 8

$$x = \frac{(A_x)(I_s)(D_f)}{(A_{is})(V_o)}$$

Where:

$\mathbf{A_x}$ = Area of characteristic ion for the compound being measured (secondary ion quantitation is allowed only when there are sample interferences with the primary ion)

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

$\mathbf{I_s}$ = Amount of internal standard added in ng

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

$\mathbf{V_o}$ = Volume of water purged, mL

12.3.5.5. Calculation of ***x*** for Medium level soils:

Equation 9

$$x = \frac{(A_x)(I_s)(V_t)(1000)(D_f)}{(A_{is})(V_a)(W_s)(D)}$$

Where:

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

$\mathbf{V_t}$ = Volume of total extract, mL (Typically 25 mL)

$\mathbf{V_a}$ = Volume of extract added for purging, µL

$\mathbf{W_s}$ = Weight of sample extracted, g

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

12.3.5.6. Calculation of ***x*** for Low level soils:

Equation 10

$$x = \frac{(A_x)(I_s)}{(A_{is})(W_s)(D)}$$

Where:

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

D is as for medium level soils

$\mathbf{W_s}$ = Weight of sample added to the purge vessel, g

12.3.5.7. Calculation of TICs: The calculation of TICs (tentatively identified compounds) is identical to the above calculations with the following exceptions:

$\mathbf{A_x}$ = Area in the total ion chromatogram for the compound being measured

$\mathbf{A_{is}}$ = Area of the total ion chromatogram for the nearest internal standard without interference

RF = 1

In other words, the concentration is equal to ***x*** as defined in equations 8, 9 and 10.

12.3.6. MS/MSD Recovery

Equation 11

$$\textbf{Matrix Spike Recovery, \%} = \frac{SSR - SR}{SA} \times 100$$

SSR = Spike sample result
SR = Sample result
SA = Spike added

12.3.7. Relative % Difference calculation for the MS/MSD

Equation 12

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

Where:

RPD = Relative percent difference

MSR = Matrix spike result

MSDR = Matrix spike duplicate result

13. METHOD PERFORMANCE

13.1. Method Detection Limit

Generally, each laboratory must generate a valid method detection limit for each analyte of interest. The MDL must be below the reporting limit for each analyte. The procedure for determination of the method detection limit is given in 40 CFR Part 136, Appendix B, and further defined in QA Policy #: QA-005. When non-standard compounds are analyzed at client request, lesser requirements are possible with client agreement. At a minimum, a standard at the reporting limit must be analyzed to demonstrate the capability of the method.

13.2. Initial Demonstration

Each laboratory must make a one time initial demonstration of capability for each individual method. Demonstration of capability for both soil and water matrices is required. This requires analysis of QC check samples containing all of the standard analytes for the method. For some tests it may be necessary to use more than one QC check mix to cover all analytes of interest. The QC check sample is made up at 20 µg/L. (Some compounds will be at higher levels, refer to the calibration standard levels for guidance.)

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

13.2.2. Calculate the average recovery and standard deviation of the recovery for each analyte of interest. The %RSD should be $\leq$ 15% for each analyte, and the % recovery should be within 80-120% *for all controlled compounds.*

13.2.3. If any analyte does not meet the acceptance criteria, check the acceptance limits in the reference methods (Table 6 of method 8240B, paragraph 8.3.5 of method 8260A). If the recovery or precision is outside the limits in the reference methods, the test must be repeated. Only those analytes that did not meet criteria in the first test need to be evaluated. Repeated failure for any analyte indicates the need for the laboratory to evaluate the analytical procedure and take corrective action.

13.3. Training Qualification

The group/team leader has the responsibility to ensure that this procedure is performed by an analyst who has been properly trained in its use and has the required experience.

14. POLLUTION PREVENTION

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

15. WASTE MANAGEMENT

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

16. REFERENCES

16.1. SW846, *Test Methods for Evaluating Solid Waste,* Third Edition, Gas Chromatography/Mass Spectrometry for Volatile Organics, Method 8260B, Update III, December 1996

17. MISCELLANEOUS

17.1. Modifications from the reference method

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

17.1.2. A retention time window of 0.2 minutes is used for all components, since some data systems do not have the capability of using the relative retention time units specified in the reference method.

17.1.3. The quantitation and qualifier ions for some compounds have been changed from those recommended in SW-846 in order to improve the reliability of qualitative identification.

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

17.1.5. SW-846 recommends that a curve be used for any analytes with %RSD of the response factors > 15%. However, some industry standard data systems and forms generation software cannot report this data with the necessary information for data validation. In addition most software available does not allow weighting of the curve. Unweighted curves may exhibit serious errors in quantitation at the low end, resulting in possible false positives or false negatives. Therefore, this SOP allows used of average response factors if the average %RSD for all compounds is $\leq$ 15%.

17.2. Modifications from previous revision

This SOP has been substantially revised to reflect the changes included in Update III to SW-846. Directions for method 524.2 and method 624 have also been added.

17.3. Facility specific SOPs

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

17.4. Flow diagrams

17.4.1. Initial Demonstration and MDL

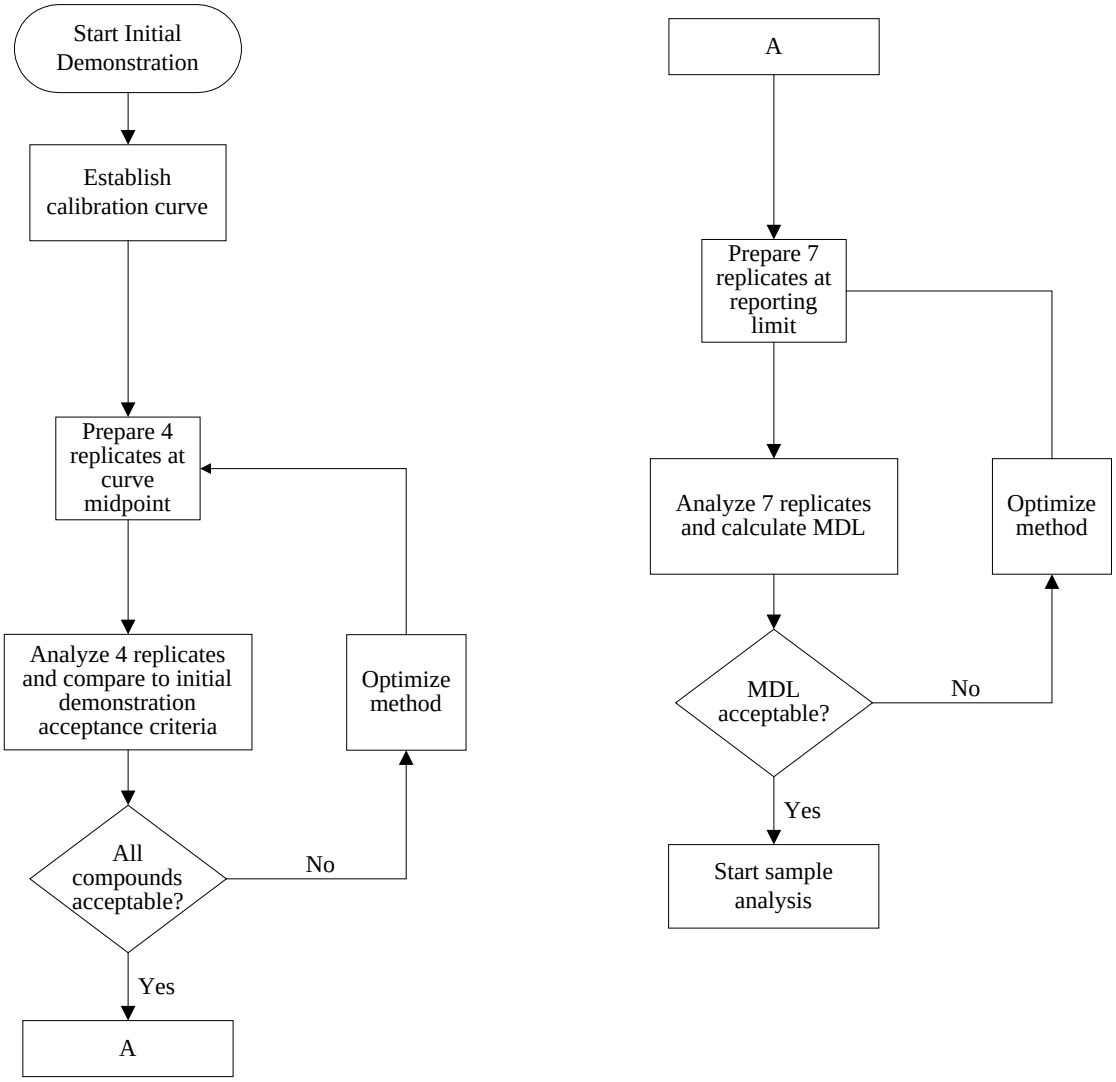


Table 1

STL Primary Standard and Reporting Limits

Compound	CAS Number	Reporting Limits[1]			
		5 mL Water µg/L	25 mL water µg/L	Low soil µg/kg	Med. Soil µg/kg
Dichlorodifluoromethane	75-71-8	10	2	10	500
Chloromethane	74-87-3	10	2	10	500
Bromomethane	74-83-9	10	2	10	500
Vinyl chloride	75-01-4	10	2	10	500
Chloroethane	75-00-3	10	2	10	500
Trichlorofluoromethane	75-69-4	10	2	10	500
Acrolein	107-02-8	100	20	100	5000
Acetone	67-64-1	20	10	20	1000
Trichlorotrifluoroethane	76-13-1	5	1	5	250
Ethanol	64-17-5	500	200	500	25,000
Iodomethane	74-88-4	5	1	5	250
Carbon disulfide	75-15-0	5	1	5	250
Methylene chloride	75-09-2	5	1	5	250
tert-Butyl alcohol	75-65-0	200	50	200	10,000
1,1-Dichloroethene	75-35-4	5	1	5	250
1,1-Dichloroethane	75-34-3	5	1	5	250
trans-1,2-Dichloroethene	156-60-5	2.5	0.5	2.5	125
Acrylonitrile	107-13-1	100	20	100	5000
Methyl *tert*-butyl ether (MTBE)	1634-04-4	20	5	20	1000
Hexane	110-54-3	5	1	5	250
cis-1,2-Dichloroethene	156-59-2	2.5	0.5	2.5	125
1,2-Dichloroethene (Total)	540-59-0	5	1	5	250
Tetrahydrofuran	109-99-9	20	5	20	1000
Chloroform	67-66-3	5	1	5	250
1,2-Dichloroethane	107-06-2	5	1	5	250
Dibromomethane	74-95-3	5	1	5	250
2-Butanone	78-93-3	20	5	20	1000
1,4-Dioxane	123-91-1	500	200	500	25000
1,1,1-Trichloroethane	71-55-6	5	1	5	250
Carbon tetrachloride	56-23-5	5	1	5	250
Bromodichloromethane	75-27-4	5	1	5	250
1,2-Dichloropropane	78-87-5	5	1	5	250
cis-1,3-Dichloropropene	10061-01-5	5	1	5	250
Trichloroethene	79-01-6	5	1	5	250
Dibromochlorometne	124-48-1	5	1	5	250

Table 1

STL Primary Standard and Reporting Limits

Compound	CAS Number	Reporting Limits[1]			
		5 mL Water µg/L	25 mL water µg/L	Low soil µg/kg	Med. Soil µg/kg
1,2-Dibromoethane	106-93-4	5	1	5	250
1,2,3-Trichloropropane	96-18-4	5	1	5	250
1,1,2-Trichloroethane	79-00-5	5	1	5	250
Benzene	71-43-2	5	1	5	250
Ethylmethacrylate	97-63-2	5	1	5	250
trans-1,3-Dichloropropene	10061-02-6	5	1	5	250
Bromoform	75-25-2	5	1	5	250
4-Methyl-2-pentanone	108-10-1	20	5	20	1000
2-Hexanone	591-78-6	20	5	20	1000
Tetrachloroethene	127-18-4	5	1	5	250
Toluene	108-88-3	5	1	5	250
1,1,2,2-Tetrachloroethane	79-34-5	5	1	5	250
2-Chloroethyl vinyl ether	110-75-8	N/A[2]	N/A	50	1000
Vinyl acetate	108-05-4	10	2	10	500
Chlorobenzene	108-90-7	5	1	5	250
Ethylbenzene	100-41-4	5	1	5	250
Styrene	100-42-5	5	1	5	250
t-1,4-Dichloro-2-butene	110-57-6	5	1	5	250
m and p Xylenes		2.5	0.5	2.5	125
o-xylene	95-47-6	2.5	0.5	2.5	125
Total xylenes	1330-20-7	5	1	5	250
1,3-Dichlorobenzene	541-73-1	5	1	5	250
1,4-Dichlorobenzene	106-46-7	5	1	5	250
1,2-Dichlorobenzene	95-50-1	5	1	5	250

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

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

Table 2

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

Compound	Calibration Level ug/L				
	Level 1	Level 2	Level 3	Level 4	Level 5
1,2-Dichloroethane-d4 (Surrogate)	5	20	50	100	200
Toluene-d8 (Surrogate)	5	20	50	100	200
4-Bromofluorobenzene (Surrogate)	5	20	50	100	200
Dichlorodifluoromethane	5	20	50	100	200
Chloromethane	5	20	50	100	200
Bromomethane	5	20	50	100	200
Vinyl chloride	5	20	50	100	200
Chloroethane	5	20	50	100	200
Trichlorofluoromethane	5	20	50	100	200
Acrolein	100	200	500	1000	2000
Acetone	5	20	50	100	200
Trichlorotrifluoroethane	5	20	50	100	200
Ethanol	1000	2000	5000	10000	20000
Iodomethane	5	20	50	100	200
Carbon disulfide	5	20	50	100	200
Methylene chloride	5	20	50	100	200
tert-Butyl alcohol	200	400	1,000	2,000	4,000
1,1-Dichloroethene	5	20	50	100	200
1,1-Dichloroethane	5	20	50	100	200
trans-1,2-Dichloroethene	5	20	50	100	200
Acrylonitrile	100	200	500	1,000	2,000
Methyl *tert*-butyl ether (MTBE)	5	20	50	100	200
Hexane	5	20	50	100	200
cis-1,2-Dichloroethene	5	20	50	100	200
Tetrahydrofuran	5	20	50	100	200
Chloroform	5	20	50	100	200
1,2-Dichloroethane	5	20	50	100	200
Dibromomethane	5	20	50	100	200
2-Butanone	5	20	50	100	200
1,4-Dioxane	500	1000	2,500	5,000	10,000
1,1,1-Trichloroethane	5	20	50	100	200
Carbon tetrachloride	5	20	50	100	200
Bromodichloromethane	5	20	50	100	200
1,2-Dichloropropane	5	20	50	100	200
cis-1,3-Dichloropropene	5	20	50	100	200
Trichloroethene	5	20	50	100	200

Table 2

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

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

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

Table 3

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

Compound	CAS Number	Reporting Limits			
		5 mL Water µg/L	25 mL water µg/L	Low Soil µg/kg	Medium Soil µg/mL
Allyl Chloride	107-05-1	10	2	10	500
Acetonitrile	75-05-8	100	20	100	5000
Dichlorofluoromethane		10	2	10	500
Isopropyl ether	108-20-3	10	2	10	500
Chloroprene	126-99-8	5	1	5	250
n-Butanol	71-36-3	200	50	200	10,000
Propionitrile	107-12-0	20	4	20	1000
Methacrylonitrile	126-98-7	5	1	5	250
Isobutanol	78-83-1	400	100	400	20,000
Methyl methacrylate	80-62-6	5	1	5	250
1,1,1,2-Tetrachloroethane	630-20-6	5	1	5	250
1,2-Dibromo-3-chloropropane	96-12-8	10	2	10	500
Ethyl ether	60-29-7	10	2	10	500
Ethyl Acetate	141-78-6	20	4	20	1,000
2-Nitropropane	79-46-9	10	2	10	500
Cyclohexanone	108-94-1	N/A[2]	N/A[2]	N/A[2]	N/A[2]
Isopropylbenzene	98-82-8	5	1	5	250

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

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

Table 4

STL Appendix IX Standard Calibration Levels, µg/L

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

Table 5

Reportable Analytes for STL Standard Tests, Primary Standard

Compound	CAS Number	STL Standard List	TCLP	TCL	Appendix IX	UTS
Dichlorodifluoromethane	75-71-8				X	X
Chloromethane	74-87-3	X		X	X	X
Bromomethane	74-83-9	X		X	X	X
Vinyl chloride	75-01-4	X	X	X	X	X
Chloroethane	75-00-3	X		X	X	X
Trichlorofluoromethane	75-69-4				X	X
Acrolein	107-02-8				X	X
Acetone	67-64-1	X		X	X	X
Trichlorotrifluoroethane	76-13-1					X
Ethanol	64-17-5					
Iodomethane	74-88-4				X	X
Carbon disulfide	75-15-0	X		X	X	X
Methylene chloride	75-09-2	X		X	X	X
tert-Butly alcohol	75-65-0					
1,1-Dichloroethene	75-35-4	X	X	X	X	X
1,1-Dichloroethane	75-34-3	X		X	X	X
trans-1,2-Dichloroethene	156-60-5	X		X	X	X
Total dichloroethene		X		X	X	X
Acrylonitrile	107-13-1				X	X
Methyl *tert*-butyl ether (MTBE)	1634-04-4					
Hexane	110-54-3					
cis-1,2-Dichloroethene	156-59-2	X		X		
Tetrahydrofuran	109-99-9					
Chloroform	67-66-3	X	X	X	X	X
1,2-Dichloroethane	107-06-2	X	X	X	X	X
Dibromomethane	74-95-3				X	X
2-Butanone	78-93-3	X	X	X	X	X
1,4-Dioxane	123-91-1				X	X
1,1,1-Trichloroethane	71-55-6	X		X	X	X
Carbon tetrachloride	56-23-5	X	X	X	X	X
Bromodichloromethane	75-27-4	X		X	X	X
1,2-Dichloropropane	78-87-5	X		X	X	X
cis-1,3-Dichloropropene	10061-01-5	X		X	X	X

Table 5

Reportable Analytes for STL Standard Tests, Primary Standard

Compound	CAS Number	STL Standard List	TCLP	TCL	Appendix IX	UTS
Trichloroethene	79-01-6	X	X	X	X	X
Dibromochloromethane	124-48-1	X		X	X	X
1,2-Dibromoethane	106-93-4				X	X
1,2,3-Trichloropropane	96-18-4				X	X
1,1,2-Trichloroethane	79-00-5	X		X	X	X
Benzene	71-43-2	X	X	X	X	X
Ethylmethacrylate	97-63-2				X	X
trans-1,3-Dichloropropene	10061-02-6	X		X	X	X
Bromoform	75-25-2	X		X	X	X
4-Methyl-2-pentanone	108-10-1	X		X	X	X
2-Hexanone	591-78-6	X		X	X	
Tetrachloroethene	127-18-4	X	X	X	X	X
Toluene	108-88-3	X		X	X	X
1,1,2,2-Tetrachloroethane	79-34-5	X		X	X	X
2-Chloroethyl vinyl ether	110-75-8					
Vinyl acetate	108-05-4				X	
Chlorobenzene	108-90-7	X	X	X	X	X
Ethylbenzene	100-41-4	X		X	X	X
Styrene	100-42-5	X		X	X	
t-1,4-Dichloro-2-butene	110-57-6				X	
m and p Xylenes		X		X	X	X
o-xylene	95-47-6	X		X	X	X
Total xylenes	1330-20-7	X		X	X	X
1,3-Dichlorobenzene	541-73-1					
1,4-Dichlorobenzene	106-46-7					
1,2-Dichlorobenzene	95-50-1					

Table 6

Reportable Analytes for STL Standard Tests, Appendix IX standard

Compound	Number	STL Standard List	TCLP	TCL	Appendix IX	UTS
Allyl Chloride	107-05-1				X	
Acetonitrile	75-05-8				X	X
Dichlorofluoromethane	75-43-4					
Isopropyl ether	108-20-3					
Chloroprene	126-99-8				X	
n-Butanol	71-36-3					
Propionitrile	107-12-0				X	
Methacrylonitrile	126-98-7				X	X
Isobutanol	78-83-1				X	X
Methyl methacrylate	80-62-6				X	X
1,1,1,2-Tetrachloroethane	630-20-6				X	X
1,2-Dibromo-3-chloropropane	96-12-8				X	X
Ethyl ether	60-29-7					X
Ethyl Acetate	141-78-6					X
2-Nitropropane	79-46-9					
Cyclohexanone	108-94-1					X
Isopropylbenzene	98-82-8					

Table 7

Internal Standards

	Standard Concentration µg/mL	Quantitation ion (5 mL purge)	Quantitation ion (25 mL purge)
Fluorobenzene	25	96	96
Chlorobenzene-d5	25	*119*	119
1,4-Dichlorobenzene-d4	25	152	152

Notes:

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

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

Table 8

Surrogate Standards

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

Notes:

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

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

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

Table 9

Matrix Spike / LCS Compounds

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

Notes:

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

2) Recovery and precision limits for LCS and MS/MSD are generated from historical data and are maintained by the QA dedartment.

3) Full analyte spikes may also be used at the laboratories option or at client request.

Table 10

BFB Key Ion Abundance Criteria

Mass	Ion Abundance Criteria
50	15% to 40% of Mass 95
75	30% to 60% of Mass 95
95	Base Peak, 100% Relative Abundance
96	5% to 9% of Mass 95
173	Less Than 2% of Mass 174
174	Greater Than 50% of Mass 95
175	5% to 9% of Mass 174
176	Greater Than 95%, But Less Than 101% of Mass 174
177	5% to 9% of Mass 176

Table 11

SPCC Compounds and Minimum Response Factors

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

Table 12

CCC compounds

Compound	Max. %RSD from Initial Calibration	Max. %D for continuing calibration
Vinyl Chloride	<30.0	<20.0
1,1-Dichloroethene	<30.0	<20.0
Chloroform	<30.0	<20.0
1,2-Dichloropropane	<30.0	<20.0
Toluene	<30.0	<20.0
Ethylbenzene	<30.0	<20.0

Table 13

Characteristic ions

Compound	Primary*	Secondary	Tertiary
1,2-Dichloroethane-d_4 (Surrogate)	65	102	
Dichlorodifluoromethane	85	87	50, 101,103
Chloromethane	50	52	49
Vinyl chloride	62	64	61
Bromomethane	94	96	79
Chloroethane	64	66	49
Trichlorofluoromethane	101	103	66
1,1-Dichloroethene	96	61	98
Acrolein	56	55	58
Iodomethane	142	127	141

Table 13

Characteristic ions

Compound	Primary*	Secondary	Tertiary
Carbon disulfide	76	78	
Trichlorotrifluoroethane	151	101	153
Ethanol	45	46	
Acetone	43	58	
Methylene chloride	84	49	51, 86
tert-Butyl alcohol	59	74	
trans-1,2-Dichloroethene	96	61	98
Acrylonitrile	53	52	51
Methyl *tert* butyl ether	73		
Hexane	57	43	
1,1-Dichloroethane	63	65	83
cis-1,2-Dichloroethene	96	61	98
2-Butanone	43	72**	
Tetrahydrofuran	42	71	
Chloroform	83	85	47
1,2-Dichloroethane	62	64	98
Dibromomethane	93	174	95, 172, 176
1,4-Dioxane	88	58	
Vinyl acetate	43	86	
1,1,1-Trichloroethane	97	99	117
Carbon tetrachloride	117	119	121
Benzene	78	52	77
Trichloroethene	130	95	97, 132
1,2-Dichloropropane	63	65	41
Bromodichloromethane	83	85	129
2-Chloroethyl vinyl ether	63	65	106
cis-1,3-Dichloropropene	75	77	39
trans-1,3-Dichloropropene	75	77	39
1,1,2-Trichloroethane	97	83	85, 99
Chlorodibromomethane	129	127	131
Bromoform	173	171	175, 252
1,2,3-Trichloropropane	75	110	77, 112, 97
Toluene-d_8 (Surrogate)	98	70	100
4-Bromofluorobenzene (Surrogate)	95	174	176
Toluene	91	92	65
4-Methyl-2-pentanone	43	58	57, 100
Tetrachloroethene	164	166	131
Ethyl methacrylate	69	41	99, 86, 114
2-Hexanone	43	58	57, 100

Table 13

Characteristic ions

Compound	Primary*	Secondary	Tertiary
Chlorobenzene	112	114	77
Ethylbenzene	106	91	
Xylenes	106	91	
Styrene	104	103	78, 51, 77
Dichlorobenzene (all isomers)	146	148	111
trans 1,4-Dichloro-2-butene	53	75	89, 77, 124
1,1,2,2-Tetrachloroethane	83	85	131, 133
Allyl Chloride	76	41	78
Acetonitrile	40	41	
Dichlorofluoromethane	67	69	
Isopropyl ether	87	59	45
Chloroprene	53	88	90
n-Butanol	56	41	42
Propionitrile	54	52	55
Methacrylonitrile	41	67	52
Isobutanol	41	43	74
Methyl methacrylate	41	69	100
1,1,1,2-Tetrachloroethane	131	133	119
1,2-Dibromo-3-chloropropane	157	155	75
Ethyl ether	59	74	
Ethyl Acetate	43	88	61
2-Nitropropane	41	43	46
Cyclohexanone	55	42	98
Isopropylbenzene	105	120	

* The primary ion should be used for quantitation unless interferences are present, in which case a secondary ion may be used.

** m/z 43 may be used for quantitation of 2-Butanone, but m/z 72 must be present for positive identification.

18. SUMMARY

This appendix lists modifications to the main body of the SOP that are necessary for analysis of drinking water by method 524.2.

18.1. A target analyte list based on the list in method 524.2 is frequently requested for analysis by method 8260B. STL's standard analyte list for this test, and the internal and surrogate standards used, are listed in Tables A-1 to A-4 below. In all other respects the method is as described in the main body of this SOP. Note that this without the modifications listed in Section 19, the method is ***not*** appropriate for drinking water analysis by method 524.2.

19. MODIFICATIONS REQUIRED FOR DRINKING WATER ANALYSIS BY METHOD 524.2

19.1. This method can be applied to surface water, ground water and drinking water.

19.2. Purge sample volume is normally 25 mL, but lesser volumes may be used if adequate sensitivity is obtained.

19.3. Sample concentrations are calculated using initial calibration curve.

19.4. Only one internal standard -- Fluorobenzene -- is used for this method, and therefore all target analytes are assigned to it.

19.5. A maximum of 25 ng of BFB is used for tuning for method 524.2

19.6. BFB tuning criteria for mass 75 are 30-80% of mass 95.

19.7. The recovery limits for the initial demonstration of capability are 80-120% with %RSD less than 20%.

19.8. Initial calibration curve requirements:

19.8.1. The number of calibration standards depends on the calibration range used. For a range of up to a factor of 20 (e.g. 1µg/L - 20µg/L) a minimum of three standards are necessary. For a factor of up to 50 four standards are necessary, and for a factor of up to 100 five standards are necessary.

19.8.2. All target compounds must have RSD ≤ 20%.

19.8.3. If this requirement can not be met, a regression curve must be constructed for the non-compliant compounds. There is no correlation coefficient requirement for the regression curve.

19.9. Continuing calibration verification (CCV) requirements:

19.9.1. All target compounds must have %D ≤ 30%.

19.9.2. The internal standards in each CCV must be over 70% of the abundance found in the CCV analysis immediately preceding it *and* over 50% of the calibration point in the initial calibration curve whose concentration matches that of the CCV.

19.9.3. The same analysis run may be used to satisfy the requirements for an LCS (also known as a laboratory fortified blank, LFB) and a continuing calibration verification. The LCS/CCV does not need to be a second source standard.

19.10. Method clarifications, modifications and additions

19.10.1. Section 7.1 requires that the trap packing materials be Tenax GC, Methyl silicone, silica gel and coconut charcoal. STL routinely employs the Supelco VOCARB 3000, which consists of Carbopack B and Carboxen 1000 and 1001.

19.10.2. Section 7.8.2 of the source method requires that each calibration standard be prepared by diluting the appropriate volume of the working standard with organic-free water adjusted to pH < 2 in a volumetric flask. STL prepares calibration standards by diluting the the appropriate volume of the working standard with organic-free water in the gas-tight syringe that will be used to inject the sample into the purge and trap device.

19.10.3. Sections 9.8 and 9.9 of the source method require that duplicate spiked blanks and a second-source initial calibration verification standard be analyzed at least quarterly. Since some STL do not normally analyze drinking waters samples, these QC samples will be analyzed only during the conduct of projects that require this method.

Table A-1

STL 8260 Drinking Water List Standard and Reporting Limits

Compound	CAS Number	Reporting Limits[1]			
		5 mL water µg/L	25 mL water µg/L	Low soil µg/kg	Med. Soil µg/kg
Dichlorodifluoromethane	75-71-8	10	2	10	500
Chloromethane	74-87-3	10	2	10	500
Bromomethane	74-83-9	10	2	10	500
Vinyl chloride	75-01-4	10	2	10	500
Chloroethane	75-00-3	10	2	10	500
Trichlorofluoromethane	75-69-4	10	2	10	500
Acetone[1]	67-64-1	20	10	20	1000
Methylene chloride	75-09-2	5	2	5	250
1,1-Dichloroethene	75-35-4	5	1	5	250
1,1-Dichloroethane	75-34-3	5	1	5	250
trans-1,2-Dichloroethene	156-60-5	2.5	0.5	2.5	125
Methyl *tert*-butyl ether (MTBE)[1]	1634-04-4	20	5	20	250
2,2-Dichloropropane	590-20-7	5	1	5	250
cis-1,2-Dichloroethene	156-59-2	2.5	0.5	2.5	125
1,2-Dichloroethene (Total)	540-59-0	5	1	5	250
Chloroform	67-66-3	5	1	5	250
Bromochloromethane	74-97-5	5	1	5	250
1,2-Dichloroethane	107-06-2	5	1	5	250
Dibromomethane	74-95-3	5	1	5	250
2-Butanone[1]	78-93-3	20	5	20	1000
1,1,1-Trichloroethane	71-55-6	5	1	5	250
Carbon tetrachloride	56-23-5	5	1	5	250
1,1-Dichloropropene	563-58-6	5	1	5	250
Bromodichloromethane	75-27-4	5	1	5	250
1,2-Dichloropropane	78-87-5	5	1	5	250
1,3-Dichloropropane	142-28-9	5	1	5	250
cis-1,3-Dichloropropene	10061-01-5	5	1	5	250
Trichloroethene	79-01-6	5	1	5	250
Dibromochloromethane	124-48-1	5	1	5	250
1,2-Dibromoethane	106-93-4	5	1	5	250
1,2,3-Trichloropropane	96-18-4	5	1	5	250
1,1,2-Trichloroethane	79-00-5	5	1	5	250
Benzene	71-43-2	5	1	5	250
trans-1,3-Dichloropropene	10061-02-6	5	1	5	250

Table A-1

STL 8260 Drinking Water List Standard and Reporting Limits

Compound	CAS Number	Reporting Limits[1]			
		5 mL water µg/L	25 mL water µg/L	Low soil µg/kg	Med. Soil µg/kg
Bromoform	75-25-2	5	1	5	250
4-Methyl-2-pentanone[1]	108-10-1	20	5	20	1000
2-Hexanone[1]	591-78-6	20	5	20	1000
Tetrachloroethene	127-18-4	5	1	5	250
Toluene	108-88-3	5	1	5	250
1,1,2,2-Tetrachloroethane	79-34-5	5	1	5	250
Chlorobenzene	108-90-7	5	1	5	250
1,1,1,2-Terrachloroethane	630-20-6	5	1	5	250
Ethylbenzene	100-41-4	5	1	5	250
Styrene	100-42-5	5	1	5	250
m and p Xylenes		2.5	0.5	2.5	125
o-xylene	95-47-6	2.5	0.5	2.5	125
Total xylenes	1330-20-7	5	1	5	250
Isopropylbenzene	98-82-8	5	1	5	250
Bromobenzene	108-86-1	5	1	5	250
n-Propylbenzene	103-65-1	5	1	5	250
2-Chlorotoluene	95-49-8	5	1	5	250
4-Chlorotoluene	106-43-4	5	1	5	250
1,3,5-Trimethylbenzene	108-67-8	5	1	5	250
tert-Butylbenzene	98-06-6	5	1	5	250
1,2,4-Trimethylbenzene	95-63-6	5	1	5	250
sec-butylbenzene	135-98-8	5	1	5	250
1,3-Dichlorobenzene	541-73-1	5	1	5	250
1,4-Dichlorobenzene	106-46-7	5	1	5	250
1,2-Dichlorobenzene	95-50-1	5	1	5	250
4-Isopropyltoluene	99-87-6	5	1	5	250
n-Butylbenzene	104-51-8	5	1	5	250
1,2-Dibromo-3-chloropropane	96-12-8	5	1	5	250
1,2,4-Trichlorobenzene	120-82-1	5	1	5	250
Napthalene	91-20-3	5	1	5	250
Hexachlorobutadiene	87-68-3	5	1	5	250
1,2,3-Trichlorobenzene	87-61-6	5	1	5	250

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

Table A-2

Internal Standards, Method 8260A Drinking water list

	Standard Concentration µg/mL	Quantitation ion
Fluorobenzene	25	96
Chlorobenzene-d5	25	119
1,4-Dichlorobenzene-d4	25	152

Notes:

1) Fluorobenzene only is used for method 524.2

2) 10 µL of the internal standard is added to the sample. This results in a concentration of each internal in the sample of 50µg/L for a 5 mL purge or 10 µg/L for a 25 mL purge.

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

Table A-3

Surrogate Standards, Drinking water list

Surrogate Compounds	Standard Concentration µg/mL
1,2-Dichloroethane-d_4[1]	25
Dibromofluoromethane[1]	25
Toluene-d_8[1]	25
1,2-Dichlorobenzene-d4[2]	25
4-Bromofluorobenzene[1,2]	25

[1] 8260B surrogate

[2] 524.2 surrogate

Notes:

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

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

Table A-4

STL Drinking water list Standard: Calibration Levels

Compound	Level 1	Level 2	Level 3	Level 4	Level 5
	25 mL	25 mL	25 mL	25 mL	25 mL
Dichlorodifluoromethane	2	5	10	20	40
Chloromethane	2	5	10	20	40
Bromomethane	2	5	10	20	40
Vinyl chloride	2	5	10	20	40
Chloroethane	2	5	10	20	40
Trichlorofluoromethane	2	5	10	20	40
Acetone[1]	10	20	30	40	50
Methylene chloride	2	5	10	20	40
1,1-Dichloroethene	2	5	10	20	40
1,1-Dichloroethane	2	5	10	20	40
trans-1,2-Dichloroethene	2	5	10	20	40
Methyl *tert*-butyl ether (MTBE)	10	20	30	40	50
2,2-Dichloropropane	2	5	10	20	40
cis-1,2-Dichloroethene	2	5	10	20	40
Chloroform	2	5	10	20	40
Bromochloromethane	2	5	10	20	40
1,2-Dichloroethane	2	5	10	20	40
Dibromomethane	2	5	10	20	40
2-Butanone[1]	10	20	30	40	50
1,1,1-Trichloroethane	2	5	10	20	40
Carbon tetrachloride	2	5	10	20	40
Bromodichloromethane	2	5	10	20	40
1,2-Dichloropropane	2	5	10	20	40
cis-1,3-Dichloropropene	2	5	10	20	40
Trichloroethene	2	5	10	20	40

Table A-4

STL Drinking water list Standard: Calibration Levels

Compound	Level 1	Level 2	Level 3	Level 4	Level 5
Dibromochloromethane	2	5	10	20	40
1,2-Dibromoethane	2	5	10	20	40
1,2,3-Trichloropropane	2	5	10	20	40
1,1,2-Trichloroethane	2	5	10	20	40
Benzene	2	5	10	20	40
trans-1,3-Dichloropropene	2	5	10	20	40
Bromoform	2	5	10	20	40
4-Methyl-2-pentanone[1]	10	20	30	40	50
2-Hexanone[1]	10	20	30	40	50
Tetrachloroethene	2	5	10	20	40
Toluene	2	5	10	20	40
1,1,2,2-Tetrachloroethane	2	5	10	20	40
Chlorobenzene	2	5	10	20	40
Ethylbenzene	2	5	10	20	40
Styrene	2	5	10	20	40
m and p Xylenes	2	5	10	20	40
o-xylene	2	5	10	20	40
Isopropylbenzene	2	5	10	20	40
Bromobenzene	2	5	10	20	40
n-Propylbenzene	2	5	10	20	40
2-Chlorotoluene	2	5	10	20	40
4-Chlorotoluene	2	5	10	20	40
1,3,5-Trimethylbenzene	2	5	10	20	40
tert-Butylbenzene	2	5	10	20	40
1,2,4-Trimethylbenzene	2	5	10	20	40
sec-butylbenzene	2	5	10	20	40
1,3-Dichlorobenzene	2	5	10	20	40
1,4-Dichlorobenzene	2	5	10	20	40

Table A-4

STL Drinking water list Standard: Calibration Levels

Compound	Level 1	Level 2	Level 3	Level 4	Level 5
1,2-Dichlorobenzene	2	5	10	20	40
4-Isopropyltoluene	2	5	10	20	40
n-Butylbenzene	2	5	10	20	40
1,2-Dibromo-3-chloropropane	2	5	10	20	40
1,2,4-Trichlorobenzene	2	5	10	20	40
Napthalene	2	5	10	20	40
Hexachlorobutadiene	2	5	10	20	40
1,2,3-Trichlorobenzene	2	5	10	20	40

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

20. REQUIREMENTS FOR EPA 624

20.1. Method 624 is required for demonstration of compliance with NPDES wastewater discharge permits. This method can be applied only to aqueous matrices. The standard analyte list and reporting limits are listed in Table B-1.

20.2. The tune period for this method is defined as 24 hours.

20.3. The initial calibration curve for this method requires at least three points.

20.4. Sample concentrations are calculated using the average RRF from the initial calibration curve.

20.5. Each target analyte is assigned to the closest eluting internal standard.

20.6. Initial demonstration of Proficiency

20.6.1. The spiking level for the four replicate initial demonstration of proficiency is 20 µg/L. The acceptance criteria are listed in Table B-2

20.7. Initial calibration curve requirements:

20.7.1. Target compounds must have RSD ≤ 35%.

20.7.2. If this requirement can not be met, a regression curve must be constructed for the non-compliant compounds. There is no correlation coefficient requirement for the regression curve.

20.8. Continuing calibration verification requirements:

20.8.1. The continuing calibration standard is from a different source than the initial calibration standard. The acceptance criteria are listed in Table B-2.

20.9. Matrix Spike and LCS requirements

20.9.1. The matrix spike and LCS are spiked at 20 µg/L. A matrix spike duplicate is not necessary for this method. The recovery limits for matrix spike and LCS recovery are listed in Table C-2.

20.10. Method clarifications, modifications and additions

20.10.1. Section 5.2.2 of the source method describes the trap packing materials as Tenax GC, Methyl silicone, silica gel and coconut charcoal. STL routinely employs the Supelco VOCARB 3000, which consists of Carbopack B and Carboxen 1000 and 1001.

20.10.2. Section 5.3.2 of the source method describes a packed analytical column. STL routinely employs capillary columns when performing this method.

20.10.3. The source method provides a suggested list of compounds for internal and surrogate standards. STL uses the following two compounds which are not on the table: Chlorobenzene-d_5 (internal standard) and 1,2-Difluorobenzene-d_4 (surrogate).

Table B-1.

Method 624 Analytes and Reporting Limits

Analytes	µg/L
Benzene	5
Bromodichloromethane	5
Bromoform	5
Bromomethane	5
Carbon tetrachloride	5
Chlorobenzene	5
Chloroethane	5
2-Chloroethyl vinyl ether	5
Chloroform	5
Chloromethane	5
Dibromochloromethane	5
1,2-Dichlorobenzene	5
1,3-Dichlorobenzene	5
1,4-Dichlorobenzene	5
1,1-Dichloroethane	5
1,2-Dichloroethane	5
1,1-Dichloroethene	5
trans-1,2-Dichloroethene	5
1,2-Dichloropropane	5
cis-1,3-Dichloropropene	5
trans-1,3-Dichloropropene	5
Ethylbenzene	5
Methylene chloride	5
1,1,2,2-Tetrachloroethane	5
Tetrachloroethene	5
Toluene	5
1,1,1-Trichloroethane	5
1,1,2-Trichloroethane	5
Trichloroethene	5
Trichlorofluoromethane	5
Vinyl chloride	5

Table B-2.

Method 624 QC Acceptance Criteria

Analytes	Daily QC check acceptance criteria (20µg/L spike)	Mean recovery, 4 replicate initial demonstration acceptance criteria (20µg/L spike)	Standard deviation, 4 replicate initial demonstration acceptance criteria (20µg/L spike)	Matrix spike and LCS acceptance criteria (% recovery)
Benzene	12.8-27.2	15.2-26.0	6.9	37-151
Bromodichloromethane	13.1-26.9	10.1-28.0	6.4	35-155
Bromoform	14.2-25.8	11.4-31.1	5.4	45-169
Bromomethane	2.8-37.2	D-41.2	17.9	D-242
Carbon tetrachloride	14.6-25.4	17.2-23.5	5.2	70-140
Chlorobenzene	13.2-26.8	16.4-27.4	6.3	37-160
Chloroethane	7.6-32.4	8.4-40.4	11.4	14-230
2-Chloroethyl vinyl ether	D-44.8	D-50.4	25.9	D-305
Chloroform	13.5-26.5	13.7-24.2	6.1	51-138
Chloromethane	D-40.8	D-45.9	19.8	D-273
Dibromochloromethane	13.5-26.5	13.8-26.6	6.1	53-149
1,2-Dichlorobenzene	12.6-27.4	11.8-34.7	7.1	18-190
1,3-Dichlorobenzene	14.6-25.4	17.0-28.8	5.5	59-156
1,4-Dichlorobenzene	12.6-27.4	11.8-34.7	7.1	18-190
1,1-Dichloroethane	14.5-25.5	14.2-28.5	5.1	59-155
1,2-Dichloroethane	13.6-26.4	14.3-27.4	6.0	49-155
1,1-Dichloroethene	10.1-29.9	3.7-42.3	9.1	D-234
trans-1,2-Dichloroethene	13.9-26.1	13.6-28.5	5.7	54-156
1,2-Dichloropropane	6.8-33.2	3.8-36.2	13.8	D-210
cis-1,3-Dichloropropene	4.8-35.2	1.0-39.0	15.8	D-227
trans-1,3-Dichloropropene	10.0-30.0	7.6-32.4	10.4	17-183
Ethylbenzene	11.8-28.2	17.4-26.7	7.5	37-162
Methylene chloride	12.1-27.9	D-41.0	7.4	D-221
1,1,2,2-Tetrachloroethane	12.1-27.9	13.5-27.2	7.4	46-157
Tetrachloroethene	14.7-25.3	17.0-26.6	5.0	64-148
Toluene	14.9-25.1	16.6-26.7	4.8	47-150
1,1,1-Trichloroethane	15.0-25.0	13.7-30.1	4.6	52-162
1,1,2-Trichloroethane	14.2-25.8	14.3-27.1	5.5	52-150
Trichloroethene	13.3-26.7	18.6-27.6	6.6	71-157
Trichlorofluoromethane	9.6-30.4	8.9-31.5	10.0	17-181
Vinyl chloride	0.8-39.2	D-43.5	20.0	D-251

CORP-MS-0001-PT

GC/MS based on Methods 8270C and 625

STL STANDARD OPERATING PROCEDURE

TITLE: GC/MS ANALYSIS BASED ON METHODS 8270C AND 625

(SUPERSEDES: Revision 1)

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1. SCOPE AND APPLICATION

1.1. This method is based upon SW846 8270C, and is applicable to the determination of the concentration of semivolatile organic compounds in extracts prepared from solid and aqueous matrices. The modifications presented in Attachment A may be followed for analysis of wastewater following method 625. Direct injection of a sample may be used in limited applications. Refer to Tables 1, 2, 3 and 4 for the list of compounds applicable for this method. Note that the compounds are listed in approximate retention time order. Additional compounds may be amenable to this method. If non-standard analytes are required, they must be validated by the procedures described in section 13 before sample analysis.

1.2. The following compounds may require special treatment when being determined by this method:

- Benzidine can be subject to oxidative losses during solvent concentration and exhibits poor chromatography. Neutral extraction should be performed if this compound is expected.
- Hexachlorocyclopentadiene is subject to thermal decomposition in the inlet of the gas chromatograph, chemical reaction in acetone solution, and photochemical decomposition.
- N-Nitrosodiphenylamine decomposes in the gas chromatographic inlet and cannot be distinguished from diphenylamine.
- Pentachlorophenol, 2,4-dinitrophenol, 4-nitrophenol, 4,6-dinitro-2-methylphenol, 4-chloro-3-methylphenol, benzoic acid, 2-nitroaniline, 3-nitroaniline, 4-chloroaniline, and benzyl alcohol are subject to erratic chromatographic behavior, especially if the GC system is contaminated with high boiling material.
- Hexachlorophene is not amenable to analysis by this method.
- 3-Methylphenol cannot be separated from 4-methylphenol by the conditions specified in this method.

1.3. The standard reporting limit (SRL) of this method for determining an individual compound is approximately 0.33 mg/kg (wet weight) for soil/sediment samples, 1 - 200 mg/kg for wastes (dependent on matrix and method of preparation), and 10 µg/L for groundwater samples. Some compounds have higher reporting limits. Refer to Tables 1 and 2 for specific SRLs. Reporting limits will be proportionately higher for sample extracts that require dilution.

2. SUMMARY OF METHOD

1.1. Aqueous samples are extracted with methylene chloride using a separatory funnel, a continuous extractor or Accelerated One-Step™. Solid samples are extracted with methylene chloride / acetone using sonication, soxhlet, accelerated soxhlet or pressurized fluid extraction. Waste dilution is used for samples that are miscible with the solvent. The extract is dried, concentrated to a volume of 1 mL, and analyzed by GC/MS. Extraction procedures are detailed in SOP# CORP-OP-0001. Qualitative identification of the parameters in the extract is performed using the retention time and the relative abundance of characteristic ions. Quantitative analysis is performed using the internal standard technique with a single characteristic ion.

3. DEFINITIONS

3.1. CCC (Calibration Check Compounds) - A subset of target compounds used to evaluate the calibration stability of the GC/MS system. A maximum percent deviation of the CCC's is specified for calibration acceptance.

3.2. SPCC (System Performance Check Compounds) - Target compounds designated to monitor chromatographic performance, sensitivity, and compound instability or degradation on active sites. Minimum response factors are specified for acceptable performance.

3.3. Batch - The batch is a set of up to 20 samples of the same matrix processed using the same procedures and reagents within the same time period. The Quality Control batch must contain a matrix spike / spike duplicate (MS/MSD), a Laboratory Control Sample (LCS), and a method blank. In some cases, at client request, the MS/MSD may be replaced with a matrix spike and sample duplicate. Batches are defined at the sample preparation stage. Batches should be kept together through the whole analytical process to the extent possible, but it is not mandatory to analyze prepared extracts on the same instrument or in the same sequence. Refer to the STL QC Program document (QA-003) for further details of the batch definition.

3.4. Method Blank - An analytical control consisting of all reagents, internal standards and surrogate standards, that is carried through the entire analytical procedure.

The method blank is used to define the level of laboratory background and reagent contamination.

3.5. LCS (Laboratory Control Sample) - A blank spiked with the parameters of interest that is carried through the entire analytical procedure. Analysis of this sample with acceptable recoveries of the spiked materials demonstrates that the laboratory techniques for this method are acceptable.

3.6. MS (Matrix Spike)- aliquot of a matrix (water or soil) fortified (spiked) with known quantities of specific compounds and subjected to the entire analytical procedure in order to indicate the appropriateness of the method for the matrix by measuring recovery.

3.7. MSD (Matrix Spike Duplicate)- a second aliquot of the same sample as the matrix spike (above) that is spiked in order to determine the precision of the method.

4. INTERFERENCES

4.1. Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus that lead to discrete artifacts. All of these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. Raw GC/MS data from all blanks, samples, and spikes must be evaluated for interferences. If an interference is detected it is necessary to determine if the source of interference is in the preparation and/or cleanup of the samples; then take corrective action to eliminate the problem.

4.2. The use of high purity reagents, solvents, and gases helps to minimize interference problems.

4.3. Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature of the sample.

4.4. Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed with solvent between samples. Whenever an unusually concentrated sample is encountered, it should be followed by the analysis of solvent to check for cross contamination.

4.5. Phthalate contamination is commonly observed in this analysis and its occurrence should be carefully evaluated as an indicator of a contamination problem in the sample preparation step of the analysis.

5. SAFETY PRECAUTIONS

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

5.1.1. Eye protection that satisfies ANSI Z87.1 (as per the Chemical Hygiene Plan), laboratory coat, and appropriate gloves must be worn while samples, standards, solvents and reagents are being handled. Disposable gloves that have become contaminated will be removed and discarded; other gloves will be cleaned immediately.

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

5.1.3. Chemicals that have been classified as carcinogens, or potential carcinogens, under OSHA include: Benzo(a)anthracene, benzidine, 3,3'-dichlorobenzidine, benzo(a)pyrene, dibenzo(a,h)anthracene, and n-nitrosodimethylamine. Primary standards should be purchased in solution. If neat materials must be obtained, they shall be handled in a hood.

5.1.4. Exposure to chemicals must be maintained as low as reasonably achievable; therefore, unless they are known to be non-hazardous, all samples should be opened, transferred, and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers should be kept closed unless transfers are being made.

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

5.1.6.

6. EQUIPMENT AND SUPPLIES

6.1. Gas Chromatograph/Mass Spectrometer System: An analytical system complete with a temperature-programmable gas chromatograph suitable for split/splitless injection and all required accessories, including syringes, analytical columns, and gases. The capillary column should be directly coupled to the source.

6.2. Column: 30 m x 0.32 mm I.D. (or 0.25 mm I.D.) 0.5-µm film thickness silicon-coated fused-silica capillary column (J & W Scientific DB-5.625 or equivalent). Alternate columns are acceptable if they provide acceptable performance.

6.3. Mass Spectrometer: Capable of scanning from 35 to 500 AMU every one second or less, using 70 volts (nominal) electron energy in the electron impact ionization

mode. The mass spectrometer must be capable of producing a mass spectrum for decafluorotriphenylphosphine (DFTPP) which meets all of the criteria in Table 6 when 50 ng of the GC/MS tuning standard is injected through the GC.

6.4. GC/MS Interface: Any GC-to-MS interface that gives acceptable calibration points and achieves acceptable tuning performance criteria may be used.

6.5. Data System: A computer system must be interfaced to the mass spectrometer. The system must allow the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that can search any GC/MS data file for ions of a specific mass and that can plot such ion abundances versus time or scan number. This type of plot is defined as the Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundances in any EICP between specified time or scan-number limits. The most recent version of the EPA/NIH Mass Spectral Library is recommended.

6.6. Syringe: 10 µL Hamilton Laboratory grade syringes or equivalent.

6.7. Carrier gas: Ultra high purity helium.

7. REAGENTS AND STANDARDS

7.1. A minimum five point calibration curve is prepared. The low point should be at or below the reporting limit. Refer to Tables 12 and 13 for typical calibration levels for all analytes. Other calibration levels may be used, depending on instrument capability, but the low standard must support the reporting limit and the high standard defines the range of the calibration.

7.2. An Internal Standard solution is prepared. Compounds in the I.S. Mix are: acenaphthene-d10, chrysene-d12, 1,4-dichlorobenzene-d4, naphthalene-d8, perylene-d12, and phenanthrene-d10.

7.2.1. Internal Standards are added to all standards and extracts to result in 40ng injected onto the column. For example, if the volume of an extract used was 200 µL, 20 µL of a 400 µg/mL internal standard solution would be added for a 1 µL injection.

7.3. Surrogate Standard Spiking Solution: Prepare as indicated in the preparative methods. See appropriate preparation SOP. Surrogate compounds and levels are listed in Table 11.

7.4. GC/MS Tuning Standard: A methylene chloride solution containing 50 µg/mL of decafluorotriphenylphosphine (DFTPP) is prepared. Pentachlorophenol, benzidine, and DDT, should also be included in the Tuning Standard at 50 µg/mL.

7.5. Laboratory Control Spiking Solution: Prepare as indicated in the preparative methods. See appropriate preparation SOP. LCS compounds and levels are listed in Tables 9 and 10.

7.6. Matrix Spike Solution: Prepare as indicated in the preparative methods. See preparation SOP. The matrix spike compounds and levels are the same as the LCS compounds.

7.7. The standards listed in 7.1 to 7.6 should be refrigerated at $\leq 6^{o}C$ when not in use. Refrigeration at $-10^{o}C$ to $-20^{o}C$ may be used if it can be demonstrated that analytes do not fall out of solution at this temperature. The standards must be replaced at least once a year. The continuing calibration standard must be replaced every week and is stored at $\leq 6^{o}C$.

8. SAMPLE PRESERVATION AND STORAGE

8.1. Reference appropriate facility SOP for sample bottle preservation and storage.

8.2. Samples are stored at $4 \pm 2^{o}C$. Samples and extracts should be stored in suitable glass containers with Teflon lined caps. (Extracts will normally be stored for 30 days after invoicing.)

8.3. Water samples are extracted within seven days of sampling and the extracts are analyzed within forty days of extraction. Solids, sludges, and organic liquids are extracted within fourteen days of sampling and the extracts are analyzed within forty days of extraction.

9. QUALITY CONTROL

9.1. Initial Demonstration of Capability

9.1.1. For the standard analyte list, the initial demonstration and method detection limit (MDL) studies described in section 13 must be acceptable before analysis of samples may begin. Refer to the flow chart in section 17.4.1.

9.1.2. For non-standard analytes an MDL study should be performed and calibration curve generated before analyzing any samples, unless lesser requirements are previously agreed to with the client. In any event, the minimum initial demonstration required is analysis of an extracted standard at the reporting limit and a single point calibration.

9.2. Control Limits

In-house historical control limits must be determined for surrogates, matrix spikes,

and laboratory control samples (LCS). These limits must be determined at least annually. The recovery limits are mean recovery +/- 3 standard deviations for surrogates, MS and LCSPrecision limits for matrix spikes / matrix spike duplicates are mean relative percent difference +/- 3 standard deviations.

9.2.1. These limits do not apply to dilutions (except for tests without a separate extraction), but surrogate and matrix spike recoveries will be reported unless the dilution is more than 5X.

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

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

9.3. Method Blank

A method blank is prepared and analyzed with each batch of samples. The method blank consists of reagent water for aqueous samples, and sodium sulfate for soil samples (Refer to SOP No. CORP-OP-0001 for details). Surrogates are added and the method blank is carried through the entire analytical procedure. The method blank must not contain any analyte of interest at or above the reporting limit (except common laboratory contaminants, see below) or at or above 5% of the measured concentration of that analyte in the associated samples, whichever is higher.

- If the analyte is a common laboratory contaminant (phthalate esters), the data may be reported with qualifiers if the concentration of the analyte is less than five times the RL. Such action must be taken in consultation with the client.

- Reanalysis of any samples with reportable concentrations of analytes found in the method blank is required unless other actions are agreed with the client.

- If there is no target analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. Such action should be taken in consultation with the client.

9.3.1. The method blank must have acceptable surrogate recoveries. If surrogate recoveries are not acceptable, the data must be evaluated to determine if the method blank has served the purpose of demonstrating that the analysis is free of contamination. If surrogate recoveries are low and there are reportable analytes in the associated samples, re-extraction of the blank and affected samples will normally be required. Consultation with the

client should take place.

9.3.2. If reanalysis of the batch is not possible due to limited sample volume or other constraints, the method blank is reported, all associated samples are flagged with a "B", and appropriate comments may be made in a narrative to provide further documentation.

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

9.3.4. Sample results are NOT blank subtracted unless specific requests and arrangements have been made with a client or agency.

9.4. Instrument Blank

9.4.1. Instruments must be evaluated for contamination during each 12 hour analytical run. This may be accomplished by analysis of a method blank. If a method blank is not available, an instrument blank must be analyzed. An instrument blank consists of methylene chloride with the internal standards added. It is evaluated in the same way as the method blank.

9.5. Laboratory Control Sample (LCS)

9.5.1. A laboratory control sample (LCS) is prepared and analyzed with every batch of samples. All analytes must be within established control limits. The LCS is spiked with the compounds listed in Tables 9 and 10 unless specified by a client or agency. The compounds must be spiked at a concentration equivalent to 100 or 150 ng on-column depending on the analyte.

9.5.2. If any analyte in the LCS is outside the laboratory established historical control limits, corrective action must occur. Corrective action may include re-extraction and reanalysis of the batch.

- If the batch is not re-extracted and reanalyzed, the reasons for accepting the batch must be clearly presented in the project records and the report. (An example of acceptable reasons for not reanalyzing might be that the matrix spike and matrix spike duplicate are acceptable, and sample surrogate recoveries are good, demonstrating that the problem was confined to the LCS).

- If re-extraction and reanalysis of the batch is not possible due to limited sample volume or other constraints, the LCS is reported, all

associated samples are flagged, and appropriate comments are made in a narrative to provide further documentation.

9.5.3. Ongoing monitoring of the LCS provides evidence that the laboratory is performing the method within accepted QC guidelines for accuracy and precision.

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

A matrix spike/matrix spike duplicate (MS/MSD) is prepared and analyzed with every batch of samples. The MS/MSD is spiked with the same subset of analytes as the LCS (See Tables 9 and 10). Compare the percent recovery and relative percent difference (RPD) to that in the laboratory specific historically generated limits.

- If any individual recovery or RPD falls outside the acceptable range, corrective action must occur. The initial corrective action will be to check the recovery of that analyte in the Laboratory Control Sample (LCS). Generally, if the recovery of the analyte in the LCS is within limits, then the laboratory operation is in control and analysis may proceed. The reasons for accepting the batch must be documented.

- If the recovery for any component is outside QC limits for both the Matrix spike / spike duplicate and the LCS, the laboratory is out of control and corrective action must be taken. Corrective action will normally include repreparation and reanalysis of the batch.

- If a MS/MSD is not possible due to limited sample, then a LCS duplicate should be analyzed. RPD of the LCS and LCSD are compared to the matrix spike limits.

- The matrix spike / duplicate must be analyzed at the same dilution as the unspiked sample, even if the matrix spike compounds will be diluted out.

9.7. Surrogates

9.7.1. Every sample, blank, and QC sample is spiked with surrogate standards. Surrogate spike recoveries must be evaluated by determining whether the concentration (measured as percent recovery) falls within the required recovery limits. Surrogate compounds must be spiked at either 100 or 150 ng on-column, depending on the surrogate. The compounds routinely included in the surrogate spiking solution, along with recommended standard concentrations, are listed in Table 11.

9.7.2. If any surrogates are outside limits the following corrective actions must

take place (except for dilutions):

- Check all calculations for error.
- Ensure that instrument performance is acceptable.
- Recalculate the data and/or reanalyze the extract if either of the above checks reveal a problem.
- Re-extract and reanalyze the sample or flag the data as "Estimated Concentration" if neither of the above resolves the problem.

The decision to reanalyze or flag the data should be made in consultation with the client. It is only necessary to reprepare / reanalyze a sample once to demonstrate that poor surrogate recovery is due to matrix effect, unless the analyst believes that the repeated out of control results are not due to matrix effect.

9.7.3. If the sample with surrogate recoveries outside the recovery limits was a sample used for an MS/MSD and the surrogate recoveries in the MS/MSD are also outside of the control limits, then the sample, the MS, and the MSD do not require reanalysis as this phenomenon would indicate a possible matrix problem.

9.7.4. If the sample is reanalyzed and the surrogate recoveries in the reanalysis are acceptable, then the problem was within the analyst's control and only the reanalyzed data should be reported. (Unless the reanalysis was outside holding times, in which case reporting both sets of results may be appropriate.)

9.7.5. If the reanalysis does confirm the original results, the original analysis is reported and the data flagged as estimated due to matrix effect.

9.8. Nonconformance and Corrective Action

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

9.9. Quality Assurance Summaries

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

9.10. STL QC Program

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

10. CALIBRATION AND STANDARDIZATION

10.1. Summary

10.1.1. The instrument is tuned for DFTPP, calibrated initially with a five-point calibration curve, and verified each 12-hour shift with one or more continuing calibration standard(s). Recommended instrument conditions are listed in Table 5.

10.2. All standards and extracts are allowed to warm to room temperature before injecting.

10.3. Instrument Tuning

At the beginning of every twelve hour shift when analyses are to be performed, the GC/MS system must be checked to see if acceptable performance criteria (Table 6) is achieved for DFTPP (decafluorotriphenylphosphine).

10.3.1. Inject 50 ng of the GC/MS tuning standard (Section 7.4) into the GC/MS system. Obtain a background-corrected mass spectra of DFTPP and confirm that all the key m/z criteria in Table 6 are achieved. If all the criteria are not achieved, the analyst must retune the mass spectrometer and repeat the test until all criteria are achieved. The performance criteria must be achieved before any samples, blanks, or standards are analyzed.

10.3.2. The GC/MS tuning standard should also be used to evaluate the inertness of the chromatographic system. Benzidine and pentachlorophenol should not exhibit excessive tailing. If DDT is an analyte of interest, it must be included in the tuning standard, and its breakdown must be < 20%. Refer to section 12 for the appropriate calculations.

10.4. Initial Calibration

10.4.1. Internal Standard Calibration Procedure: Internal standards are listed in Table 7. Use the base peak m/z as the primary m/z for quantitation of the standards. If interferences are noted, use one of the next two most intense masses for quantitation.

10.4.2. Compounds should be assigned to the IS with the closest retention time.

10.4.3. Prepare calibration standards at a minimum of five concentration levels for each parameter of interest. Six standards must be used for a quadratic least squares calibration. It may also be useful to analyze six calibration levels and use the lower five for most analytes and the upper five for analytes that have poor response. Add the internal standard mixture to result in 40 ng on column. (For example, if the volume of the calibration standard used is 1 mL, add 100 µL of the 400 µg/mL internal standard solution for a 1 µL injection). The concentrations of all analytes are listed in tables 12 and 13.

10.4.4. Analyze each calibration standard and tabulate the area of the primary characteristic m/z against concentration for each compound and internal standard. Calculate response factors (RF), average response factors, and the percent RSD of the response factors for each compound using the equations in section 12 and verify that the CCC and SPCC criteria in section 10.4.5 and 10.4.6 are met. **No sample analysis may be performed unless these criteria are met.**

10.4.5. System Performance Check Compounds (SPCCs): The minimum average RF for semivolatile SPCCs is 0.050. If the minimum response factors are not met, the system must be evaluated and corrective action must be taken before sample analysis begins. Some possible problems are standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, and active sites in the column or chromatographic system. This check must be met before analysis begins.

SPCC Compounds:

N-nitroso-di-n-propylamine
Hexachlorocyclopentadiene
2,4-Dinitrophenol
4-Nitrophenol

10.4.6. Calibration Check Compounds (CCCs): The %RSD of the response factors for each CCC in the initial calibration must be less than 30% for the initial calibration to be considered valid. This criterion must be met before sample analysis begins. Problems similar to those listed under SPCCs could affect this criterion.

10.4.6.1. If none of the CCCs are required analytes, project specific calibration specifications must be agreed with the client.

10.4.6.2. CCC Compounds:

Phenol
Acenaphthene
1,4-Dichlorobenzene
N-nitrosodiphenylamine
2-Nitrophenol
Pentachlorophenol
2,4-Dichlorophenol
Fluoranthene
Hexachlorobutadiene
Di-n-octylphthalate
4-Chloro-3-methylphenol
Benzo(a)pyrene
2,4,6-Trichlorophenol

10.4.7. If the average of all %RSDs in the initial calibration is $\leq$ 15%, then all analytes may use average response factor for calibration.

10.4.7.1. If the software in use is capable of routinely reporting curve coefficients for data validation purposes, and the necessary calibration reports can be generated, then the analyst should evaluate analytes with %RSD > 15% for calibration on a curve. If it appears that substantially better accuracy would be obtained using quantitation from a curve then the appropriate curve should be used for quantitation.

10.4.7.2. If the average of all the %RSDs in the initial calibration is > 15%, then calibration on a curve must be used for those analytes with %RSD > 15%. Linear or quadratic curve fits may be used. Use of $1/\text{Concentration}^2$ weighting is recommended to improve the accuracy of quantitation at the low end of the curve. The analyst should consider instrument maintenance to improve the linearity of response. If Relative Standard Error (RSE) is used to evaluate the curve it must be better than 15%. Otherwise the correlation coefficient (coefficient of determination for non-linear curves) must be $\geq$ 0.990.

10.4.8. Weighting of data points

In a linear or quadratic calibration fit, the points at the lower end of the calibration

curve have less weight in determining the curve generated than points at the high concentration end of the curve. However, in environmental analysis, accuracy at the low end of the curve is very important. For this reason it is preferable to increase the weighting of the lower concentration points. 1/Concentration^2 weighting (often called $1/X^2$ weighting) will improve accuracy at the low end of the curve and should be used if the data system has this capability.

10.4.9. If time remains in the 12 hour period initiated by the DFTPP injection before the initial calibration, samples may be analyzed. Otherwise, proceed to continuing calibration.

10.4.10. **Quantitation is performed using the calibration curve or average response factor form the initial curve, not the continuing calibration.**

10.5. Continuing Calibration

10.5.1. At the start of each 12-hour period, the GC/MS tuning standard must be analyzed. A 50 ng injection of DFTPP must result in a mass spectrum for DFTPP which meets the criteria given in Table 6.

10.5.2. Following a successful DFTPP analysis the continuing calibration standard(s) are analyzed. The standards must contain all semivolatile analytes, including all required surrogates. A mid level calibration standard is used for the continuing calibration.

10.5.3. The following criteria must be met for the continuing calibration to be acceptable:

- The SPCC compounds must have a response factor of $\geq$ 0.05.
- The percent difference or drift of the CCC compounds from the initial calibration must be $\leq$ 20%. (see section 12 for calculations) In addition, the percent difference or drift of all analytes must be $\leq$ 50%, with allowance being made for up to six target compounds to have percent drift greater than 50%.
- The internal standard response must be within 50-200% of the response in the mid level of the initial calibration.
- The internal standard retention times must be within 30 seconds of the retention times in the mid-level of the initial calibration.

10.5.3.1. If none of the CCCs are required analytes, project specific calibration specifications must be agreed with the client.

10.5.4. Once the above criteria have been met, sample analysis may begin. Initial calibration average RFs (or the calibration curve) will be used for sample quantitation, not the continuing calibration RFs. Analysis may proceed until 12 hours from the injection of the DFTPP have passed. (A sample *injected* less than 12 hours after the DFTPP is acceptable.)

11. PROCEDURE

11.1. Sample Preparation

Samples are prepared following SOP CORP-OP-0001.

11.2. Sample Analysis Procedure

11.2.1. Calibrate the instrument as described in section 10. Depending on the target compounds required by the client, it may be necessary to use more than one calibration standard.

11.2.2. All samples must be analyzed using the same instrument conditions as the preceeding continuing calibration standard.

11.2.3. Add internal standard to the extract to result in 40 ng injected on column (for example, 1 µL of a 2000µL/mL internal standard solution in 100 µL of extract for a 2 µL injection). Mix thoroughly before injection into the instrument.

11.2.4. Inject the sample extract into the GC/MS system using the same injection technique as used for the standards.

11.2.5. The data system will determine the concentration of each analyte in the extract using calculations equivalent to those in section 12. Quantitation is based on the initial calibration, not the continuing calibration.

11.2.6. Identified compounds are reviewed for proper integration. Manual integrations are performed if necessary and are documented by the analyst or automatically by the data system.

11.2.7. Target compounds identified by the data system are evaluated using the criteria listed in section 12.1.

11.2.8. Library searches of peaks present in the chromatogram that are not target compounds (Tentatively Identified Compounds, TIC) may be performed if required by the client. They are evaluated using the criteria in section 12.3. At least 20 TICs will be generated.

11.3. Dilutions

If the response for any compound exceeds the working range of the GC/MS system, a dilution of the extract is prepared and analyzed. An appropriate dilution should be in the upper half of the calibration range. Samples may be screened to determine the appropriate dilution for the initial run. If the initial diluted run has no hits or hits below 20% of the calibration range and the matrix allows for analysis at a lesser dilution, the sample must be reanalyzed at a dilution targeted to bring the largest hit above 50% of the calibration range.

11.3.1. Guidance for Dilutions Due to Matrix

If the sample is initially run at a dilution and the baseline rise is less than the height of the internal standards, or if individual non-target peaks are less than two times the height of the internal standards, the sample should be reanalyzed at a more concentrated dilution. This requirement is approximate and subject to analyst judgement. For example, samples containing organic acids may need to be analyzed at a higher dilution to avoid destroying the column.

11.3.2. Reporting Dilutions

The most concentrated dilution with no target compounds above the calibration range will be reported. Other dilutions will only be reported at client request.

11.4. Perform all qualitative and quantitative measurements. When the extracts are not being used for analyses, refrigerate them at $4 \pm 2^{o}C$, protected from light in screw cap vials equipped with unpierced Teflon lined septa.

11.5. Retention time criteria for samples

If the retention time for any internal standard changes by more than 0.5 minutes from the last continuing calibration standard, the chromatographic system must be inspected for malfunctions and corrected. Reanalysis of samples analyzed while the system was malfunctioning is required.

11.5.1. If the retention time of any internal standard in any sample varies by more than 0.1 minute from the preceeding continuing calibration standard, the data must be carefully evaluated to ensure that no analytes have shifted outside their retention time windows.

11.6. Percent Moisture

Analytical results may be reported as dry or wet weight, as required by the client. Percent moisture must be determined if results will be reported as dry weight. Refer to the facility specific SOP for determination of percent moisture.

11.7. Procedural Variations

11.7.1. One-time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and approved by a Technical Specialist and QA Manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file. Any unauthorized deviations from this procedure must also be documented as a non-conformance, with a cause and corrective action described.

11.8. Troubleshooting Guide

11.8.1. Daily Instrument Maintenance

In addition to the checks listed in the instrument maintenance schedule in the STL QAMP, the following daily maintenance should be performed.

11.8.1.1.Clip Column as necessary.

11.8.1.2.Install new or cleaned injection port liner as necessary.

11.8.1.3.Install new septum as necessary.

11.8.1.4.Perform mass calibration as necessary.

11.8.2. Major Maintenance

11.8.2.1.A new initial calibration is necessary following major maintenance. Major maintenance includes changing the column, cleaning the ion volume or repeller, cleaning the source, and replacing the multiplier. Refer to the manufacturer's manual for specific guidance.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Qualitative identification

An analyte is identified by retention time and by comparison of the sample mass spectrum with the mass spectrum of a standard of the suspected compound (standard reference spectrum). Mass spectra for standard reference may be obtained on the user's GC/MS by analysis of the calibration standards or from the NBS library. Two criteria must be satisfied to verify identification: (1) elution of sample component at the same GC retention time as the standard component; and (2) correspondence of the sample component and the standard component characteristic ions. (Note: Care must be taken to ensure that spectral distortion due to co-elution is evaluated.)

- The sample component retention time must compare to within ± 0.2 min. of the retention time of the standard component. For reference, the standard must be run within the same twelve hours as the sample.

- All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100%) should be present in the sample spectrum.

- The characteristic ions of a compound must maximize in the same scan or within one scan of each other.

- The relative intensities of ions should agree to within ±30% between the standard and sample spectra. (Example: For an ion with an abundance of 50% in the standard spectra, the corresponding sample abundance must be between 20% and 80%.)

12.1.1. If a compound cannot be verified by all the above criteria, but in the technical judgment of the analyst the identification is correct, the analyst shall report that identification and proceed with quantitation.

12.2. Mass chromatogram searches.

Certain compounds are unstable in the calibration standard and cannot be calibrated in the normal way. In particular, the compound hexachlorophene (CAS 70-30-4) falls into this category, and is required for Appendix IX analysis. For this analyte a mass chromatogram search is made.

12.2.1. Hexachlorophene

Display the mass chromatograms for mass 196 and mass 198 for the region of the chromatogram from at least 2 minutes before chrysene-d12 to at least 4 minutes

after chrysene-d12. If peaks for both ions coincide then the analyst evaluates the spectrum for the presence of hexachlorophene. No quantitation is possible.

12.3. For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the type of analyses being conducted. Computer generated library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other. Only after visual comparison of sample spectra with the nearest library searches shall the mass spectral interpretation specialist assign a tentative identification. Guidelines for making tentative identification are:

- Relative intensities of major ions in the reference spectrum (ions >10% of the most abundant ion) should be present in the sample spectrum.
- The relative intensities of the major ions should agree within ±20%. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance should be between 30%and 70%.)
- Molecular ions present in the reference spectrum should be present in the sample spectrum.
- Ions present in the sample spectrum, but not in the reference spectrum, should be reviewed for possible background contamination or presence of coeluting compounds.
- Ions present in the reference spectrum, but not in the sample spectrum, should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks. Data system library reduction programs can sometimes create these discrepancies.
- Automatic background subtraction can severely distort spectra from samples with unresolved hydrocarbons.

12.4. Anyone evaluating data is trained to know how to handle isomers with identical mass spectra and close elution times. These include:

Dichlorobenzenes
Methylphenols
Trichlorophenols
Phenanthrene, anthracene
Fluoranthene, pyrene
Benzo(b) and (k)fluoranthene
Chrysene, benzo(a)anthracene

Extra precautions concerning these compounds are to more closely scrutinize retention time vs. the calibration standard and also to check that all isomers have distinct retention times.

A second category of problem compounds would be the poor responders or compounds that chromatograph poorly. Included in this category would be:

Benzoic acid
Chloroanilines
Nitroanilines
2,4-Dinitrophenol
4-Nitrophenol
Pentachlorophenol
3,3'-Dichlorobenzidine
Benzyl alcohol
4,6-Dinitro-2-methylphenol

Manually checking the integrations would be appropriate for these compounds.

12.5. Calculations

12.5.1. Percent Relative Standard Deviation for Initial Calibration

$$\%RSD = \frac{SD}{\overline{RF}} \times 100$$

$RF =$ Mean of RFs from intial caibration for a compound

$SD =$ Standard deviation of RFs from initial calibration for a compound,

$$= \sqrt{\sum_{i=1}^{N} \frac{\left(RFi - \overline{RF}\right)^2}{N-1}}$$

$RFi =$ RF for each of the calibration levels

$N =$ Number of RF values

12.5.2. Continuing calibration percent drift

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

$C_{actual} =$ Known concentration in standard

$C_{found} =$ Measured concentration using selected quantitation method

12.5.3. Concentration in the extract

The concentration of each identified analyte and surrogate in the extract is calculated from the linear or quadratic curve fitted to the initial calibration points, or from the average RF of the initial calibration.

12.5.3.1.Average response factor

If the average of all the %RSDs of the response factors in the initial calibration is ≤ 15%, the average response factor from the initial calibration may be used for quantitation.

$$C_{ex} = \frac{R_x C_{is}}{R_{is}\overline{RF}}$$

12.5.3.2.Linear fit

$$C_{ex} = A + B\frac{(R_x C_{is})}{R_{is}}$$

C_{ex}= Concentration in extract, µg/mL

R_x= Response for analyte

R_{is}= Response for internal standard

C_{is}= Concentration of internal standard

A= Intercept

B= Slope

12.5.3.3.Quadratic fit

$$C_{ex} = A + B\left(\frac{R_x C_{is}}{R_{is}}\right) + C\left(\frac{R_x C_{is}}{R_{is}}\right)$$

C= Curvature

12.5.4. The concentration in the sample is then calculated.

12.5.4.1. Aqueous Calculation

$$\text{Concentration, } \mu\text{g / L} = \frac{C_{ex}V_t}{V_o}$$

Where:

V_t = Volume of total extract, µL, taking into account dilutions (i.e., a 1-to-10 dilution of a 1 mL extract will mean V_t = 10,000 µL. If half of the base/neutral extract and half of the acid extract are combined, V_t = 2,000.)

V_o = Volume of water extracted (mL)

12.5.5. Sediment/Soil, Sludge (on a dry-weight basis) and Waste (normally on a wet-weight basis:

$$\text{Concentration, } \mu\text{g / kg} = \frac{C_{ex}V_t}{W_s D}$$

W_s = Weight of sample extracted or diluted in grams

D = (100 - % moisture in sample)/100, for a dry weight basis or 1 for a wet weight basis

12.6. MS/MSD percent recovery calculation.

$$\text{Matrix Spike Recovery} = \frac{S_{SR} - S_R}{S_A} \times 100\%$$

S_{SR} = Spike sample result

S_R=Sample result

S_A = Spike added

12.7. Relative % Difference calculation for the MS/MSD

$$RPD = \frac{MS_R - MSD_R}{1/2(MS_R + MSD_R)} \times 100$$

RPD = Relative percent difference

MS_R = Matrix spike result

MSD_R = Matrix spike duplicate result

12.8. Relative response factor calculation.

$$RF = \frac{A_x C_{is}}{A_{is} C_x}$$

A_x=Area of the characteristic ion for the compound being measured

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

C_x=Concentration of the compound being measured (µg/L)

C_{is} =Concentration of the specific internal standard (µg/L)

12.9. Calculation of TICs: The calculation of TICs (tentatively identified compounds) is identical to the above calculations with the following exceptions:

A_x=Area of the total ion chromatogram for the compound being measured

A_{is}=Area of the total ion chromatogram for the nearest internal standard without interference

RF=1

12.10. Percent DDT breakdown

$$\text{\% DDT breakdown} = \frac{\text{DDEarea + DDDarea}}{\text{DDTarea + DDEarea + DDarea}}$$

The total ion current areas are used for this calculation

13. METHOD PERFORMANCE

13.1. Method Detection Limit

Each laboratory must generate a valid method detection limit for each analyte of interest. The MDL must be below the reporting limit for each analyte. The procedure for determination of the method detection limit is given in 40 CFR Part 136, Appendix B, and further defined in QA Policy #: QA-005.

13.2. Initial Demonstration

Each laboratory must make an initial demonstration of capability for each individual method. Demonstration of capability for both soil and water matrices is required. This requires analysis of QC check samples containing all of the standard analytes for the method. For some tests it may be necessary to use more than one QC check mix to cover all analytes of interest.

13.2.1. Four aliquots of the QC check sample are analyzed using the same procedures used to analyze samples, including sample preparation. The concentration of the QC check sample should be equivalent to the level 4 calibration standard.

13.2.2. Calculate the average recovery and standard deviation of the recovery for each analyte of interest. Compare these results with the acceptance criteria given in table 14.

13.2.3. If any analyte does not meet the acceptance criteria the test must be repeated. Only those analytes that did not meet criteria in the first test need to be evaluated. Repeated failure for any analyte indicates the need for the laboratory to evaluate the analytical procedure and take corrective action.

13.3. Non-standard analytes

For non-standard analytes, an MDL study must be performed and calibration curve generated before analyzing any samples, unless lesser requirements are previously agreed to with the client. In any event, the minimum initial demonstration required is analysis of an extracted standard at the reporting limit and a single point calibration.

13.4. Training Qualification

The group/team leader has the responsibility to ensure that this procedure is performed by an analyst who has been properly trained in its use and has the required experience.

13.5. Data Quality Objectives (DQO). Refer to project-specific Quality Assurance plans for DQO information.

14. POLLUTION PREVENTION

14.1. This section is not applicable to this procedure.

15. WASTE MANAGEMENT

15.1. Waste generated during aliquotting and from used vials must be disposed of in accordance with the facility hazardous waste procedures. The Health and Safety Director should be contacted if additional information is required.

16. REFERENCES

16.1. SW846, Test Methods for Evaluating Solid Waste, Third Edition, Update II, October 1994, Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS): Capillary Column Technique, Method 8270B.

16.2. J. W. Eichelberger, L. E. Harris, and W. L. Budde, "Reference Compound to Calibrate Ion Abundance Measurement in Gas Chromatography/Mass Spectrometry," Analytical Chemistry, 47, 995 (1975)

17. MISCELLANEOUS

17.1. Modifications from Reference Method

17.1.1. A retention time window of 0.2 minutes is used for all components, since some data systems do not have the capability of using the relative retention time units specified in the reference method.

17.1.2. The quantitation and qualifier ions for some compounds have been changed from those recommended in SW-846 in order to improve the reliability of qualitative identification.

17.2. Modifications from Previous Revision

17.2.1. This SOP has been substantially revised to meet the requirements of method 8270C.

17.2.2. Directions for analysis be method 625 have been added as an attachment.

17.3. Facility Specific SOPs

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

17.4. Tables

Table 1

STL Primary Standard[1] and Standard Reporting Limits

Analytes	CAS Number	Standard Reporting Limits	
		Aqueous µg/L	Low Soil/Sediment µg/kg
Pyridine	110-86-1	20	660
N-nitrosodimethylamine	62-75-9	10	330
Aniline	62-53-3	10	330
Phenol	108-95-2	10	330
Bis(2-chloroethyl)ether	111-44-4	10	330
2-Chlorophenol	95-57-8	10	330
1,3-Dichlorobenzene	541-73-1	10	330
1,4-Dichlorobenzene	106-46-7	10	330
Benzyl alcohol	100-51-6	10	330
1,2-Dichlorobenzene	95-50-1	10	330
2-Methylphenol	95-48-7	10	330
2,2'-oxybis(1-chloropropane)[2]	108-60-1	10	330
4-Methylphenol	106-44-5	10	330
N-Nitroso-di-n-propylamine	621-64-7	10	330
Hexachloroethane	67-72-1	10	330
Nitrobenzene	98-95-3	10	330
Isophorone	78-59-1	10	330
2-Nitrophenol	88-75-5	10	330
2,4-Dimethylphenol	105-67-9	10	330
Benzoic acid	65-85-0	50	1600
Bis(2-chloroethoxy)methane	111-91-1	10	330
2,4-Dichlorophenol	120-83-2	10	330
1,2,4-Trichlorobenzene	120-82-1	10	330
Naphthalene	91-20-3	10	330
4-Chloroaniline	106-47-8	10	330
Hexachlorobutadiene	87-68-3	10	330
4-Chloro-3-methylphenol	59-50-7	10	330
2-Methylnaphthalene	91-57-6	10	330
Hexachlorocyclopentadiene	77-47-4	50	1600
2,4,6-Trichlorophenol	88-06-2	10	330
2,4,5-Trichlorophenol	95-95-4	10	330
2-Chloronaphthalene	91-58-7	10	330
2-Nitroaniline	88-74-4	50	1600
Dimethyl phthalate	131-11-3	10	330
Acenaphthylene	208-96-8	10	330
3-Nitroaniline	99-09-2	50	1600
Acenaphthene	83-32-9	10	330
2,4-Dinitrophenol	51-28-5	50	1600
4-Nitrophenol	100-02-7	50	1600
Dibenzofuran	132-64-9	10	330
2,4-Dinitrotoluene	121-14-2	10	330

Table 1

STL Primary Standard[1] and Standard Reporting Limits

Analytes	CAS Number	Standard Reporting Limits	
		Aqueous µg/L	Low Soil/Sediment µg/kg
2,6-Dinitrotoluene	606-20-2	10	330
Diethylphthalate	84-66-2	10	330
4-Chlorophenyl phenyl ether	7005-72-3	10	330
Fluorene	86-73-7	10	330
4-Nitroaniline	100-01-6	50	1600
4,6-Dinitro-2-methylphenol	534-52-1	50	1600
N-Nitrosodiphenylamine	86-30-6	10	330
Azobenzene	103-33-3	10	330
4-Bromophenyl phenyl ether	101-55-3	10	330
Hexachlorobenzene	118-74-1	10	330
Pentachlorophenol	87-86-5	50	1600
Phenanthrene	85-01-8	10	330
Anthracene	120-12-7	10	330
Carbazole	86-74-8	10	330
Di-n-butyl phthalate	84-74-2	10	330
Fluoranthene	206-44-0	10	330
Benzidine	92-87-5	100	3300
Pyrene	129-00-0	10	330
Butyl benzyl phthalate	85-68-7	10	330
3,3'-Dichlorobenzidine	91-94-1	50	1600
Benzo(a)anthracene	56-55-3	10	330
Bis(2-ethylhexyl)phthalate	117-81-7	10	330
Chrysene	218-01-9	10	330
Di-n-octylphthalate	117-84-0	10	330
Benzo(b)fluoranthene	205-99-2	10	330
Benzo(k)fluoranthene	207-08-9	10	330
Benzo(a)pyrene	50-32-8	10	330
Indeno(1,2,3-cd)pyrene	193-39-5	10	330
Dibenz(a,h)anthracene	53-70-3	10	330
Benzo(g,h,i)perylene	191-24-2	10	330

[1] The STL primary standard is the standard normally used at STL. Additional standards, such as the Appendix IX standard may be necessary to include all target analytes required for some clients.

[2] 2,2’oxybis(1-chloropropane) was formally known as bis(2-chloroisopropyl)ether

Table 2

STL Appendix IX[1] Standard Reporting Limits

Semivolatiles	CAS Number	Standard Reporting Limits	
		Aqueous µg/L	Low Soil/Sediment µg/kg
2-Picoline	109-06-8	20	660
N-Nitrosomethylethylamine	10595-95-6	10	330
Methyl methanesulfonate	66-27-3	10	330
N-Nitrosodiethylamine	55-18-5	10	330
Ethyl methanesulfonate	62-50-0	10	330
Pentachloroethane	76-01-7	50	1600
Acetophenone	98-86-2	10	330
N-Nitrosopyrrolidine	930-55-2	10	330
N-Nitrosomorpholine	59-89-2	10	330
o-Toluidine	95-53-4	20	660
3-Methylphenol	108-39-4	10	330
N-Nitrosopiperidine	100-75-4	10	330
o,o,o-Triethyl-Phosphorothioate[2]	126-68-1	50	1600
a,a-Dimethyl-phenethylamine	122-09-8	50	1600
2,6-Dichlorophenol	87-65-0	10	330
Hexachloropropene	1888-71-7	100	3300
p-Phenylenediamine	106-50-3	100	3300
n-Nitrosodi-n-butylamine	924-16-3	10	330
Safrole	94-59-7	20	660
1,2,4,5-Tetrachlorobenzene	95-94-3	10	330
Isosafrole	120-58-1	20	660
1,4-Dinitrobenzene	100-25-4	10	330
1,4-Naphthoquinone	130-15-4	50	1600
1,3-Dinitrobenzene	99-65-0	10	330
Pentachlorobenzene	608-93-5	10	330
1-Naphthylamine	134-32-7	10	330
2-Naphthylamine	91-59-8	10	330
2,3,4,6-Tetrachlorophenol	58-90-2	50	1600
5-Nitro-o-toluidine	99-55-8	20	660
Thionazin[2]	297-97-2	50	1600
1,3,5-Trinitrobenzene	99-35-4	50	1600
Sulfotepp[2]	3689-24-5	50	1600
Phorate[2]	298-02-2	50	1600
Phenacetin	62-44-2	20	660
Diallate[3]	2303-16-4	20	660
Dimethoate[2]	60-51-5	20	660
4-Aminobiphenyl	92-67-1	50	1600
Pentachloronitrobenzene	82-68-8	50	1600
Pronamide	23950-58-5	20	660
Disulfoton[2]	298-04-4	50	1600
2-secbutyl-4,6-dinitrophenol (Dinoseb)	88-85-7	20	660
Methyl Parathion[2]	298-00-0	50	1600
4-Nitroquinoline-1-oxide	56-57-5	100	3300

Table 2

STL Appendix IX[1] Standard Reporting Limits

Semivolatiles	CAS Number	Standard Reporting Limits	
		Aqueous µg/L	Low Soil/Sediment µg/kg
Parathion[2]	56-38-2	50	1600
Methapyrilene	91-80-5	50	1600
Aramite	140-57-8	20	660
Isodrin[3]	465-73-6	10	330
Kepone[2]	143-50-0	100	3300
Famphur[3]	52-85-7	100	3300
p-(Dimethylamino)azobenzene	60-11-7	20	660
p-Chlorobenzilate[3]	510-15-6	10	330
3,3'-Dimethylbenzidine	119-93-7	50	1600
2-Acetylaminofluorene	53-96-3	100	3300
Dibenz(a,j)acridine	224-42-0	20	660
7,12-Dimethylbenz(a)anthracene	57-97-6	20	660
3-Methylcholanthrene	56-49-5	20	660

[1] The Appendix IX standard contains additional analytes required for the Appendix IX list. The STL primary standard must also be analyzed to include all of the Appendix IX list.

[2] May also be analyzed by method 8140 or 8141, which can achieve lower reporting limits.

[3] May also be analyzed by method 8080 or 8081, which can achieve lower reporting limits

Table 3

Reportable Analytes for STL Standard Tests, Primary Standard

Analyte	CAS Number	STL Standard List	TCLP	TCL	Appendix IX
Pyridine	110-86-1		X		X
N-nitrosodimethylamine	62-75-9				X
Aniline	62-53-3				X
Phenol	108-95-2	X		X	X
Bis(2-chloroethyl)ether	111-44-4	X		X	X
2-Chlorophenol	95-57-8	X		X	X
1,3-Dichlorobenzene	541-73-1	X		X	X
1,4-Dichlorobenzene	106-46-7	X	X	X	X
Benzyl alcohol	100-51-6				X
1,2-Dichlorobenzene	95-50-1	X		X	X
2-Methylphenol	95-48-7	X	X	X	X
2,2'-oxybis(1-chloropropane)[1]	180-60-1	X		X	X
4-Methylphenol	106-44-5	X	X	X	X
N-Nitroso-di-n-propylamine	621-64-7	X		X	X
Hexachloroethane	67-72-1	X	X	X	X
Nitrobenzene	98-95-3	X	X	X	X
Isophorone	78-59-1	X		X	X
2-Nitrophenol	88-75-5	X		X	X
2,4-Dimethylphenol	105-67-9	X		X	X
Benzoic acid	65-85-0				
Bis(2-chloroethoxy)methane	111-91-1	X		X	X
2,4-Dichlorophenol	120-83-2	X		X	X
1,2,4-Trichlorobenzene	120-82-1	X		X	X
Naphthalene	91-20-3	X		X	X
4-Chloroaniline	106-47-8	X		X	X
Hexachlorobutadiene	87-68-3	X	X	X	X
4-Chloro-3-methylphenol	59-50-7	X		X	X
2-Methylnaphthalene	91-57-6	X		X	X
Hexachlorocyclopentadiene	77-47-4	X		X	X
2,4,6-Trichlorophenol	88-06-2	X	X	X	X
2,4,5-Trichlorophenol	95-95-4	X	X	X	X
2-Chloronaphthalene	91-58-7	X		X	X
2-Nitroaniline	88-74-4	X		X	X
Dimethyl phthalate	131-11-3	X		X	X
Acenaphthylene	208-96-8	X		X	X
3-Nitroaniline	99-09-2	X		X	X
Acenaphthene	83-32-9	X		X	X
2,4-Dinitrophenol	51-28-5	X		X	X
4-Nitrophenol	100-02-7	X		X	X
Dibenzofuran	132-64-9	X		X	X
2,4-Dinitrotoluene	121-14-2	X	X	X	X
2,6-Dinitrotoluene	606-20-2	X		X	X
Diethylphthalate	84-66-2	X		X	X
4-Chlorophenyl phenyl ether	7005-72-3	X		X	X

Table 3

Reportable Analytes for STL Standard Tests, Primary Standard

Analyte	CAS Number	STL Standard List	TCLP	TCL	Appendix IX
Fluorene	86-73-7	X		X	X
4-Nitroaniline	100-01-6	X		X	X
4,6-Dinitro-2-methylphenol	534-52-1	X		X	X
N-Nitrosodiphenylamine	86-30-6	X		X	X
Azobenzene[4]	103-33-3				
4-Bromophenyl phenyl ether	101-55-3	X		X	X
Hexachlorobenzene	118-74-1	X	X	X	X
Pentachlorophenol	87-86-5	X	X	X	X
Phenanthrene	85-01-8	X		X	X
Anthracene	120-12-7	X		X	X
Carbazole	86-74-8	X		X	
Di-n-butyl phthalate	84-74-2	X		X	X
Fluoranthene	206-44-0	X		X	X
Benzidine	92-87-5				
Pyrene	129-00-0	X		X	X
Butyl benzyl phthalate	85-68-7	X		X	X
3,3'-Dichlorobenzidine	91-94-1	X		X	X
Benzo(a)anthracene	56-55-3	X		X	X
Bis(2-ethylhexyl)phthalate	117-81-7	X		X	X
Chrysene	218-01-9	X		X	X
Di-n-octylphthalate	117-84-0	X		X	X
Benzo(b)fluoranthene	205-99-2	X		X	X
Benzo(k)fluoranthene	207-08-9	X		X	X
Benzo(a)pyrene	50-32-8	X		X	X
Indeno(1,2,3-cd)pyrene	193-39-5	X		X	X
Dibenz(a,h)anthracene	53-70-3	X		X	X
Benzo(g,h,i)perylene	191-24-2	X		X	X

[1] 2,2’oxybis(1-chloropropane) was formally known as bis(2-chloroisopropyl)ether

[2] Azobenzene is formed by decomposition of 1,2-diphenlyhydrazine. If 1,2-diphenylhydrazine is requested, it will be analyzed as azobenzene.

Table 4

Reportable analytes for STL Standard Tests, Appendix IX Standard

Semivolatiles	CAS Number	STL Standard List	TCLP	TCL	Appendix IX
2-Picoline	109-06-8				X
N-Nitrosomethylethylamine	10595-95-6				X
Methyl methanesulfonate	66-27-3				X
N-Nitrosodiethylamine	55-18-5				X
Ethyl methanesulfonate	62-50-0				X
Pentachloroethane	76-01-7				X
Acetophenone	98-86-2				X
N-Nitrosopyrrolidine	930-55-2				X
N-Nitrosomorpholine	59-89-2				X
o-Toluidine	95-53-4				X
3-Methylphenol	108-39-4				X
N-Nitrosopiperidine	100-75-4				X
o,o,o-Triethyl-Phosphorothioate[2]	126-68-1				X
a,a-Dimethyl-phenethylamine	122-09-8				X
2,6-Dichlorophenol	87-65-0				X
Hexachloropropene	1888-71-7				X
p-Phenylenediamine	106-50-3				X
n-Nitrosodi-n-butylamine	924-16-3				X
Safrole	94-59-7				X
1,2,4,5-Tetrachlorobenzene	95-94-3				X
Isosafrole	120-58-1				X
1,4-Dinitrobenzene	100-25-4				
1,4-Naphthoquinone	130-15-4				X
1,3-Dinitrobenzene	99-65-0				X
Pentachlorobenzene	608-93-5				X
1-Naphthylamine	134-32-7				X
2-Naphthylamine	91-59-8				X
2,3,4,6-Tetrachlorophenol	58-90-2				X
5-Nitro-o-toluidine	99-55-8				X
Thionazin[2]	297-97-2				X
1,3,5-Trinitrobenzene	99-35-4				X
Sulfotepp[2]	3689-24-5				X
Phorate[2]	298-02-2				X
Phenacetin	62-44-2				X
Diallate	2303-16-4				X
Dimethoate[2]	60-51-5				X
4-Aminobiphenyl	92-67-1				X
Pentachloronitrobenzene	82-68-8				X
Pronamide	23950-58-5				X
Disulfoton[2]	298-04-4				X
2-secbutyl-4,6-dinitrophenol (Dinoseb)[2]	88-85-7				X
Methyl parathion[2]	298-00-0				X
4-Nitroquinoline-1-oxide	56-57-5				X
Parathion[2]	56-38-2				X

Table 4

Reportable analytes for STL Standard Tests, Appendix IX Standard

Semivolatiles	CAS Number	STL Standard List	TCLP	TCL	Appendix IX
Isodrin[3]	465-73-6				X
Kepone [2]	143-50-0				X
Famphur[2]	52-85-7				X
Methapyrilene	91-80-5				X
Aramite	140-57-8				X
p-(Dimethylamino)azobenzene	60-11-7				X
p-Chlorobenzilate[3]	510-15-6				X
3,3'-Dimethylbenzidine	119-93-7				X
2-Acetylaminofluorene	53-96-3				X
Dibenz(a,j)acridine	224-42-0				
7,12-Dimethylbenz(a)anthracene	57-97-6				X
3-Methylcholanthrene	56-49-5				X
Hexachlorophene[4]	70-30-4				X
Diphenylamine[5]	122-39-4				X

[2] May also be analyzed by method 8140 or 8141, which can achieve lower reporting limits.

[3] May also be analyzed by method 8080 or 8081, which can achieve lower reporting limits

[4] Hexachlorophene is a required analyte for Appendix IX. This compound is not stable, and therefore not included in the calibration standard. The characteristic ions for hexachlorophene are searched for in the chromatogram. (See section 12.2.1)

[5] Diphenylamine is a required compound for Appendix IX. N-nitrosodiphenylamine decomposes in the injection port to form diphenylamine. Therefore these two compounds cannot be distinguished. Diphenylamine is not included in the calibration standard.

Table 5

Suggested Instrumental Conditions

Mass Range	35-500 amu
Scan Time	≤1 second/scan
Initial Column Temperature/Hold Time	40°C for 2 minutes
Column Temperature Program	40 - 320°C at 11.5°C/min
Final Column Temperature/Hold Time	320°C (until at least one minute after benzo(g,h,i)perylene has eluted)
Injector Temperature	250 - 300°C
Transfer Line Temperature	250 - 300°C
Source Temperature	According to manufacturer's specifications
Injector	Grob-type, split / splitless
Sample Volume	1 or 2 µl
Carrier Gas	Helium at 30 cm/sec

Table 6

DFTPP Key Ions and Ion Abundance Criteria

Mass	Ion Abundance Criteria
51	30 - 60% of mass 198
68	<2% of mass 69
70	<2% of mass 69
127	40 - 60% of mass 198
197	<1% of mass 198
198	Base peak, 100% relative abundance
199	5 - 9% of mass 198
275	10 - 30% of mass 198
365	>1% of mass 198
441	Present, but less than mass 443
442	>40% of mass 198
443	17 - 23% of mass 442

Table 7

Analytes in Approximate Retention Time Order and Characteristic Ions, Primary Standard

Analyte	Primary	Secondary	Tertiary
N-nitrosodimethylamine	74	42	
Pyridine	79	52	
2-Fluorophenol (Surrogate Standard)	112	64	63
Phenol-d5 (Surrogate Standard)	99	42	71
Aniline	93	66	
Phenol	94	65	66
Bis(2-chloroethyl)ether	93	63	95
2-Chlorophenol	128	64	130
1,3-Dichlorobenzene	146	148	111
1,4-Dichlorobenzene-d4 (Internal Standard)	152	150	115
1,4-Dichlorobenzene	146	148	111
Benzyl Alcohol	108	79	77
1,2-Dichlorobenzene	146	148	111
2-Methylphenol	108	107	79
2,2'-oxybis(1-chloropropane)[1]	45	77	121
4-Methylphenol	108	107	79
N-Nitroso-di-n-propylamine	70	42	101,130
Hexachloroethane	117	201	199
Nitrobenzene-d5 (Surrogate Standard)	82	128	54
Nitrobenzene	77	123	65
Isophorone	82	95	138
2-Nitrophenol	139	65	109
2,4-Dimethylphenol	107	121	122
Benzoic Acid	122	105	77
Bis(2-chloroethoxy)methane	93	95	123
2,4-Dichlorophenol	162	164	98
1,2,4-Trichlorobenzene	180	182	145
Naphthalene-d8 (Internal Standard)	136	68	54
Naphthalene	128	129	127
4-Chloroaniline	127	129	65
Hexachlorobutadiene	225	223	227
4-Chloro-3-methylphenol	107	144	142
2-Methylnaphthalene	142	141	115
Hexachlorocyclopentadiene	237	235	272
2,4,6-Trichlorophenol	196	198	200
2,4,5-Trichlorophenol	196	198	200
2-Fluorobiphenyl (Surrogate Standard)	172	171	170
2-Chloronaphthalene	162	164	127
2-Nitroaniline	65	92	138
Dimethylphthalate	163	194	164
Acenaphthylene	152	151	153
2,6-Dinitrotoluene	165	89	63

Table 7

Analytes in Approximate Retention Time Order and Characteristic Ions, Primary Standard

Analyte	Primary	Secondary	Tertiary
Acenaphthene-d10 (Internal Standard)	164	162	160
3-Nitroaniline	138	108	92
Acenaphthene	153	152	154
2,4-Dinitrophenol	184	63	154
Dibenzofuran	168	139	84
4-Nitrophenol	139	109	65
2,4-Dinitrotoluene	165	63	89
Diethylphthalate	149	177	150
Fluorene	166	165	167
4-Chlorophenylphenylether	204	206	141
4-Nitroaniline	138	92	108
4,6-Dinitro-2-methylphenol	198	51	105
N-Nitrosodiphenylamine	169	168	167
2,4,6-Tribromophenol (Surrogate Standard)	330	332	141
Azobenzene	77	182	105
4-Bromophenylphenylether	248	250	141
Hexachlorobenzene	284	142	249
Pentachlorophenol	266	264	268
Phenanthrene-d10 (Internal Standard)	188	94	80
Phenanthrene	178	179	176
Anthracene	178	179	176
Carbazole	167	166	168
Di-n-butylphthalate	149	150	104
Fluoranthene	202	101	203
Benzidine	184	92	185
Pyrene	202	200	203
Terphenyl-d14 (Surrogate Standard)	244	122	212
Butylbenzylphthalate	149	91	206
Benzo(a)Anthracene	228	229	226
Chrysene-d12 (Internal Standard)	240	120	236
3,3'-Dichlorobenzidine	252	254	126
Chrysene	228	226	229
Bis(2-ethylhexyl)phthalate	149	167	279
Di-n-octylphthalate	149	167	43
Benzo(b)fluoranthene	252	253	125
Benzo(k)fluoranthene	252	253	125
Benzo(a)pyrene	252	253	125
Perylene-d12 (Internal Standard)	264	260	265
Indeno(1,2,3-cd)pyrene	276	138	277
Dibenz(a,h)anthracene	278	139	279
Benzo(g,h,i)perylene	276	138	277

Table 8

Analytes in Approximate Retention Time Order and Characteristic Ions, Appendix IX Standard

Analyte	Primary	Secondary	Tertiary
2-Picoline	93	66	92
N-Nitrosomethylethylamine	88	42	43
Methyl methanesulfonate	80	79	65
N-Nitrosodiethylamine	102	44	57
Ethyl methanesulfonate	79	109	97
Pentachloroethane	117	119	167
Acetophenone	105	77	120
N-Nitrosopyrrolidine	100	41	42
N-Nitrosomorpholine	116	56	86
o-Toluidine	106	107	
3-Methylphenol	108	107	77
N-Nitrosopiperidine	114	42	55
o,o,o-Triethyl-Phosphorothioate	198	121	93
a,a-Dimethyl-phenethylamine	58	91	
2,6-Dichlorophenol	162	164	63
Hexachloropropene	213	215	211
p-Phenylenediamine	108	80	
n-Nitrosodi-n-butylamine	84	57	41
Safrole	162	104	77
1,2,4,5-Tetrachlorobenzene	216	214	218
Isosafrole 1	162	104	131
Isosafrole 2	162	104	131
1,4-Dinitrobenzene	168	75	122
1,4-Naphthoquinone	158	104	102
1,3-Dinitrobenzene	168	75	76
Pentachlorobenzene	250	248	252
1-Naphthylamine	143	115	
2-Naphthylamine	143	115	
2,3,4,6-Tetrachlorophenol	232	230	131
5-Nitro-o-toluidine	152	77	106
Thionazin	97	96	143
1,3,5-Trinitrobenzene	213	75	120
Sulfotepp	97	322	202
Phorate	121	75	260
Phenacetin	108	179	109
Diallate	86	234	
Dimethoate	87	93	125
4-Aminobiphenyl	169		
Pentachloronitrobenzene	237	142	214
Pronamide	173	175	255
Disulfoton	88	97	89
2-secbutyl-4,6-dinitrophenol (Dinoseb)	211	163	147
Methyl parathion	109	125	263
4-Nitroquinoline-1-oxide	190	128	160
Parathion	109	97	291

Table 8

Analytes in Approximate Retention Time Order and Characteristic Ions, Appendix IX Standard

Analyte	Primary	Secondary	Tertiary
Isodrin	193	66	195
Kepone	272	274	237
Famphur	218	125	93
Methapyrilene	97	58	
Aramite 1	185	319	
Aramite 2	185	319	
p-(Dimethylamino)azobenzene	120	225	77
p-Chlorobenzilate	251	139	253
3,3'-Dimethylbenzidine	212	106	
2-Acetylaminofluorene	181	180	223
Dibenz(a,j)acridine	279	280	
7,12-Dimethylbenz(a)anthracene	256	241	120
3-Methylcholanthrene	268	252	253

Table 9

8270C LCS Compounds

LCS Compounds	Spiking Level, ng/µL in extract[1]
1,2,4-Trichlorobenzene	100
Acenaphthene	100
2,4-Dinitrotoluene	100
Pyrene	100
N-Nitroso-di-n-propylamine	100
1,4-Dichlorobenzene	100
Pentachlorophenol	150
Phenol	150
2-Chlorophenol	150
4-Chloro-3-methylphenol	150
4-Nitrophenol	150

[1] Levels are 50 and 75 ng/µL if 2 µL injection is used

Table 10

TCLP LCS Compounds

LCS Compounds	Spiking Level, ng/µL in extract[1]
1,4-Dichlorobenzene	100
2,4-Dinitrotoluene	100
Hexachlorobenzene	100
Hexachlorobutadiene	100
Hexachloroethane	100
2-Methylphenol	100
3-Methylphenol	100
4-Methylphenol	100
Nitrobenzene	100
Pentachlorophenol	100
Pyridine	100
2,4,5-Trichlorophenol	100
2,4,6-Trichlorophenol	100

[1] Levels are 50 ng/µL if 2 µL injection is used

Recovery limits for the LCS and for matrix spikes are generated from historical data and are maintained by the QA department.

Table 11

8270C Surrogate Compounds

Surrogate Compounds	Spiking Level, ng/µL in extract[2]
Nitrobenzene-d5	100
2-Fluorobiphenyl	100
Terphenyl-d14	100
1,2-Dichlorobenzene-d4[1]	100
Phenol-d5	150
2-Fluorophenol	150
2,4,6-Tribromophenol	150
2-Chlorophenol-d4[1]	150

[1] Included in standard mix, but not routinely evaluated for method 8270B

[2] Levels are 50 and 75 ng/µL if 2 µL injection is used

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

Table 12

Calibration Levels, Primary Standard, ug/ml (for 2ul injection)

Analyte	Level 1	Level 2	Level 3	Level 4	Level 5
Pyridine	10	25	40	60	80
N-nitrosodimethylamine	10	25	40	600	800
Aniline	10	25	400	600	800
Phenol	10	25	40	60	80
Bis(2-chloroethyl)ether	10	25	40	60	80
2-Chlorophenol	10	25	40	60	80
1,3-Dichlorobenzene	10	25	40	60	80
1,4-Dichlorobenzene	10	25	40	60	80
Benzyl alcohol	10	25	40	60	80
1,2-Dichlorobenzene	10	25	40	60	80
2-Methylphenol	10	25	40	60	80
2,2'-oxybis(1-chloropropane)[1]	10	25	40	60	80
4-Methylphenol	10	25	40	60	80
N-Nitroso-di-n-propylamine	10	25	40	60	80
Hexachloroethane	10	25	40	60	80
Nitrobenzene	10	25	40	60	80
Isophorone	10	25	40	60	80
2-Nitrophenol	10	25	40	60	80
2,4-Dimethylphenol	10	25	40	60	80
Benzoic acid	20	50	80	120	160
Bis(2-chloroethoxy)methane	10	25	40	60	80
2,4-Dichlorophenol	10	25	40	60	80
1,2,4-Trichlorobenzene	10	25	40	60	80
Naphthalene	10	25	40	60	80
4-Chloroaniline	10	25	40	60	80
Hexachlorobutadiene	10	25	40	60	80
4-Chloro-3-methylphenol	10	25	40	60	80
2-Methylnaphthalene	10	25	40	60	80
Hexachlorocyclopentadiene	10	25	40	60	80
2,4,6-Trichlorophenol	10	25	40	60	80
2,4,5-Trichlorophenol	10	25	40	60	80
2-Chloronaphthalene	10	25	40	60	80
2-Nitroaniline	20	50	80	120	160
Dimethyl phthalate	10	25	40	60	80
Acenaphthylene	10	25	40	60	80
3-Nitroaniline	20	50	80	120	160
Acenaphthene	10	25	40	60	80
2,4-Dinitrophenol	20	50	80	120	160
4-Nitrophenol	20	50	80	120	160
Dibenzofuran	10	25	40	60	80
2,4-Dinitrotoluene	10	25	40	60	80
2,6-Dinitrotoluene	10	25	40	60	80
Diethylphthalate	10	25	40	60	80
4-Chlorophenyl phenyl ether	10	25	40	60	80
Fluorene	10	25	40	60	80

Table 12

Calibration Levels, Primary Standard, ug/ml (for 2ul injection)

Analyte	Level 1	Level 2	Level 3	Level 4	Level 5
4-Nitroaniline	10	25	40	60	80
4,6-Dinitro-2-methylphenol	20	50	80	120	160
N-Nitrosodiphenylamine	10	25	40	60	80
Azobenzene[2]	10	25	40	60	80
4-Bromophenyl phenyl ether	10	25	40	60	80
Hexachlorobenzene	10	25	40	60	80
Pentachlorophenol	20	50	80	120	160
Phenanthrene	10	25	40	60	80
Anthracene	10	25	40	60	80
Carbazole	10	25	40	60	80
Di-n-butyl phthalate	10	25	40	60	80
Fluoranthene	10	25	40	60	80
Benzidine	20	50	80	120	160
Pyrene	10	25	40	60	80
Butyl benzyl phthalate	10	25	40	60	80
3,3'-Dichlorobenzidine	20	50	80	120	160
Benzo(a)anthracene	10	25	40	60	80
Bis(2-ethylhexyl)phthalate	10	25	40	60	80
Chrysene	10	25	40	60	80
Di-n-octylphthalate	10	25	40	60	80
Benzo(b)fluoranthene	10	25	40	60	80
Benzo(k)fluoranthene	10	25	40	60	80
Benzo(a)pyrene	10	25	40	60	80
Indeno(1,2,3-cd)pyrene	10	25	40	60	80
Dibenz(a,h)anthracene	10	25	40	60	80
Benzo(g,h,i)perylene	10	25	40	60	80

[1] 2,2'oxybis(1-chloropropane) was formally known as bis(2-chloroisopropyl)ether

[2]Azobenzene is formed by decomposition of 1,2-diphenlyhydrazine. If 1,2-diphenylhydrazine is requested, it will be analyzed as azobenzene.

Table 13
Calibration Levels, Appendix IX Standard, µg/mL (for 2ul injection)

Semivolatiles	Level 1	Level 2	Level 3	Level 4	Level 5
2-Picoline	10	25	40	60	80
N-Nitrosomethylethylamine	10	25	40	60	80
Methyl methanesulfonate	10	25	40	60	80
N-Nitrosodiethylamine	10	25	40	60	80
Ethyl methanesulfonate	10	25	40	60	80
Pentachloroethane	10	25	40	60	80
Acetophenone	10	25	40	60	80
N-Nitrosopyrrolidine	10	25	40	60	80
N-Nitrosomorpholine	10	25	40	60	80
o-Toluidine	10	25	40	60	80
3-Methylphenol	10	25	40	60	80
N-Nitrosopiperidine	10	25	40	60	80
o,o,o-Triethyl-Phosphorothioate	20	50	80	120	160
a,a-Dimethyl-phenethylamine	10	25	40	60	80
2,6-Dichlorophenol	10	25	40	60	80
Hexachloropropene	20	50	80	120	160
p-Phenylenediamine	10	25	40	60	80
n-Nitrosodi-n-butylamine	10	25	40	60	80
Safrole	10	25	40	60	80
1,2,4,5-Tetrachlorobenzene	10	25	40	60	80
Isosafrole 1 + 2	20	50	80	120	160
1,4-Dinitrobenzene	10	25	40	60	80
1,4-Naphthoquinone	10	25	40	60	80
1,3-Dinitrobenzene	10	25	40	60	80
Pentachlorobenzene	10	25	40	60	80
1-Naphthylamine	10	25	40	60	80
2-Naphthylamine	10	25	40	60	80
2,3,4,6-Tetrachlorophenol	10	25	40	60	80
5-Nitro-o-toluidine	10	25	40	60	80
Thionazin	10	25	40	60	80
1,3,5-Trinitrobenzene	20	50	80	120	160
Sulfotepp	10	25	40	60	80
Phorate	10	25	40	60	80
Phenacetin	10	25	40	60	80
Diallate 1 + 2	20	50	80	120	160
Dimethoate	10	25	40	60	80
4-Aminobiphenyl	10	25	40	60	80
Pentachloronitrobenzene	20	50	80	120	160
Pronamide	10	25	40	60	80
Disulfoton	10	25	40	60	80
2-secbutyl-4,6-dinitrophenol (Dinoseb)	20	50	80	120	160
Methyl parathion	10	25	40	60	80
4-Nitroquinoline-1-oxide	20	50	80	120	160
Parathion	10	25	40	60	80
Isodrin	10	25	40	60	80
Kepone	20	50	80	120	160

Table 13
Calibration Levels, Appendix IX Standard, µg/mL (for 2ul injection)

Semivolatiles	Level 1	Level 2	Level 3	Level 4	Level 5
Famphur	20	50	80	120	160
Methapyrilene	10	25	40	60	80
Aramite 1 and 2	20	50	80	120	160
p-(Dimethylamino)azobenzene	10	25	40	60	80
p-Chlorobenzilate	10	25	40	60	80
3,3'-Dimethylbenzidine	10	25	40	60	80
2-Acetylaminofluorene	10	25	40	60	80
Dibenz (a,j)acridine	10	25	40	60	80
7,12-Dimethylbenz(a)anthracene	10	25	40	60	80
3-Methylcholanthrene	10	25	40	60	80

Table 14
Initial demonstration recovery and precision limits

Compound	Spiking concentration µg/L	Limit for Relative Standard Deviation	Limit for average recovery, %
Acenaphthene	50	27.6	60.1-132.3
Acenaphthylene	50	40.0	53.5-126.0
Aldrin[1]	50	39.0	7.2-152.2
Anthracene	50	32.0	43.4-118.0
Benz(a)anthracene	50	27.6	41.8-133.0
Benzo(b)fluoranthene	50	38.8	42.0-140.4
Benzo(k)fluoranthene	50	32.3	25.2-145.7
Benzo(a)pyrene	50	39.0	31.7-148.0
Benzo(ghi)perylene	50	58.9	D-195.0
Benzylbutyl phthalate	50	23.4	D-139.9
B-BHC[1]	50	31.5	41.5-130.6
d-BHC[1]	50	21.6	D-100.0
Bis(2-chloroethyl) ether	50	55.0	42.9-126.0
Bis(2-chloroethoxy)methane	50	34.5	49.2-164.7
Bis(2-chloroisopropyl) ether	50	46.3	62.8-138.6
Bis(2-ethylhexyl) phthalate	50	41.1	28.9-136.8
4-Bromophenyl phenyl ether	50	23.0	64.9-114.4
2-Chloronaphthalene	50	13.0	64.5-113.5
4-Chlorophenyl phenyl ether	50	33.4	38.4-144.7
Chrysene	50	48.3	44.1-139.9
4,4'-DDD[1]	50	31.0	D-134.5
4,4'-DDE[1]	50	32.0	19.2-119.7
4,4'-DDT[1]	50	61.6	D-170.6
Dibenzo(a,h)anthracene	50	70.0	D-199.7
Di-n-butyl phthalate	50	16.7	8.4-111.0
1,2-Dichlorobenzene	50	30.9	48.6-112.0
1,3-Dichlorobenzene	50	41.7	16.7-153.9

Table 14
Initial demonstration recovery and precision limits

Compound	Spiking concentration µg/L	Limit for Relative Standard Deviation	Limit for average recovery, %
1,4-Dichlorobenzene	50	32.1	37.3-105.7
3,3'-Dichlorobenzidine	50	71.4	8.2-212.5
Dieldrin[1]	50	30.7	44.3-119.3
Diethyl phthalate	50	26.5	D-100.0
Dimethyl phthalate	50	23.2	D-100.0
2,4-Dinitrotoluene	50	21.8	47.5-126.9
2,6-Dinitrotoluene	50	29.6	68.1-136.7
Di-n-octylphthalate	50	31.4	18.6-131.8
Endosulfan sulfate[1]	50	16.7	D-103.5
Endrin aldehyde	50	32.5	D-188.8
Fluoranthene	50	32.8	42.9-121.3
Fluorene	50	20.7	71.6-108.4
Heptachlor[1]	50	37.2	D-172.2
Heptachlor epoxide[1]	50	54.7	70.9-109.4
Hexachlorobenzene	50	24.9	7.8-141.5
Hexachlorobutadiene	50	26.3	37.8-102.2
Hexachloroethane	50	24.5	55.2-100.0
Indeno(1,2,3-cd)pyrene	50	44.6	D-150.9
Isophorone	50	63.3	46.6-180.2
Naphthalene	50	30.1	35.6-119.6
Nitrobenzene	50	39.3	54.3-157.6
N-Nitrosodi-n-propylamine	50	55.4	13.6-197.9
PCB-1260[1]	50	54.2	19.3-121.0
Phenanthrene	50	20.6	65.2-108.7
Pyrene	50	25.2	69.6-100.0
1,2,4-Trichlorobenzene	50	28.1	57.3-129.2
4-Chloro-3-methylphenol	50	37.2	40.8-127.9
2-Chlorophenol	50	28.7	36.2-120.4
2,4-Chlorophenol	50	26.4	52.5-121.7
2,4-Dimethylphenol	50	26.1	41.8-109.0
2,4-Dinitrophenol	50	49.8	D-172.9
2-Methyl-4,6-dinitrophenol	50	93.2	53.0-100.0
2-Nitrophenol	50	35.2	45.0-166.7
4-Nitrophenol	50	47.2	13.0-106.5
Pentachlorophenol	50	48.9	38.1-151.8
Phenol	50	22.6	16.6-100.0
2,4,6-Trichlorophenol	50	31.7	52.4-129.2

[1]Since the organochlorine pesticides and PCBs are normally determined by method 8080 at STL, they will not be included in the initial demonstration of capability for method 8270B.

ATTACHMENT A

MODIFICATIONS REQUIRED FOR ANALYSIS OF WASTEWATER FOLLOWING METHOD 625

18. REQUIREMENTS FOR METHOD 625

18.1. Method 625 is required for demonstration of compliance with NPDES wastewater discharge permits. The standard analyte list and reporting limits are listed in Table A-1.

18.2. This method can be applied only to aqueous matrices.

18.3. The tune period for this method is defined as 24 hours.

18.4. Initial calibration curve requirements:

18.4.1. The initial calibration curve for this method requires at least three points.

18.4.2. Target compounds must have RSD ≤ 35%.

18.4.3. If this requirement can not be met, a regression curve must be constructed for the non-compliant compounds.

18.5. Continuing calibration verification requirements: All target compounds must have %D ≤ 20%.

18.6. Matrix Spike and LCS requirements:

18.6.1. A full analyte spike is required for method 625. The spiking levels are given in Table A-2.

Table A-1. STL Method 625 standard reporting list and reporting limits.

Analytes	CAS Number	Aqueous µg/L
Phenol	108-95-2	10
Bis(2-chloroethyl)ether	111-44-4	10
2-Chlorophenol	95-57-8	10
1,3-Dichlorobenzene	541-73-1	10
1,4-Dichlorobenzene	106-46-7	10
1,2-Dichlorobenzene	95-50-1	10
2,2'-oxybis(1-chloropropane)	108-60-1	10
N-Nitroso-di-n-propylamine	621-64-7	10
Hexachloroethane	67-72-1	10
Nitrobenzene	98-95-3	10
Isophorone	78-59-1	10
2-Nitrophenol	88-75-5	10
2,4-Dimethylphenol	105-67-9	10
Bis(2-chloroethoxy)methane	111-91-1	10
2,4-Dichlorophenol	120-83-2	10
1,2,4-Trichlorobenzene	120-82-1	10
Naphthalene	91-20-3	10
Hexachlorobutadiene	87-68-3	10
4-Chloro-3-methylphenol	59-50-7	10
Hexachlorocyclopentadiene	77-47-4	50
2,4,6-Trichlorophenol	88-06-2	10
2-Chloronaphthalene	91-58-7	10
Dimethyl phthalate	131-11-3	10
Acenaphthylene	208-96-8	10
Acenaphthene	83-32-9	10
2,4-Dinitrophenol	51-28-5	50
4-Nitrophenol	100-02-7	50
2,4-Dinitrotoluene	121-14-2	10
2,6-Dinitrotoluene	606-20-2	10
Diethylphthalate	84-66-2	10
4-Chlorophenyl phenyl ether	7005-72-3	10
Fluorene	86-73-7	10
4,6-Dinitro-2-methylphenol	534-52-1	50
N-Nitrosodiphenylamine	86-30-6	10
4-Bromophenyl phenyl ether	101-55-3	10
Hexachlorobenzene	118-74-1	10
Pentachlorophenol	87-86-5	50
Phenanthrene	85-01-8	10
Anthracene	120-12-7	10
Di-n-butyl phthalate	84-74-2	10
Fluoranthene	206-44-0	10
Benzidine	92-87-5	100
Pyrene	129-00-0	10
Butyl benzyl phthalate	85-68-7	10

Analytes	CAS Number	Aqueous µg/L
3,3'-Dichlorobenzidine	91-94-1	50
Benzo(a)anthracene	56-55-3	10
Bis(2-ethylhexyl)phthalate	117-81-7	10
Chrysene	218-01-9	10
Di-n-octylphthalate	117-84-0	10
Benzo(b)fluoranthene	205-99-2	10
Benzo(k)fluoranthene	207-08-9	10
Benzo(a)pyrene	50-32-8	10
Indeno(1,2,3-cd)pyrene	193-39-5	10
Dibenz(a,h)anthracene	53-70-3	10
Benzo(g,h,i)perylene	191-24-2	10

Table A-2. Method 625 LCS and MS compounds and spike concentrations.

LCS Compounds	Spiking Level, ng/µL in extract[1]
Phenol	100
Bis(2-chloroethyl)ether	100
2-Chlorophenol	100
1,3-Dichlorobenzene	100
1,4-Dichlorobenzene	100
1,2-Dichlorobenzene	100
2,2'-oxybis(1-chloropropane)	100
N-Nitroso-di-n-propylamine	100
Hexachloroethane	100
Nitrobenzene	100
Isophorone	100
2-Nitrophenol	100
2,4-Dimethylphenol	100
Bis(2-chloroethoxy)methane	100
2,4-Dichlorophenol	100
1,2,4-Trichlorobenzene	100
Naphthalene	100
Hexachlorobutadiene	100
4-Chloro-3-methylphenol	100
Hexachlorocyclopentadiene	100
2,4,6-Trichlorophenol	100
2-Chloronaphthalene	100
Dimethyl phthalate	100
Acenaphthylene	100
Acenaphthene	100
2,4-Dinitrophenol	100
4-Nitrophenol	100
2,4-Dinitrotoluene	100
2,6-Dinitrotoluene	100
Diethylphthalate	100
4-Chlorophenyl phenyl ether	100
Fluorene	100
4,6-Dinitro-2-methylphenol	100
N-Nitrosodiphenylamine	100
4-Bromophenyl phenyl ether	100
Hexachlorobenzene	100
Pentachlorophenol	100
Phenanthrene	100
Anthracene	100
Di-n-butyl phthalate	100
Fluoranthene	100
Benzidine	100
Pyrene	100
Butyl benzyl phthalate	100
3,3'-Dichlorobenzidine	100

LCS Compounds	Spiking Level, ng/µL in extract[1]
Benzo(a)anthracene	100
Bis(2-ethylhexyl)phthalate	100
Chrysene	100
Di-n-octylphthalate	100
Benzo(b)fluoranthene	100
Benzo(k)fluoranthene	100
Benzo(a)pyrene	100
Indeno(1,2,3-cd)pyrene	100
Dibenz(a,h)anthracene	100
Benzo(g,h,i)perylene	100

[1] **Levels are 50 and 75 ng/µL if 2 µL injection is used**

CORP-GC-0001PT

Gas Chromatography Analysis based on
Method 8000B, 8021A, 8081A, 8082, and 8151A;
SW-846 8141A and 8310

STL STANDARD OPERATING PROCEDURE

TITLE: GAS CHROMATOGRAPHIC ANALYSIS BASED ON METHOD 8000B, 8021B, 8081A, 8082 and 8151A, SW-846,

WITH LAB SPECIFIC APPENDICES FOR 8141A & 8310

(SUPERSEDES: Revision 4)

Prepared by: Richard Burrows

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1. SCOPE AND APPLICATION

This SOP describes procedures for analysis of organic analytes by Gas Chromatography (GC). The procedures are based on SW-846 methodology and are applicable for measurements made to comply with the Resource Conservation and Recovery Act (RCRA). Individual analytes and methods are described in the appendices.

2. SUMMARY OF METHOD

In general, semivolatile analytes in aqueous samples are prepared for analysis using continuous or separatory funnel liquid / liquid extraction or solid phase extraction (SOP # CORP-OP-0001) Solid samples are prepared using sonication, Soxhlet or pressurized fluid extraction (SOP # CORP-OP-0001). Volatile analytes are prepared for analysis using purge and trap methodology (Appendix A).

After the initial preparation step, the sample is introduced to the GC and concentrations of target analytes are measured by the detector response within a defined retention time window, relative to the response to standard concentrations. Internal or external standardization procedures are used as specified in the method appendices.

3. DEFINITIONS

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

4. INTERFERENCES

Contamination by carryover can occur when a low concentration sample is analyzed after a high concentration sample. In addition, some purge and trap autosamplers are susceptible to port specific contamination. Co-elution of target analytes with non-targets can occur, resulting in false positives or biased high results. In particular, this is a problem with non-selective detectors such as the Flame Ionization Detector (FID). See the appendices for interferences specific to individual tests and suggested corrective actions.

5. SAFETY

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

Eye protection that satisfies ANSI Z87.1 (as per the Chemical Hygiene Plan), laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have become contaminated will be removed and discarded; other gloves will be cleaned immediately. Refer to the STL Chemical Hygiene plan for a complete description of personal protection equipment.

The health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the MSDS files maintained in the laboratory. Specific hazards are covered in the appendices.

5.1.1. Opened containers of neat standards will be handled in a fume hood.

5.2. Sample extracts and standards which are in a flammable solvent shall be stored in an explosion-proof refrigerator.

5.3. When using hydrogen gas as a carrier, all precautions listed in the CHP shall be observed.

5.4. Standard preparation and dilution shall be performed inside an operating fume hood.

6. EQUIPMENT AND SUPPLIES

An analytical system complete with a gas chromatograph is required. A data system capable of measuring peak area and/or height is required. Recommended equipment and supplies for individual methods are listed in each method appendix.

7. REAGENTS AND STANDARDS

7.1. Stock Standards

Stock standards are purchased as certified solutions or prepared from pure solutions. Stock standards for method 8021B are stored at -10 to -20°C. Other stock standard solutions are stored at $\leq$6°C. All stock standards must be protected from light. Stock standard solutions should be brought to room temperature before using.

Semivolatile stock standard solutions must be replaced after one year. Stock standards of gases must be replaced at least every week, unless the acceptability of the standard is demonstrated (Less than 20% drift from the initial calibration is an acceptable demontration). Other volatile stock standards must be replaced every 6 months or sooner if comparison with check standards prepared from an independent source indicates a problem.

7.1.1. Expiration times for all standards are measured from the time the standard is prepared or from the time that the standard ampoule is opened, if the standard is supplied in a sealed ampoule. If a vendor supplied standard has an earlier expiration date then that date is used.

7.2. Calibration Standards

7.2.1. Volatile Calibration Standards

The procedure for preparation of volatile standards is given in Appendix A.

7.2.2. Semivolatile Calibration Standards

Semivolatile calibration standards are prepared as dilutions of the stock standards. Surrogates and internal standards are used as specified in the method appendices. Semivolatile calibration solutions must be refrigerated at $\leq$6°C and protected from light. The standards must be replaced at least every six months or sooner if comparison with check standards indicates a problem.

7.3. Gases for carrier and make-up: Hydrogen, Helium, Nitrogen, Argon/Methane.

7.4. Quality control (QC) Standards

QC standards (matrix spiking and LCS standards) are prepared and stored in the same way as calibration standards. They must be made from a stock independent from the calibration standards.

8. SAMPLE PRESERVATION AND STORAGE

Semivolatile extracts must be refrigerated at $\leq$6°C and analyzed within 40 days of the end of the extraction. Volatile sample storage conditions and holding times are given in Appendix A.

9. QUALITY CONTROL

9.1. Initial Demonstration of Capability

9.1.1. For the standard analyte list, the initial demonstration and method detection limit (MDL) studies described in section 13 must be acceptable before analysis of samples may begin.

9.1.2. For non-standard analytes, a MDL study must be performed and calibration curve generated before analyzing any samples, unless lesser requirements are previously agreed to with the client. In any event the minimum initial demonstration required is analysis of an extracted standard at the reporting limit and a single point calibration.

9.2. Batch Definition

Batches are defined at the sample preparation stage. Batches should be kept together through the whole analytical process as far as possible, but it is not mandatory to analyze prepared extracts on the same instrument or in the same sequence. Refer to the STL QC Program document (QA-003) for further details of the batch definition.

9.2.1. Quality Control Batch

The batch is a set of up to 20 samples of the same matrix processed using the same procedures and reagents within the same time period. The Quality Control batch must contain a matrix spike / spike duplicate (MS/MSD), a Laboratory Control Sample (LCS), and a method blank. Laboratory generated QC samples (Blank, LCS, MS/MSD) do not count towards the maximum 20 samples in a batch. Field QC samples are included in the batch count. In some cases, at client request, the MS/MSD may be replaced with a matrix spike and sample duplicate. If insufficient sample is available for an MS/MSD a LCSD may be substituted.

9.3. Control Limits

In-house historical control limits must be determined for surrogates, matrix spikes, and laboratory control samples (LCS). These limits must be determined at least annually. The recovery limits are mean recovery +/- 3 standard deviations, unless that limit is tighter than the calibration criteria, in which case limits may be widened. Refer to policy QA-003 for more details.

9.3.1. These limits do not apply to dilutions (except for tests without a separate extraction), but surrogate and matrix spike recoveries will be reported unless the dilution is more than 5X.

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

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

9.4. Surrogates

All methods must use surrogates to the extent possible. Surrogate recoveries in samples and QC samples must be assessed to ensure that recoveries are within established limits. If any surrogates are outside limits, the following corrective actions must take place (except for dilutions):

- Check all calculations for error.
- Ensure that instrument performance is acceptable.
- Recalculate the data and/or reanalyze the extract if either of the above checks reveal a problem.
- Reprepare and reanalyze the sample or flag the data as “Estimated Concentration” if neither of the above resolves the problem. Repreparation is not necessary is there is obvious chromatographic interference.
- The decision to reanalyze or flag the data should be made in consultation with the client. It is only necessary to reprepare / reanalyze a sample once to demonstrate that poor surrogate recovery is due to matrix effect, unless the analyst believes that the repeated out of control results are not due to matrix effect.

9.4.1. If dual column analysis is used the choice of which result to report is made in the same way as for samples (Section 12.1.2) unless one column is out of control, in which case the in-control result is reported.

9.4.2. If the surrogates are out of control for the sample, matrix spike, and matrix spike duplicate, then matrix effect has been demonstrated for that sample and repreparation is not necessary. If the sample is out of control and the MS and/or MSD is in control, then repreparation or flagging of the data is required.

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

9.5. Method Blanks

For each batch of samples, analyze a method blank. The method blank consists of reagent water for aqueous semivolatiles samples, and sodium sulfate for semivolatiles soils tests (Refer to SOP No. CORP-OP-0001 for details). For low level volatiles, the method blank consists of reagent water. For medium level volatiles, the method blank consists of methanol as described in Appendix A. Surrogates are added and the method blank is carried through the entire analytical procedure. The method blank must not contain any analyte of interest at or above the reporting limit (except common laboratory contaminants, see below) or at or above 5% of the measured concentration of that analyte in the associated samples, whichever is higher.

If the analyte is a common laboratory contaminant (methylene chloride, acetone, 2-butanone, phthalate esters) the data may be reported with qualifiers if the concentration of the analyte is less than five times the reporting limit. Such action must be taken in consultation with the client.

Re-extraction and reanalysis of samples associated with an unacceptable method blank is required when reportable concentrations are determined in the samples.

If there is no target analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. Such action should be taken in consultation with the client.

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

9.6. Instrument Blanks

9.6.1. An instrument blank must be analyzed during any 12 hour period of analysis that does not contain a method blank.

9.6.2. An instrument blank consists of the appropriate solvent with internal standards added. If internal standards are not used the surrogates should be added.

9.6.3. Control criteria are the same as for the method blank, except that only reanalysis of affected samples would be required, not re-extraction.

9.7. Laboratory Control Samples (LCS)

For each batch of samples, analyze a LCS. The LCS contains a representative subset of the analytes of interest, and must contain the same analytes as the matrix spike. The LCS may also contain the full set of analytes. If any analyte or surrogate is outside established control limits, the system is out of control and corrective action must occur. Corrective action will normally be repreparation and reanalysis of the batch; however, if the matrix spike and matrix spike duplicate are within limits, the batch may be acceptable.

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

9.7.2. If dual column analysis is used the choice of which result to report is made in the same way as for samples (Section 12.1.2) unless one column is out of control, in which case the in control result is reported.

9.7.3. LCS compound lists are included in the appendices.

9.7.4. If full analyte spike lists are used at client request, it will be necessary to allow a percentage of the components to be outside control limits as this would be expected statistically. These requirements should be negotiated with the client.

9.8. Matrix Spikes

For each QC batch, analyze a matrix spike and matrix spike duplicate. Spiking compounds and levels are given in the appendices. Compare the percent recovery and relative percent difference (RPD) to those in the laboratory specific historically generated limits.

- If any individual recovery or RPD falls outside the acceptable range, corrective action must occur. The initial corrective action will be to check the recovery of that analyte in the Laboratory Control Sample (LCS). Generally, if the recovery of the analyte in the LCS is within limits, then the laboratory operation is in control and analysis may proceed.
- If the recovery for any component is outside QC limits for both the Matrix spike / spike duplicate and the LCS, the laboratory is out of control and corrective action must be taken. Corrective action will normally include repreparation and reanalysis of the batch.
- If a MS/MSD is not possible due to limited sample, then a LCS duplicate should be analyzed.
- The matrix spike / duplicate must be analyzed at the same dilution as the unspiked sample, unless the matrix spike components would then be above the calibration range.

9.8.1. If dual column analysis is used the choice of which result to report is made in the same way as for samples (Section 12.1.2) unless one column is out of control, in which case the in control result is reported.

9.9. Quality Assurance Summaries

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

9.10. STL QC Program

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

10. CALIBRATION AND STANDARDIZATION

Internal or external calibration may be used. Internal calibration is recommended unless the sample matrix is likely to interfere with the quantitation of the internal standard. In either event prepare standards containing each analyte of interest at a minimum of five concentration levels. The low level standard should be at or below the reporting limit. The other standards define the working range of the detector. Recommended calibration levels are given in the appendices.

10.1. A new calibration curve must be generated after major changes to the system or when the continuing calibration criteria cannot be met. Major changes include new columns, changing PID lamps or FID jets or replacing the ECD detector. A new calibration is not required after clipping the column, replacing the septum or syringe, or other minor maintenance.

10.2. With the exception of 10.3 below, it is NOT acceptable to remove points from a calibration curve for the purpose of meeting criteria, unless the points are the highest or lowest on the curve AND the reporting limit and/or linear range is adjusted accordingly. In any event, at least 5 points must be included in the calibration curve. Quadratic (second order) calibrations require at least six points. Third order calibrations require at least seven points.

10.3. A level may be removed from the calibration if the reason can be clearly documented, for example a broken vial or no purge run. A minimum of five levels must remain in the calibration. The documentation must be retained with the initial calibration. Alternatively, if the analyst believes that a point on the curve is inaccurate, the point may be reanalyzed and the reanalysis used for the calibration. All initial calibration points must be analyzed without any changes to instrument conditions, and all points must be analyzed within 24 hours.

10.4. External standard calibration

Quantitation by the external standard method assumes a proportional relationship between the calibration run and the analyte in the sample. To use this approach, introduce each calibration standard into the GC using the technique that will be used for samples. The ratio of the peak height or area response to the mass or concentration injected may be used to prepare a calibration curve.

$$Calibration\ Factor\ (CF) = \frac{Area\ or\ Height\ of\ Peak}{Mass\ Injected\ (ng)}$$

Some data systems may use the inverse of this formula. This is acceptable so long as the same formula is used for standards and samples. It is also possible to use the concentration of the standard rather than the mass injected. (This would require changes in the equations used to calculate the sample concentrations). Use of peak area or height must be consistent. However, if matrix interferences would make quantitation using peak area inaccurate for a particular sample, then peak height may be used as a substitute.

10.5. Internal standard calibration

10.5.1. The internal standard approach assumes that variations in instrument sensitivity, amount injected etc. can be corrected by determining the ratio of the response of the analyte to the response of an internal standard that has been added to the extract. To use this approach, select one or more internal standard(s) that are similar in analytical behavior to the compounds of interest. Recommended internal standards are given in the appendices. The analyst must demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. If the sample matrix interferes with quantitation of the internal standard, then the external standard approach must be used instead. In this event use the response factors from the previous continuing calibration to quantitate the analytes in the sample with the interference (applies only to the sample with the interference).

10.5.2. Introduce each calibration standard into the GC using the technique that will be used for samples. Response factors (RF) for each compound are calculated as follows:

$$RF = \frac{A_s \times C_{is}}{A_{is} \times C_s}$$

Where:

A_s = Response for the analyte to be measured
A_{is} = Response for the internal standard
C_{is} = Concentration of internal standard
C_s = Concentration of the analyte to be determined in the standard

10.6. Calibration curve fits

Average response factor, linear regression, or quadratic curves may be used to fit the data. Average response factor may be used if the average % RSD of the response factors or calibration factors of all the analytes in the calibration standard taken together is $\leq$ 20%. The average %RSD is calculated by summing the RSD value for each analyte and dividing by the total number of analytes.

10.6.1. In general, for environmental analysis, average response factors are the most appropriate calibration model. Linear or curved regression fits should only be used if the analyst has reason to believe that the average RF model does not fit the normal concentration/response behavior of the detector.

10.6.2. Average response factor

The average response factor may be used if the average percent relative standard deviation (%RSD) of all the response factors taken together is $\leq$ 20%.

The equation for average response factor is:

$$\textit{Average response factor} = \overline{RF} = \frac{\sum_{i=1}^{n} RF_i}{n}$$

Where: n = Number of calibration levels

$\sum_{i=1}^{n} RF_i$ = Sum of response factors for each calibration level

10.6.3. Linear regression

The linear fit uses the following functions:

10.6.3.1. External Standard

$$y = ax + b$$

or

$$x = \frac{(y - b)}{a}$$

Where: y = Instrument response
x = Concentration
a = Slope
b = Intercept

10.6.3.2. Internal Standard

$$C_s = \frac{\left[\frac{A_s C_{is}}{A_{is}} - b\right]}{a}$$

Where: C_s = Concentration in the sample
A_s = Area of target peak in the sample
A_{is} = Area of internal standard in the sample
C_{is} = Concentration of the internal standard

10.6.4. Quadratic curve

The quadratic curve uses the following functions:

10.6.4.1. External standard

$$y = ax + cx^2 + b$$

Where c is the curvature

10.6.4.2. Internal Standard

$$y = a\left(\frac{A_s \times C_{is}}{A_{is}}\right) + c\left(\frac{A_s \times C_{is}}{A_{is}}\right)^2 + b$$

10.7. Evaluation of calibration curves

10.7.1. The percent relative standard error (%RSE) from the calibration curve is used to evaluate the initial calibration. This provides a measure of how much error is associated with using the calibration curve for quantitation.

10.7.2. The least squares regression line is calculated and used to calculate the predicted concentration for each level. The percent relative standard error is calculated as follows:

$$\%\,RSE = 100\% \times \sqrt{\frac{\sum_{i=1}^{N}\left[\frac{C_i - PC_i}{C_i}\right]^2}{(N-P)}}$$

Where:
N = Number of points in the curve
P = Number of parameters in the curve (= 1 for average response factor, 2 for linear, 3 for quadratic)
C_i = True concentration for level i
PC_i = Predicted concentration for level i

Note that when average response factors are used, %RSE is equivalent to %RSD.

10.8. The following requirements must be met for any calibration to be used:

- Response must increase with increasing concentration.
- If a curve is used, the intercept of the curve at zero response must be less than ± the reporting limit for the analyte.
- The average Relative Standard Error (RSD for average response factors) of the calibration points from the curve used must be ≤ 20%.
- Some data systems will not measure the %RSE from a linear or quadratic fit. For the linear case, the correlation coefficient may be used as an alternative to the %RSE, and must be greater than or equal to 0.990. For the quadratic case the Coefficient of Determination may be used, and must be greater or equal to 0.990.

Note: The Relative Standard Error (RSE) is superior to the Correlation Coefficient (r) and Coefficient of Determination (r^2) for testing the fit of a set of calibration points to a line. The lower points on a curve have little effect on r. As a result a curve may have a very good correlation coefficient (>0.995), while also having > 100% error at the low point.

10.9. Weighting of data points

10.9.1. In linear and quadratic calibration fits, the points at the lower end of the calibration curve have less absolute variance than points at the high concentration end of the curve. This can cause severe errors in quantitation at the low end of the calibration. However, in environmental analysis, accuracy at the low end of the curve is very important. For this reason it is preferable to increase the weighting of the lower concentration points. $1/\text{Concentration}^2$ weighting (often called $1/X^2$ weighting) will improve accuracy at the low end of the curve and should be used if the data system has this capability.

10.10. Non-standard analytes are sometimes requested. For these analytes, it may be acceptable to analyze a single standard at the reporting limit with each continuing calibration rather than a five point initial calibration. This action must be with client approval. If the analyte is detected in any of the samples, a five point initial calibration must be generated and the sample(s) reanalyzed for quantitation.

10.11. Calibration Verification

10.11.1. 12 hour Calibration

The working calibration curve or RF must be verified by the analysis of a mid point calibration standard at the beginning, after every 12 hours, and at the end of the analysis sequence. The center of each retention time window is updated with each 12 hour calibration.

10.11.2. Calibration Verification

It may be appropriate to analyze a mid point standard more frequently than every 12 hours. If these calibration verification standards are analyzed, requirements are the same as the 12 hour calibration with the exception that retention times are not updated.

10.11.3. Any individual compounds with %D $\leq$ 15% meet the calibration criteria. The calibration verification is also acceptable if the average of the %D for all the analytes is $\leq$ 15%. This average is calculated by summing all the absolute %D results in the calibration (including surrogates) and dividing by the number of analytes.

10.11.4. It is not necessary to run a calibration verification standard at the beginning of the sequence if samples are analyzed immediately after the completion of the initial calibration.

10.11.5. Samples quantitated by external standard methods must be bracketed by calibration verification standards that meet the criteria listed above. Bracketing is not necessary for internal standard methods.

10.11.6. If the analyst notes that a CCV has failed and can document the reason for failure (e.g. no purge, broken vial, carryover from the previous sample etc.) then a second CCV may be analyzed without any adjustments to the instrument. If this CCV meets criteria then the preceding samples have been successfully bracketed. If adjustments to the instrument are performed before the repeat CCV then the preceding samples have not been successfully bracketed but analysis may continue.

10.11.7. In general, it is not advisable to analyze repeat CCVs on unattended runs. If repeat CCVs are analyzed then the first will serve as the bracketing standard for the preceding samples and the last will serve as the CCV for the following samples.

10.11.8. If highly contaminated samples are expected it is acceptable to analyze blanks or primers at any point in the run.

10.11.9. % Difference calculation

% Difference for internal and external methods is calculated as follows

Internal Standard:

$$\%D = \frac{RF_c - \overline{RF}}{\overline{RF}} \times 100$$

External standard:

$$\%D = \frac{CF_c - \overline{CF}}{\overline{CF}} \times 100$$

Where RF_c and CF_c are the response and calibration factors from the continuing calibration

$\overline{RF}$ and $\overline{CF}$ are the average response and calibration factors from the initial calibration

10.11.10.% Drift calculation

% Drift is used for comparing the continuing calibration to a linear or quadratic curve. The criteria for % drift are the same as for % difference

$$\%\,Drift = \frac{Calculated\ Conc. - Theoretical\ Conc.}{Theoretical\ Conc.} \times 100\%$$

10.11.11.Corrective Actions for Continuing Calibration

If the overall average %D of all analytes is greater than ± 15% corrective action must be taken. This may include clipping the column, changing the liner or other minor instrument adjustments, followed by reanalyzing the standard. If the overall average %D still varies by more than ± 15%, a new calibration curve must be prepared.

10.11.12.Corrective Action for Samples

For internal standard methods, any samples injected after a standard not meeting the calibration criteria must be reinjected.

For external standard methods, any samples injected after the last good continuing calibration standard must be reinjected.

If the average %D for all the analytes in the calibration is over 15%, but all of the analytes requested for a particular sample have %D ≤ 15%, then the analysis is acceptable for that sample.

11. PROCEDURE

11.1. Extraction

Extraction procedures are referenced in the appendices.

11.2. Cleanup

Cleanup procedures are referenced in the appendices.

11.3. Gas Chromatography

Chromatographic conditions for individual methods are presented in the appendices.

11.4. Sample Introduction

In general, volatiles analytes are introduced using purge and trap as described in Appendix A. Semivolatile analytes are introduced by direct injection of the extract. Samples, standards, and QC must be introduced using the same procedure.

11.5. Analytical Sequence

An analytical sequence starts with an initial calibration or a daily calibration. Refer to the individual method appendices for method specific details of daily calibrations and analytical sequences.

11.5.1. The daily calibration includes analysis of standards containing all single response analytes and updating the retention time windows.

11.5.2. If there is a break in the analytical sequence of greater than 12 hours, a new analytical sequence must be started with a daily calibration.

11.6. Retention Time Windows

11.6.1. Retention time windows must be specified for all analytes. *A Fixed retention time windows (±.05 minutes) will be used for all GC methods. Alternatively, if it is determined through calculation that wider limits are necessary, the limits will be developed as follows:* Make an injection of all analytes of interest each day over a three day period. Calculate the standard deviation of the three retention times for each analyte (relative retention times may also be used). For multiresponse analytes (e.g., Aroclors) use the retention time of major peaks. Plus or minus three times the standard deviation of the retention times of each analyte defines the retention time window.

11.6.2. The center of the retention time window is the retention time from the last of the three standards. The centers of the windows are updated with the mid point of the initial calibration and each 12 hour calibration. The widths of the windows will remain the same until new windows are generated following the installation of a new column.

11.6.3. *Where calculated limits are being used, if* the retention time window as calculated above is less than +/- 0.05 minutes, use +/- 0.05 minutes as the retention time window. This allows for slight variations in retention times caused by sample matrix.

11.6.4. *Where calculated limits are being used, t*he laboratory must calculate new retention time windows each time a new column is installed. The new windows must be generated within one week of the installation of the new column. Until these standards have been run on the new column, the retention time windows from the old column may be used, updated with the retention times from the new initial calibration.

11.6.5. Corrective Action for Retention Times

The retention times of all compounds in each continuing calibration must be within the retention time windows established by the 12 hour calibration. If this condition is not met, all samples analyzed after the last compliant standard must be reanalyzed unless the following conditions are met for any compound that elutes outside the retention time window:

The retention time of that compound in the standard must be within a retention time range equal to twice the original window.

No peak that would be reportable may be present on the sample chromatogram within an elution time range equal to three times the original retention time window.

11.7. Daily Retention Time Windows

The center of the retention time windows determined in section 11.6 are adjusted to the retention time of each analyte as determined in the 12 hour calibration standards. (See the method 8081A and 8082 appendices for exceptions for multi-response components.) The retention time windows must be updated at the beginning of each analytical sequence and with each 12 hour calibration, but not for any other calibration verification standards.

11.8. Percent Moisture

Analytical results may be reported as dry or wet weight, as required by the client. Percent moisture must be determined if results will be reported as dry weight. Refer to SOP CORP-OP-0001 for determination of percent moisture.

11.9. Procedural Variations

Procedural variations are allowed only if deemed necessary in the professional judgment of the supervisor to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and approved by a supervisor and QA/QC manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file. The nonconformance is also addressed in the case narrative. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Qualitative Identification

12.1.1. Tentative identification occurs when a peak is found within the retention time window for an analyte, at a concentration above the reporting limit, or above the MDL if J flags are required. Normally confirmation is required on a second column, but if the detector is sufficiently specific or if the sample matrix is well enough defined, single column analysis may be adequate. In some cases GC/MS confirmation may be required. Client specific requirements may also define the need for second column confirmation and / or GC/MS confirmation. Refer to the appendices for test specific requirements for confirmation. Identification is confirmed if a peak is also present in the retention time window for that analyte on the confirmatory column, at a concentration greater than the reporting limit (MDL if J flag confirmation required).

12.1.2. Dual column quantitation

For confirmed results, two approaches are available to the analyst;
A) The primary column approach
Or
B) The better result approach
Both are acceptable to avoid the reporting of erroneous or unconfirmed data.

12.1.2.1. Primary column approach:

The result from the primary column is normally reported. The result from the secondary column is reported if any of the following three bulleted possibilities are true.

- There is obvious chromatographic interference on the primary column
- The result on the primary column is > 40% greater than the result on the secondary column
- Continuing or bracketing standard fails on the primary column but is acceptable on the secondary column. (If the primary column result is > 40% higher than the secondary and the primary column calibration fails, then the sample must be evaluated for reanalysis.)

12.1.2.2. Better result approach

The lower of the two results is normally reported. The lower result is considered better because the higher result is generally higher because of chromatographic interference. The higher result is reported if any of the following two bulleted possibilities are true.

- There is obvious chromatographic interference on the column with the lower result
- The continuing or bracketing calibration on the column with the lower result fails. (If the higher result is > 40% higher and the calibration on the column with the lower result fails, then the sample must be evaluated for reanalysis.)

12.1.3. If the Relative percent difference (RPD) between the response on the two columns is greater than 40%, or if the opinion of an experienced analyst is that the complexity of the matrix is resulting in false positives, the confirmation is suspect and the results are qualified. RPD is calculated using the following formula:

$$RPD = \frac{R_1 - R_2}{\frac{1}{2}(R_1 + R_2)} x100$$

Where R=Result

12.1.4. Multi-response Analytes

For multi-response analytes, the analyst should use the retention time window, but should rely primarily on pattern recognition. The pattern of peaks will normally serve as confirmation.

12.1.5. The experience of the analyst should weigh heavily in the interpretation of the chromatogram. For example, sample matrix or laboratory temperature fluctuation may result in variation of retention times.

12.2. Calibration Range

If concentrations of any analytes exceed the working range as defined by the calibration standards, then the sample must be diluted and reanalyzed. Dilutions should target the most concentrated analyte in the upper half (over 50% of the high level standard) of the calibration range. It may be necessary to dilute samples due to matrix.

12.3. Dilutions

Samples may be screened to determine the appropriate dilution for the initial run. If the initial diluted run has no hits or hits below 20% of the calibration range and the matrix allows for analysis at a lesser dilution, then the sample must be reanalyzed at a dilution targeted to bring the largest hit above 50% of the calibration range.

12.3.1. Guidance for Dilutions Due to Matrix

If the sample is initially run at a dilution and only minor matrix peaks are, then the sample should be reanalyzed at a more concentrated dilution. Analyst judgement is required to determine the most concentrated dilution that will not result in instrument contamination.

12.3.2. Reporting Dilutions

The most concentrated dilution with no target compounds above the calibration range will be reported. Other dilutions will only be reported at client request.

12.4. Interferences

If peak detection is prevented by interferences, further cleanup should be attempted. If no further cleanup is reasonable, then elevation of reporting levels and/or lack of positive identification must be addressed in the case narrative.

12.5. Internal Standard Criteria for Continuing Calibration

If internal standard calibration is used, then the internal standard response in a continuing calibration standard must be within 50 to 150% of the response in the mid level of the initial calibration.

12.6. Calculations

Capabilities of individual data systems may require the use of different formulas than those presented here. When this is the case, the calculations used must be shown to be equivalent and must be documented in an appendix attached to this document.

12.6.1. External Standard Calculations

12.6.1.1. Aqueous samples

$$Concentration\ (mg\ /\ L) = \frac{(A_x \times V_t \times D_f)}{(CF \times V_i \times V_s)}$$

Where:

A_x = Response for the analyte in the sample
V_i = Volume of extract injected, µL
D_f = Dilution factor
V_t = Volume of total extract, µL
V_s = Volume of sample extracted or purged, mL
CF = Calibration factor, area or height/ng, Section 10.1

12.6.1.2. Non-aqueous Samples

$$Concentration\ (mg\ /\ kg) = \frac{(A_x \times V_t \times D_f)}{(CF \times V_i \times W \times D)}$$

Where:

W = Weight of sample extracted or purged, g

$$D = \frac{100 - \%\,Moisture}{100}$$ (D = 1 if wet weight is required)

12.6.2. Internal Standard Calculations

12.6.2.1. Aqueous Samples

$$Concentration\ (mg\ /\ L) = \frac{(A_x \times C_{is} \times D_f)}{(A_{is} \times RF \times V_s)}$$

Where:

C_{is} = Amount of internal standard added, ng
A_{is} = Response of the internal standard
RF = Response factor for analyte

12.6.2.2. Non-aqueous Samples

$$Concentration\ (mg / kg) = \frac{(A_x \times C_{is} \times D_f)}{(A_{is} \times RF \times W \times D)}$$

12.6.3. Surrogate Recovery

Concentrations of surrogate compounds are calculated using the same equations as for the target compounds. The response factor from the initial calibration is used. Surrogate recovery is calculated using the following equation:

$$\%\ \text{Recovery} = \frac{Concentration\ (or\ amount)\ found}{Concentration\ (or\ amount)\ spiked} \times 100$$

13. METHOD PERFORMANCE

13.1. Method Detection Limit

Each laboratory must generate a valid method detection limit for each analyte of interest. The MDL must be below the reporting limit for each analyte. The procedure for determination of the method detection limit is given in 40 CFR Part 136, Appendix B, and further defined in QA Policy #: QA-005.

13.2. Initial Demonstration

Each laboratory must make a one time initial demonstration of capability for each individual method. Demonstration of capability for both soils and water matrices is required. This requires analysis of QC check samples containing all of the standard analytes for the method. For some tests it may be necessary to use more than one QC check mix to cover all analytes of interest.

13.2.1. Four aliquots of the QC check sample are analyzed using the same procedures used to analyze samples, including sample preparation. The concentration of the QC check sample should be equivalent to a mid level calibration.

13.2.2. Calculate the average recovery and standard deviation of the recovery for each analyte of interest. Compare these results with the acceptance criteria given in each appendix.

13.2.3. If any analyte does not meet the acceptance criteria, the test must be repeated. Only those analytes that did not meet criteria in the first test need to be evaluated. Repeated failure for any analyte indicates the need for the laboratory to evaluate the analytical procedure and take corrective action.

13.3. Training Qualification

The group/team leader has the responsibility to ensure that this procedure is performed by an analyst who has been properly trained in its use and has the required experience.

14. POLLUTION PREVENTION

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

15. WASTE MANAGEMENT

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

16. REFERENCES

Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW846, 3rd Edition, Final Update III, December 1996, Section 8000B

17. MISCELLANEOUS

17.1. Modifications from Reference Method

17.1.1. Chapter 1 of SW-846 states that the method blank should not contain any analyte of interest at or above the Method Detection Limit. This SOP states that the Method Blank must not contain any analyte of interest at or above the reporting limit. Common lab contaminants are allowed to be up to 5 times the reporting limit in the blank following consultation with the client.

17.2. Modifications from Previous Revision

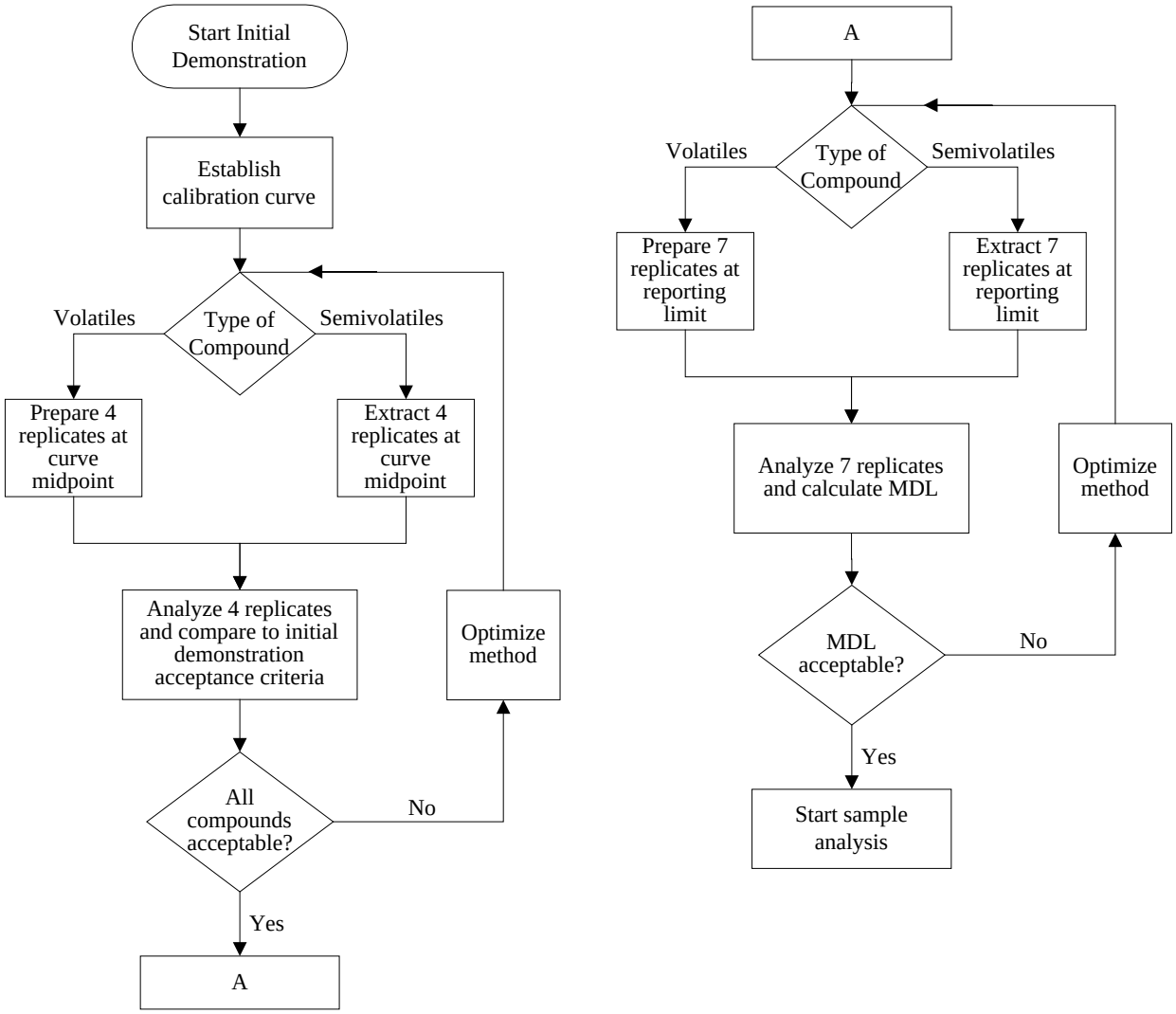
The calibration criteria in section 10.11 have been rewritten to improve consistency with SW-846 and to improve clarity.

17.3. Facility Specific SOPs

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

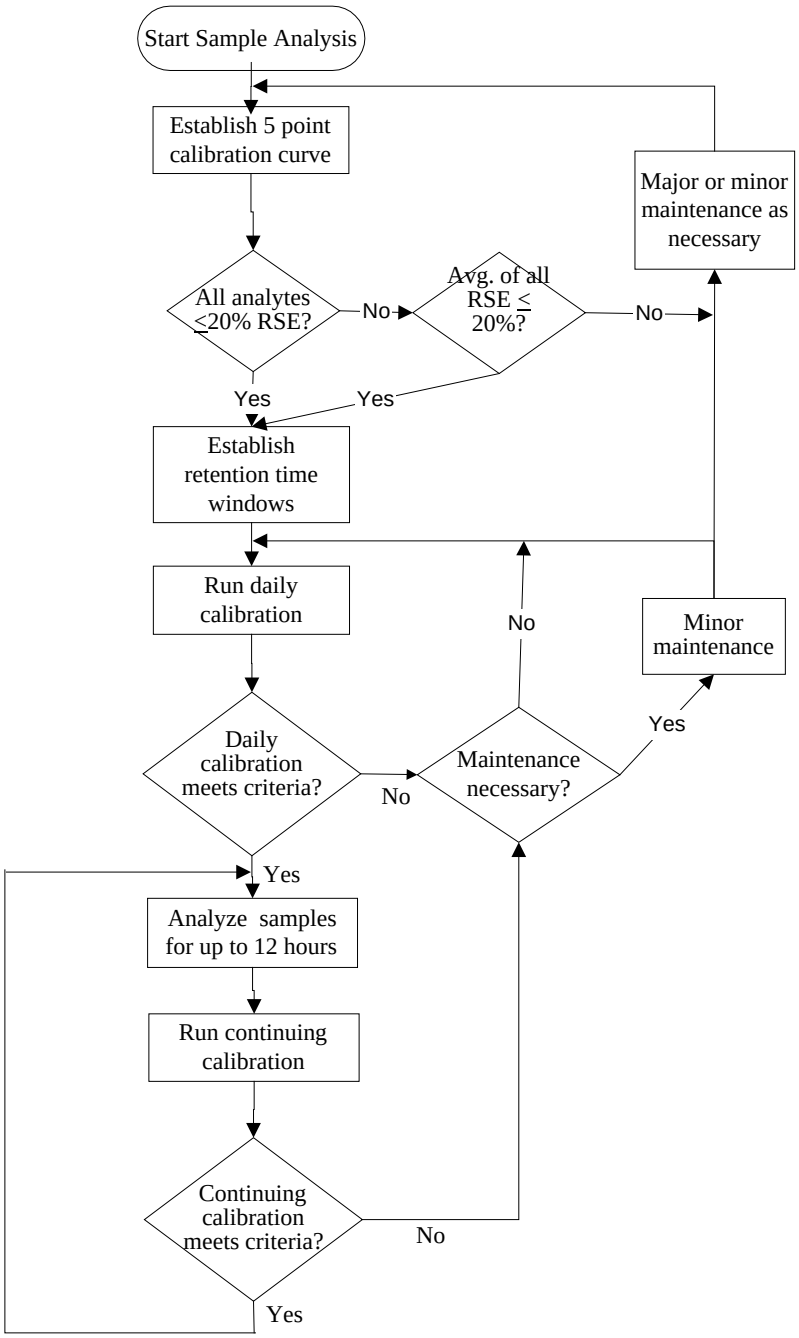
17.4. Flow Diagrams

17.4.1. Initial demonstration and MDL[1]



[1] This flow diagram is for guidance and cannot cover all eventualities. Consult the SOP text and a supervisor if in doubt.

17.4.2. Sample Analysis[1]



[1] This flow diagram is for guidance and cannot cover all eventualities. Consult the SOP text and a supervisor if in doubt.

1. SCOPE AND APPLICATION

1.1. This method describes sample preparation and extraction for the analysis of volatile organics by a purge and trap procedure, following method 8021B. However, where required by a client QAPP this section may also be used to analyze aromatic volatiles by discontinued methods 8020A and 8010B. All requirements of the 8000B section of this SOP must be met except when superseded by this Appendix. Refer to Table A-1 for the individual analytes normally determined by these procedures.

1.2. Compounds within the scope of this method have boiling points below 200°C and are soluble or slightly soluble in water. Classes of compounds best suited to purge-and-trap analysis include low molecular weight halogenated hydrocarbons, aromatics, ketones, nitriles, acetates, acrylates, ethers, and sulfides.

1.3. Water samples and soils samples with low levels of contamination may be analyzed directly by purge-and-trap extraction and gas chromatography. Higher concentrations of these analytes in soil may be determined by the medium level methanol extraction procedure.

1.4. This method also describes the preparation of water-miscible liquids, non-water-miscible liquids, solids, wastes, and soils/sediments for analysis by the purge-and-trap procedure.

2. SUMMARY OF METHOD

2.1. An inert gas is bubbled through the sample at ambient temperature or at 40°C (40°C required for low level soils), and the volatile components are transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent column where the volatile components are adsorbed. After purging is completed, the sorbent column is heated and backflushed with inert gas to desorb the components onto a gas chromatographic column. Analytes are detected using a photoionization Detector, an electrolytic conductivity detector or a combination of both.

2.2. For soil samples, a portion of the sample is dispersed in methanol to dissolve the volatile organic constituents. A portion of the methanolic solution is combined with water. It is then analyzed by purge-and-trap GC following the normal water method. If very low detection limits are needed for soil samples then direct purge using sodium bisulfate preservation may be necessary.

3. DEFINITIONS

Refer to the QAMP for definitions of terms used in this SOP.

4. INTERFERENCES

4.1. Refer to section 4 of the method 8000B part of this SOP for general information on chromatographic interferences.

4.2. Impurities in the purge gas, and from organic compounds out-gassing from the plumbing ahead of the trap, account for the majority of contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running laboratory reagent blanks. The use of non-TFE plastic tubing, non-TFE thread sealants, or flow controllers with rubber components in the purging device should be avoided.

4.3. Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride and fluorocarbons) through the septum seal of the sample vial during shipment and storage. A trip blank prepared from organic-free reagent water and carried through sampling and handling protocols serves as a check on such contamination.

4.4. Contamination by carryover can occur whenever high-concentration and low-concentration samples are analyzed sequentially. Whenever an unusually concentrated sample is analyzed, it should be followed by an analysis of organic-free reagent water to check for cross-contamination. The trap and other parts of the system are subject to contamination. Therefore, frequent bake-out and purging of the system may be required.

4.5. When utilizing an autosampler system which has multiple ports for sample analysis, it is likely that only a single stage or port may be contaminated by a highly concentrated sample. If a port is suspect, a water blank should be analyzed to verify lack of contamination. If the water blank and subsequent blanks on that port show contamination consistent with the concentrated sample, further maintenance is required. This may include replacing or cleaning the multi-port valve, transfer lines, etc.

4.6. A holding blank is kept in the sample refrigerator. This is analyzed and replaced every 14 days. If the holding blank does not meet the method blank criteria, the source of contamination must be found and corrected. Evaluation of all samples analyzed in the 14 day period prior to the analysis of the contaminated holding blank is required.

4.7. Acidification of samples may result in hydrolysis of 2-chloroethyl vinyl ether.

5. SAFETY

5.1. Refer to section 5 of the Method 8000B section of this SOP for general safety requirements.

5.2. Often, purge vessels on purge-and-trap instrumentation are pressurized by the time analysis is completed. Therefore, vent the pressure prior to removal of these vessels to prevent the contents from spraying out.

5.3. The toxicity or carcinogenicity of each chemical used in this procedure has not been fully defined. Additional health and safety information can be obtained from the MSDS files maintained in the laboratory. The following specific hazards are known:

Methanol -- Flammable and toxic

5.4. Methanol shall not be used in a CaptAir hood.

6. EQUIPMENT AND SUPPLIES

6.1. Microsyringes -- 10µL, 25µL, 100µL, 250µL, 500µL, and 1000µL. These should be equipped with a 20 gauge (0.006" ID) needle. These will be used to measure and dispense methanolic solutions and aqueous samples.

6.2. Gas tight syringes -- 5 mL and 25 mL. Used for measuring sample volumes.

6.3. Purge and Trap Apparatus -- A device capable of extracting volatile compounds, trapping on a sorbent trap, and introducing onto a gas chromatograph.

6.4. Purge and Trap Autosampler -- In order to maintain high sample throughput, an autosampler is highly recommended.

6.5. Trap -- The trap used is dependent on the class of compound to be analyzed. Refer to Table A-2 for suggested traps for specific tests.

6.6. Purge Vessels -- These are dependent on the purge and trap unit/autosampler used. Both disposable culture tubes (needle sparge units) and specially designed vessels with fritted bottoms may be used. Follow the manufacturer’s suggestions for configuration.

6.7. Columns - Refer to Table A-2 for details of columns.

6.8. Volumetric flasks, Class A: 5 mL to 250 mL

6.9. pH paper

6.10. Balance capable of weighing to 0.01g for samples.

7. REAGENTS AND SUPPLIES

7.1. Refer to the method 8000B section of this SOP for general requirements for reagents and supplies.

7.2. Organic Free Water

Organic free water is defined as water in which an interferent is not observed at the reporting limit of the compounds of interest. Suggested methods for generating organic free water include:

- Filtration through a carbon bed.
- Continuously sparging water with helium or nitrogen.
- Use of commercial water purification systems.

Other methods may be used, so long as the requirement that the water not show any interferences is met. The procedure used should be documented in a lab specific attachment.

7.3. Sodium Bisulfate

7.4. Methanol -- Purge and Trap Grade

7.5. Standards

Refer to tables A-5 and A-6 for details of surrogate, matrix spiking and internal standards. Calibration standard levels are not specified, since they may depend on the sensitivity and linear range of specific detectors. However, the low level standard must be equivalent to the reporting limits specified in Table A-1.

7.5.1. Volatile standards are prepared by injecting a measured volume of the stock standard into a syringe containing the appropriate volume of organic free water. The calibration standard is then loaded into the purge device.

8. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1. Holding times for all volatile analysis are 14 days from sample collection.

8.2. Water samples are normally preserved at pH < 2 with 1:1 hydrochloric acid. If residual chlorine is present, 2 drops of 10% sodium thiosulfate are added.

1.3. Solid samples are field preserved with sodium bisulfate solution for low level analysis, or with methanol for medium level analysis. Soil samples can also be taken using the EnCore™ sampler and preserved in the lab within 48 hours of sampling. At specific client request, unpreserved soil samples may be accepted.

8.4. There are several methods of sampling soil. The recommended method, which provides the minimum of field difficulties, is to take a EnCore sample. (The 5 g or 25 g sampler can be used, depending on client preference). Following shipment back to the lab the soil is preserved in methanol. This is the medium level procedure. If very low detection limits are needed (< 50 µg/kg for most analytes) then it will be necessary to use two additional 5 g EnCore samplers or to use field preservation.

8.5. Sample collection for medium level analysis using EnCore samplers.

8.5.1. Ship one 5 g (or 25 g) EnCore sampler per field sample position.

8.5.2. An additional bottle must be shipped for percent moisture determination.

8.5.3. When the samples are returned to the lab, extrude the (nominal) 5g (or 25 g) sample into a tared VOA vial containing 5 mL methanol (25 mL methanol for the 25 g sampler). Obtain the weight of the soil added to the vial and note on the label.

8.5.4. Add the correct amount of surrogate spiking mixture. (Add 100 µL of 250 µg/mL solution for a nominal 25 g sample, 20µL for a nominal 5 g sample.)

8.5.5. Add the correct amount of matrix spiking solution to the matrix spike and matrix spike duplicate samples. (Add 100 µL of 250 µg/mL solution for a nominal 25 g sample, 20µL for a nominal 5 g sample.) The addition of spike introduces a slight error, (0.4%) which can be neglected, into the calculations.

8.5.6. Prepare an LCS for each batch by adding the correct amount of matrix spiking solution to clean methanol. (100 µL of spike to 25 mL methanol or 20 µL spike to 5 mL methanol).

8.5.7. Shake the samples for two minutes to distribute the methanol throughout the soil.

8.5.8. Allow to settle, then remove a portion of methanol and store in a clean Teflon capped vial at $4+2^{o}C$ until analysis.

8.6. Sample collection for medium level analysis using field methanol preservation

8.6.1. Prepare a VOA vial by adding 5 mL purge and trap grade methanol. (If a 25 g sample is to be used, add 25 mL methanol to the VOA vial).

8.6.2. Seal the bottle and attach a label.

8.6.3. Weigh the bottle to the nearest 0.01g and note the weight on the label.

8.6.4. Ship with appropriate sampling instructions.

8.6.5. Each sample will require an additional bottle with no preservative for percent moisture determination.

8.6.6. At client request, the methanol addition and weighing may also be performed in the field.

8.6.7. When the samples are returned to the lab, obtain the weight of the soil added to the vial and note on the label.

8.6.8. Add the correct amount of surrogate spiking mixture. (Add 100 µL of 250 µg/mL solution for a nominal 25 g sample, 20µL for a nominal 5 g sample.)

8.6.9. Add the correct amount of matrix spiking solution to the matrix spike and matrix spike duplicate samples. (Add 100 µL of 250 µg/mL solution for a nominal 25 g sample, 20µL for a nominal 5 g sample.) The addition of spike introduces a slight error, (0.4%) which can be neglected, into the calculations.

8.6.10. Prepare an LCS for each batch by adding the correct amount of matrix spiking solution to clean methanol. (100 µL of spike to 25 mL methanol or 20 µL spike to 5 mL methanol).

8.6.11. Shake the samples for two minutes to distribute the methanol throughout the soil.

8.6.12. Allow to settle, then remove a portion of methanol and store in a clean Teflon capped vial at 4+2°C until analysis.

8.7. Low level procedure

8.7.1. If low detection limits are required (typically < 50 µg/kg) sodium bisulfate preservation must be used. However, it is also necessary to take a sample for the medium level (methanol preserved) procedure, in case the concentration of analytes in the soil is above the calibration range of the low-level procedure.

8.7.2. A purge and trap autosampler capable of sampling from a sealed vial is required for analysis of samples collected using this method. (Varian Archon or O.I. 4552).

8.7.3. The soil sample is taken using a 5g EnCore sampling device and returned to the lab. It is recommended that two EnCore samplers be used for each field sample position, to allow for any reruns than may be necessary. A separate sample for % moisture determination is also necessary.

8.7.4. Prepare VOA vials by adding a magnetic stir bar, approximately 1 g of sodium bisulfate and 5 mL of reagent water.

8.7.5. Seal the vial and attach a label. The label must not cover the neck of the vial or the autosampler will malfunction.

8.7.6. Weigh the vial to the nearest 0.01g and note the weight on the label.

8.7.7. Extrude the soil sample from the EnCore sampler into the prepared VOA vial. Reweigh the vial to obtain the weight of soil and note on the label.

8.7.8. **Note:** Soils containing carbonates may effervesce when added to the sodium bisulfate solution. If this is the case at a specific site, add 5 mL of water instead, and freeze at $\geq$ -10°C until analysis.

8.7.9. Alternatively the sodium bisulfate preservation may be performed in the field. Ship at least two vials per sample. The field samplers must determine the weight of soil sampled. Each sample will require an additional bottle with no preservative for percent moisture determination, and an additional bottle preserved with methanol for the medium level procedure.

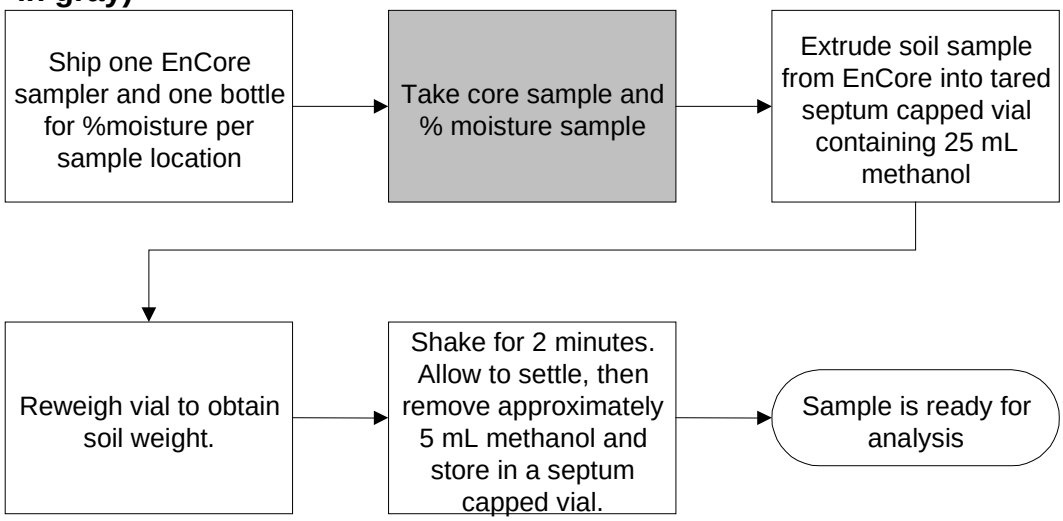
8.8. Aqueous samples are stored in glass containers with Teflon lined septa at 4°C +/- 2°C, with minimum headspace.

8.9. Medium level solid extracts are aliquoted into 2 - 5 mL glass vials with Teflon lined caps and stored at 4°C +/- 2°C. The extracts are stored with minimum headspace.

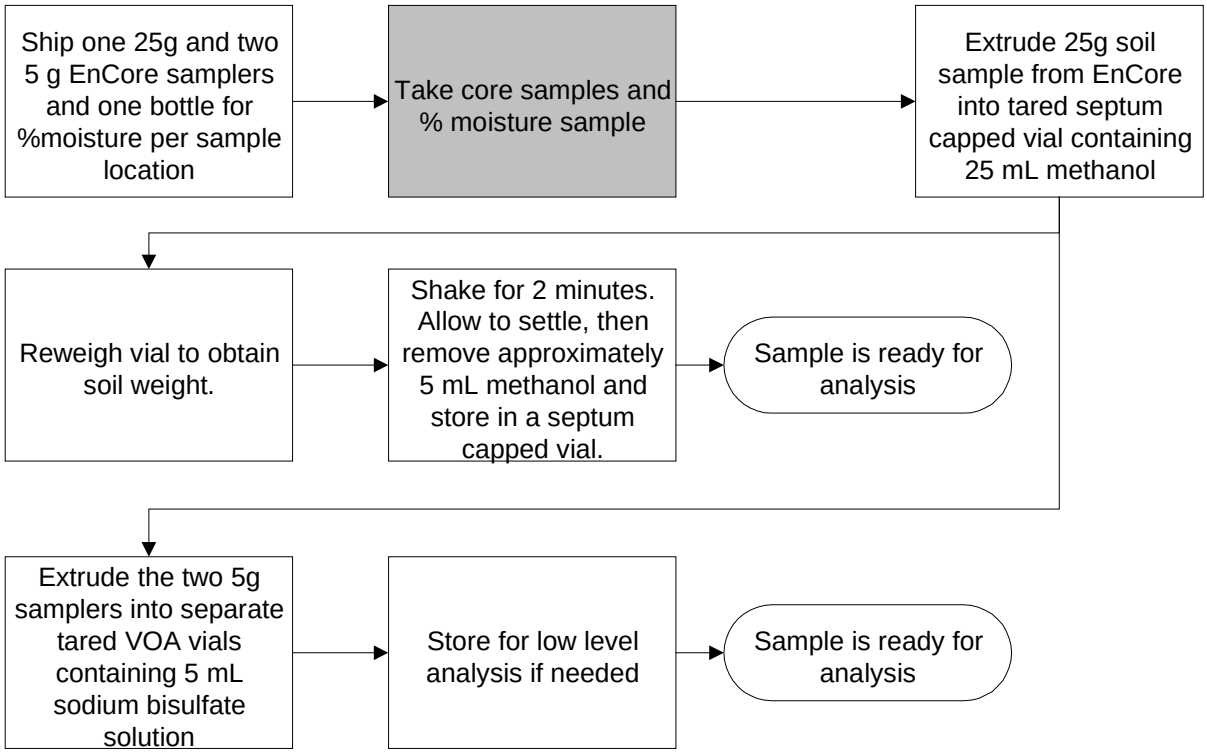
8.10. The maximum holding time is 14 days from sampling until the sample is analyzed. (Samples that are found to be unpreserved still have a 14 day holding time. However they should be analyzed as soon as possible. The lack of preservation should be addressed in the case narrative). Maximum holding time for the EnCore sampler (before the sample is added to methanol or sodium bisulfate) is 48 hours.

8.11. A holding blank is stored with the samples. This is analyzed and replaced if any of the trip blanks show any contamination. Otherwise it is replaced every 14 days.

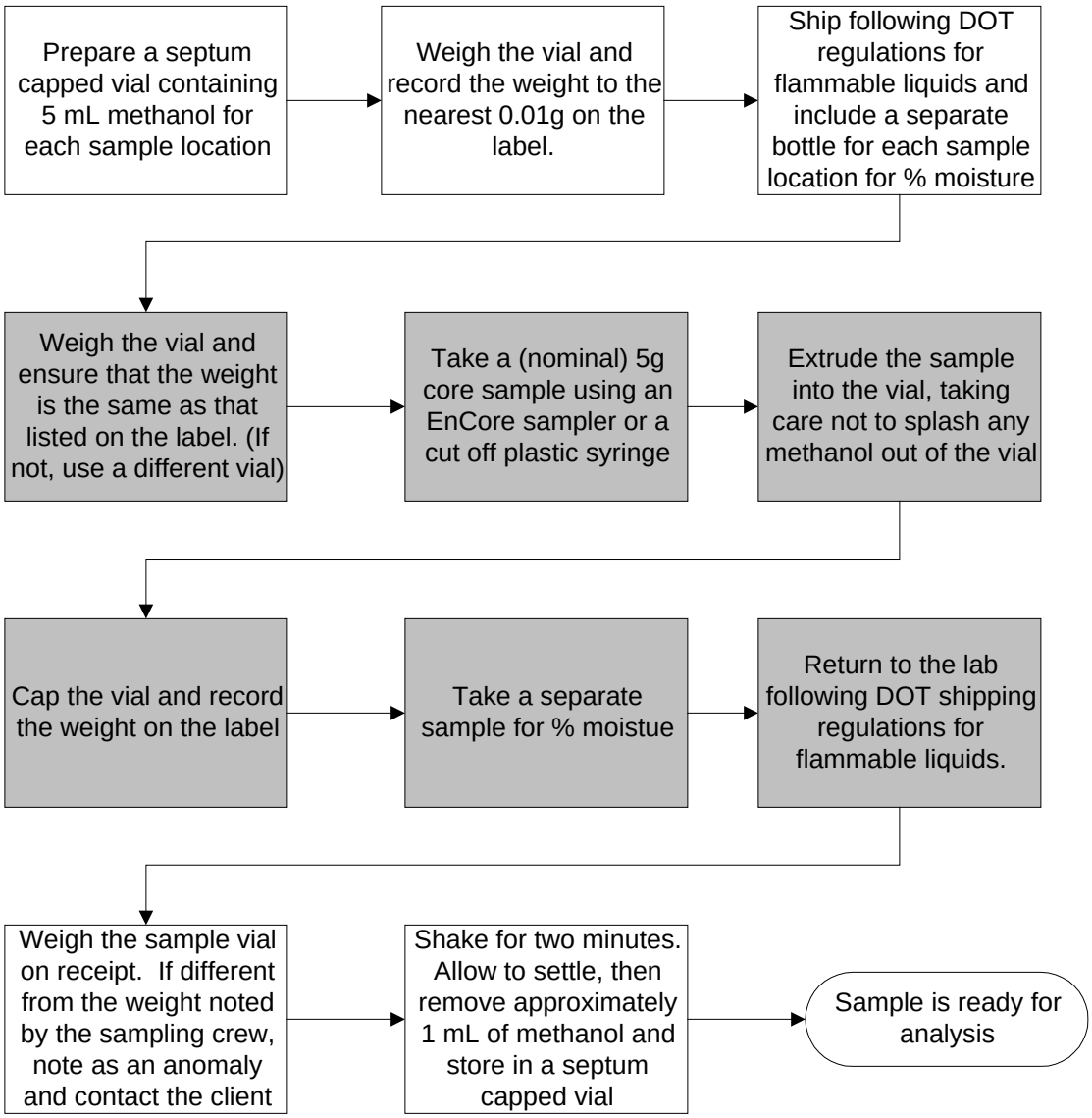
EnCore procedure when low level is not required (field steps in gray)



EnCore procedure when low level is required



Field methanol extraction procedure (field steps in gray)



9. QUALITY CONTROL

9.1. Refer to the method 8000B section of this SOP, section 9, for general quality control procedures, including batch definition, requirements for method blanks, LCS, matrix spikes, surrogates, and control limits.

10. CALIBRATION AND STANDARDIZATION

10.1. Refer to the method 8000B section of this SOP, section 10, for general calibration procedures.

10.2. Gas Chromatograph Operating Conditions

Various column configurations are possible. If dual column confirmation is necessary, the sample may be split using a Y splitter at the injector end to direct the sample to two columns and two detectors. For simultaneous determination of aromatic and halogenated volatiles, a single column is used and the PID and ELCD detectors are connected in series.

10.2.1. Refer to Table A-2, A-3 and A-4 for GC operating conditions.

10.3. Initial Calibration

10.3.1. Refer to Section 10 of the 8000B section of this SOP for details of initial calibration criteria.

10.3.2. Low level soil samples must be purged at 40°C, therefore the calibration curve must also be purged at 40°C. In addition, the low level soil calibration solutions should contain approximately the same amount of sodium bisulfate as the samples.

10.3.3. The low level calibration must be at the reporting limit or below. The remaining standards encompass the working range of the detector.

10.3.4. Calibrate the instrument using the same volume that will be used during sample analysis.

10.4. Calibration Verification

10.4.1. A mid level calibration standard is used for the calibration verification. The gases have 20 % D criteria rather than the 15% used for other analytes.

10.4.2. A calibration verification run is performed after every 10 samples for this method.

10.4.3. Bracketing of samples with calibration verification runs is only necessary for external standard analysis.

11. PROCEDURE

11.1. Refer to the method 8000B section of this SOP for general procedural requirements.

11.2. Analytical Sequence

The analytical sequence starts with an initial calibration of at least five points, or a 12 hour calibration that meets % difference criteria from an existing initial calibration.

11.3. Confirmation

The PID and ELCD detectors are sufficiently selective that second column confirmation is not always necessary. Requirements for second column confirmation should be decided in consultation with the client. If the PID and ELCD are used in series confirmatory information for many analytes can be gained by comparing the relative response from the two detectors.

11.4. Aqueous Sample Analysis (Purge and Trap units using sparge vessels)

11.4.1. Depending on the sensitivity of the instrument and capabilities of the purge and trap device, 5, 10, 20, or 25 mL sample volumes may be analyzed. A 5 mL sample volume is recommended.

11.4.2. Rinse a 5 mL (or 25 mL for larger sample volumes) gas-tight syringe with organic free water. Fill the syringe with the sample to be analyzed, and compress to volume.

11.4.3. Check and document the pH of the sample remaining in the VOA vial after loading the syringe.

11.4.4. This procedure invalidates the contents of the VOA vial for further analysis, unless an aliquot is transferred to a smaller VOA vial with no headspace (e.g., 20 mL) at the same time the analysis aliquot is removed.

11.4.5. Spike with the appropriate volume of surrogate/internal standard solution and spike solution (if required) through the barrel of the syringe. The method blank is spiked with surrogates only, the LCS and matrix spikes with the surrogate and matrix spiking solutions. Refer to Tables A-5 and A-6 for volumes and concentrations of spiking solutions.

11.4.6. Load onto the purge and trap device and start the run.

11.4.7. If the initial analysis of a sample or a dilution of the sample has a concentration of analytes that exceeds the initial calibration range, the sample must be reanalyzed at a higher dilution. When a sample has a high response for a compound, analysis should be followed by an organic free water blank. It is recognized that during automated unattended analysis, this may not occur. If any potential carryover hits are present in samples following highly contaminated samples, the sample must be reanalyzed to determine if any of these hits are a result of carryover or are actually present in the sample.

11.4.8. Dilutions may be made in gas tight syringes unless the volume of sample used is less than 5 µL, in which case dilution in volumetric flasks will be necessary.

11.4.8.1. Spike with the same volume of surrogate/internal standard solution as used for undiluted samples prior to loading onto the purge and trap device.

11.4.8.2. For Matrix spike / matrix spike duplicates where the sample requires dilution, the sample is spiked <u>after</u> the dilution is performed.

11.5. Aqueous and Soil Sample Analysis (Purge and Trap units that sample directly from the VOA vial)

11.5.1. Units which sample from the VOA vial should be equipped with a module which automatically adds surrogate and internal standard solution to the sample prior to purging the sample.

11.5.2. If the autosampler uses automatic IS/SS injection, no further preparation of the VOA vial is needed. Otherwise the internal and surrogate standards must be added to the vial. *Note:* Aqueous samples with high amounts of sediment present in the vial may not be suitable for analysis on this instrumentation, or they may need to analyzed as soils.

11.5.3. Sample remaining in the vial after sampling with one of these mechanisms is no longer valid for further analysis. A fresh VOA vial must be used for further sample analysis.

11.5.4. Check the pH of the sample remaining in the VOA vial after analysis is completed.

11.6. Low-Level Solids Analysis using discrete autosamplers

Note: This technique may seriously underestimate analyte concentration and must not be used except at specific client request for the purpose of comparability with previous data. It is no longer part of SW-846.

This method is based on purging a heated sediment/soil sample mixed with reagent water containing the surrogate and, if applicable, internal and matrix spiking standards. Analyze all reagent blanks and standards under the same conditions as the samples (e.g., heated). The calibration curve is also heated during analysis. Purge temperature is 40°C.

11.6.1. Do not discard any supernatant liquids. Mix the contents of the container with a narrow metal spatula.

11.6.2. Weigh out 5 g (or other appropriate aliquot) of sample into a disposable culture tube or other purge vessel. Record the weight to the nearest 0.1 g. If method sensitivity is demonstrated, a smaller aliquot may be used. Do not use aliquots less than 1.0 g. If the sample is contaminated with analytes such that a purge amount less than 1.0 g is appropriate, use the medium level method described in section 11.7.

11.6.3. Connect the purge vessel to the purge and trap device.

11.6.4. Rinse a 5 mL gas-tight syringe with organic free water, and fill. Compress to 5 mL. Add surrogate/internal standard (and matrix spike solutions if required.) (See Tables A-5, A-6, A-7 and A-8.) Add directly to the sample from 11.6.2.

11.6.5. The above steps should be performed rapidly and without interruption to avoid loss of volatile organics.

11.6.6. Add the heater jacket or other heating device and start the purge and trap unit.

11.6.7. Soil samples that have low IS recovery when analyzed (<50%) should be reanalyzed once to confirm matrix effect. If external standard calibration is used, samples with surrogate recovery below the control limit should be reanalyzed once to confirm matrix effect.

11.7. Methanol Extract Soils

11.7.1. Rinse a gas-tight syringe with organic free water. Fill the syringe with the same volume of organic free water as used in the calibrations. Add no more than 2% (v/v) (100 µL for a 5 mL purge) methanolic extract (from Section 8.5 or 8.6) to the syringe. Add internal standard (if used). Load the sample onto the purge and trap device and analyze as for aqueous samples. If less than 5µL of methanolic extract is to be added to the water, dilute the methanolic extract such that a volume greater than 5µL will be added to the water in the syringe.

12. DATA ANALYSIS AND CALCULATIONS

Refer to section 12 of the 8000B section of this SOP.

13. METHOD PERFORMANCE

13.1. Performance limits for the four replicate initial demonstration of capability required under Section 13.1 of the 8000B section of this SOP are 70-130%, with %RSD $\leq$ 25% The spiking level should be 20 µg/L. These limits are for guidance, and certain “difficult” analytes may fall outside this range. Any outliers must be discussed with STL’s Director of Quality Assurance and/or Director of Technology before proceeding with sample analysis.

14. POLLUTION PREVENTION

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

15. WASTE MANAGEMENT

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

16. REFERENCES

16.1. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW846, 3rd Edition, Final Update III, December 1996, Sections 5000, 5030B, 5035 and 8021B

17. MISCELLANEOUS

17.1. Modifications from Reference Method

17.2. Modifications from previous revision

17.2.1. No revisions were made to this appendix.

17.3. Facility Specific SOPs

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

17.4. Tables

Table A-1					
Standard Analyte List					
Test	Compound	CAS number	Reporting Limit, µg/L or µg/kg		
			Aqueous	Low Soil	Medium Soil
Halogenated volatiles by 8021B	Bromodichloromethane	75-27-4	1.0	1.0	50
	Bromoform	75-25-2	1.0	1.0	50
	Bromomethane	74-83-9	1.0	1.0	50
	Carbon Tetrachloride	56-23-5	1.0	1.0	50
	Chlorobenzene	108-90-7	1.0	1.0	50
	Chloroethane	70-00-3	1.0	1.0	50
	2-Chloroethyl vinyl ether	110-75-8	5.0	5.0	250
	Chloroform	67-66-3	1.0	1.0	50
	Chloromethane	74-87-3	1.0	1.0	50
	Dibromochloromethane	124-48-1	1.0	1.0	50
	1,2-Dichlorobenzene	95-50-1	1.0	1.0	50
	1,3-Dichlorobenzene	541-73-1	1.0	1.0	50
	1,4-Dichlorobenzene	106-46-7	1.0	1.0	50
	Dichlorodifluoromethane	75-71-8	1.0	1.0	50
	1,1-Dichloroethane	75-34-3	1.0	1.0	50
	1,2-Dichloroethane	107-06-2	1.0	1.0	50
	1,1-Dichloroethene	75-45-4	1.0	1.0	50
	cis-1,2 Dichloroethene	156-59-4	1.0	1.0	50
	trans-1,2-Dichloroethene	156-60-5	1.0	1.0	50
	Dichloromethane(DCM)	75-09-2	5.0	5.0	250
	1,2-Dichloropropane	78-87-5	1.0	1.0	50
	cis-1,3-Dichloropropene	10061-01-5	1.0	1.0	50
	trans-1,3-Dichloropropene	10061-02-6	1.0	1.0	50
	1,1,2,2-Tetrachloroethane	79-34-5	1.0	1.0	50
	Tetrachloroethene	127-18-4	1.0	1.0	50
	1,1,1-Trichloroethane	71-55-6	1.0	1.0	50
	1,1,2-Trichloroethane	79-00-5	1.0	1.0	50
	Trichloroethene	79-01-6	1.0	1.0	50
	Trichlorofluoromethane	75-69-4	1.0	1.0	50
	Vinyl Chloride	75-01-4	1.0	1.0	50
Additional halogenated volatiles	Benzyl Chloride	100-44-7	5.0	5.0	250
	Bromobenzene	108-86-1	1.0	1.0	50
	Dibromomethane	74-95-3	1.0	1.0	50
	1,1,1,2-Tetrachloroethane	630-20-6	1.0	1.0	50
	1,2,3-Trichloropropane	96-18-4	1.0	1.0	50
BTEX by 8021B	Benzene	71-43-2	1.0	1.0	50
	Ethyl Benzene	100-41-4	1.0	1.0	50
	Toluene	108-88-3	1.0	1.0	50
	Xylenes (total)	1330-20-7	1.0	1.0	50
Aromatic volatiles by 8021B	Benzene	71-43-2	1.0	1.0	50

Table A-1

Standard Analyte List

Test	Compound	CAS number	Reporting Limit, µg/L or µg/kg		
			Aqueous	Low Soil	Medium Soil
	Chlorobenzene	108-90-7	1.0	1.0	50
	1,2-Dichlorobenzene	75-34-3	1.0	1.0	50
	1,3-Dichlorobenzene	107-06-2	1.0	1.0	50
	1,4-Dichlorobenzene	75-45-4	1.0	1.0	50
	Ethyl Benzene	100-41-4	1.0	1.0	50
	Toluene	108-88-3	1.0	1.0	50
	Xylenes (total)	1330-20-7	1.0	1.0	50
Additional aromatic and unsaturated volatiles	1,2,4 Trimethylbenzene	95-63-6	1.0	1.0	50
	1,3,5 Trimethylbenzene	108-67-8	1.0	1.0	50
	Acetone	67-64-1	10	10	500
	MEK (2-butanone)	78-93-3	5.0	5.0	250
	MIBK (4-methyl-2-pentanone)	108-10-1	5.0	5.0	250
	Naphthalene	91-20-3	2.0	2.0	250
	Styrene	100-42-5	1.0	1.0	50
	Methyl tert-butyl ether (MTBE)	1634-04-4	1.0	1.0	50
Combined halogenated and aromatic volatiles by 8021B	Benzene	71-43-2	1.0	1.0	50
	Bromobenzene	108-86-1	1.0	1.0	50
	Bromochloromethane	74-97-5	1.0	1.0	50
	Bromodichloromethane	75-27-4	1.0	1.0	50
	Bromoform	75-25-2	1.0	1.0	50
	Bromomethane	74-83-9	1.0	1.0	50
	n-butylbenzene	104-51-8	1.0	1.0	50
	sec-Butylbenzene	135-98-8	1.0	1.0	50
	tert-Butylbenzene	98-06-6	1.0	1.0	50
	Carbon Tetrachloride	56-23-5	1.0	1.0	50
	Chlorobenzene	108-90-7	1.0	1.0	50
	Chlorodibromomethane	124-48-1	1.0	1.0	50
	Chloroethane	75-00-3	1.0	1.0	50
	Chloroform	67-66-3	1.0	1.0	50
	Chloromethane	74-87-3	1.0	1.0	50
	2-Chlorotoluene	95-49-8	1.0	1.0	50
	4-Chlorotoluene	106-43-4	1.0	1.0	50
	1,2-Dibromo-3-Chloropropane(DBCP)	96-12-8	1.0	1.0	50
	1,2-Dibromoethane(EDB)	106-93-4	1.0	1.0	50
	Dibromomethane	74-95-3	1.0	1.0	50
	1,2-Dichlorobenzene	95-50-1	1.0	1.0	50
	1,3-Dichlorobenzene	541-73-1	1.0	1.0	50
	1,4-Dichlorobenzene	106-46-7	1.0	1.0	50
	Dichlorodifluoromethane	75-71-8	1.0	1.0	50
	1,1-Dichloroethane	75-34-3	1.0	1.0	50
	1,2-Dichloroethane	107-06-2	1.0	1.0	50
	1,1-Dichloroethene	75-35-4	1.0	1.0	50
	cis-1,2-Dichloroethene	156-59-4	1.0	1.0	50
	trans-1,2-Dichloroethene	156-60-5	1.0	1.0	50
	1,2-Dichloropropane	78-87-5	1.0	1.0	50

Table A-1
Standard Analyte List

Test	Compound	CAS number	Reporting Limit, µg/L or µg/kg		
			Aqueous	Low Soil	Medium Soil
	1,3-Dichloropropane	142-28-9	1.0	1.0	50
	2,2-Dichloropropane	590-20-7	1.0	1.0	50
	1,1-Dichloropropene	563-58-6	1.0	1.0	50
	cis-1,3-Dichloropropene	10061-01-5	1.0	1.0	50
	trans-1,3-Dichloropropene	10061-02-6	1.0	1.0	50
	Ethylbenzene	100-41-4	1.0	1.0	50
	Hexachlorobutadiene	87-68-3	1.0	1.0	50
	Isopropylbenzene	98-82-8	1.0	1.0	50
	p-Isopropyltoluene	99-87-6	1.0	1.0	50
	Methylene Chloride	75-09-2	5.0	5.0	250
	Naphthalene	91-20-3	2.0	2.0	250
	n-Propylbenzene	10306501	1.0	1.0	50
	Styrene	100-42-5	1.0	1.0	50
	1,1,1,2-Tetrachloroethane	630-20-6	1.0	1.0	50
	1,1,2,2-Tetrachloroethane	79-34-5	1.0	1.0	50
	Tetrachloroethene	127-18-4	1.0	1.0	50
	Toluene	108-88-3	1.0	1.0	50
	1,2,3-Trichlorobenzene	87-61-6	1.0	1.0	50
	1,2,4-Trichlorobenzene	120-82-1	1.0	1.0	50
	1,1,1-Trichloroethane	71-55-6	1.0	1.0	50
	1,1,2-Trichloroethane	79-00-5	1.0	1.0	50
	Trichloroethene	79-01-6	1.0	1.0	50
	Trichlorofluoromethane	75-69-4	1.0	1.0	50
	1,2,3-Trichloropropane	96-18-4	1.0	1.0	50
	1,2,4-Trimethylbenzene	95-63-6	1.0	1.0	50
	1,3,5-Trimethylbenzene	108-67-8	1.0	1.0	50
	Vinyl Chloride	75-01-4	1.0	1.0	50
	Xylenes (total)	1330-20-7	1.0	1.0	50

Table A-2
Recommended Conditions for Aromatic Volatiles

Parameter	**Recommended Conditions**
Temperature program	50°C, 1min, 10°C/min to 200°C,1min
Column 1	Rtx-502.2 or DB-502.2 60m x 0.53mm 3.0um
Column 2	Rtx-1 or DB-1 60m x 0.53mm 3.0 um
Carrier gas	Helium or hydrogen
Purge Flow / time	40 mL/min, 11 minutes
Desorb Temp / time	180°C, 2 minutes (220°C for Vocarb 3000)
Bake Time / temp	200°C, 12 minutes (230°C for Vocarb 3000)
Transfer line / valve temp	115°C

Table A-3
Recommended Conditions for Method Halogenated Volatiles

Parameter	Recommended Conditions
Temperature program	35°C, 12 min, then 4°C/min to 200°C, hold for 5 min
Column 1	DB-VRX or RTX-502.2 105m x 0.53 mm id df = 3.0um
Column 2	DB-1 or RTX-1 105m x 0.53 mm ID df = 3.0um
Column 3	Rtx - Volatiles 120m x 0.53mm ID df=2.0um
Carrier gas	Helium
Purge Flow / time	40 mL/min, 11 minutes
Desorb Temp / time	180°C, 2 minutes (220°C for Vocarb 3000)
Bake Time / temp	200°C, 12 minutes (230°C for Vocarb 3000)
Transfer line / valve temp	115°C

Table A-4
Recommended Conditions for Method Combined Aromatic and Halogenated Volatiles

Parameter	Recommended Conditions
Temperature program	35°C, 12 min, then 4°C/min to 200°C, hold for 5 min
Column 1	DB-VRX or RTX-502.2 105m x 0.53 mm id df = 3.0um
Column 2	DB-1 or RTX-1 105m x 0.53 mm ID df = 3.0um
Column 3	Rtx - Volatiles 120m x 0.53mm ID df=2.0um
Carrier gas	Helium
Purge Flow / time	40 mL/min, 11 minutes
Desorb Temp / time	180°C, 2 minutes (220°C for Vocarb 3000)
Bake Time / temp	200°C, 12 minutes (230°C for Vocarb 3000)
Transfer line / valve temp	115°C

Table A-5
Surrogate and Internal Standard Concentrations

Standard	Components	Working Solution µg/mL	Spike amount µL (for 5 mL purge)	Final concentration µg/L (µg/kg)
Aromatic volatiles IS/SS	4-Chlorotoluene (SS) 1-Chloro-4-fluorobenzene (IS)	20 40	5	20 40
Halogenated volatiles IS/SS	4-chlorotoluene (SS) 1-Chloro-4-fluorobenzene (IS)	20 40	5	20 40
Combined Aromatic and halogenated volatiles IS/SS	Fluorobenzene (SS)	20	5	20
	1,4-Dichlorobutane (SS)	20	5	20
	1-Chloro-4-fluorobenzene (IS)	40	10	40

It may be necessary to select different surrogates in order to minimize sample interferences. 1-chloro-4-fluorobenzene and 4-chlorotoluene are fairly well resolved from analytes listed in this SOP. However 4-chlorotoluene may sometimes be requested as a target analyte. Other surrogates that may be considered, and issues associated with their use are:

Bromochloromethane: Elutes very close to chloroform and cis-1,2-dichloroethene on the 502.2 column. May be a target analyte.

1,2-Bromochloroethane:

1-Chloro-2-fluorobenzene: Elutes close to ethylbenzene on DB-1 or Rtx-1 and close to m,p-xylene on 502.2

a,a,a-Trifluorotoluene: Good for aromatic volatiles, coelutes or very close to trichloroethene

Bromofluorobenzene: Close to 1,1,2,2-trichloroethane and 1,2,3-trichloropropane on the 502.2 column. Good on DB-1 or Rtx-1.

2-Bromo-1-chloropropane: May coelute with 1,1,2-trichloroethane

Table A-6
Concentrations for LCS and MS/MSD compounds

Standard	Components	Working Solution µg/mL	Spike amount µL (5 mL purge)	Final concentration µg/L (µg/kg)
Aromatic	Benzene	20	5	20
	Toluene	20		20
	Chlorobenzene	20		20
Halogenated	Chlorobenzene	20	5	20
	1,1-Dichloroethene	20		20
	Trichloroethene	20		20
Combination aromatic / halogenated	Benzene	20	5	20
	Toluene	20		20
	Chlorobenzene	20		20
	1,1-Dichloroethene	20		20
	Trichloroethene	20		20

1. SCOPE AND APPLICATION

This SOP Appendix describes procedures to be used when SW-846 Method 8081A is applied to the analysis of organochlorine pesticides by GC/ECD. This Appendix may also to be applied when discontinued SW-846 Method 8080A is requested, and is applicable to extracts derived from any matrix which are prepared according to the appropriate STL sample extraction SOPs. (CORP-OP-0001)

Table B-1 lists compounds which are routinely determined by this method and gives the Reporting Limits (RL) for each matrix. RLs given are based on the low level standard and the sample preparation concentration factors. Matrix interferences may result in higher RLs than those listed.

At client request, this method may also be used for the analysis of PCBs (Arochlors) in combination with pesticides, although these are normally analyzed following method 8082, as described in Appendix C of this SOP. In any event, if samples for PCB analysis do not need the acid clean up procedure, then the same injection may be used for method 8081B and 8082, assuming all calibration and QC requirements for both methods are met. Extracts that have been acid cleaned may not be analyzed for pesticides, since several of the pesticides will be degraded.

2. SUMMARY OF METHOD

This method presents conditions for the analysis of prepared extracts of organochlorine pesticides. The pesticides are injected onto the column and separated and detected by electron capture detection. Quantitation may be by internal or external standard methods.

3. DEFINITIONS

Refer to the QAMP for definitions of terms used in this document.

4. INTERFERENCES

4.1. Refer to the method 8000B section of this SOP for information regarding chromatographic interferences.

4.2. Interferences in the GC analysis arise from many compounds amenable to gas chromatography that give a measurable response on the electron capture detector. Phthalate esters, which are common plasticizers, can pose a major problem in the determinations. Interferences from phthalates are minimized by avoiding contact with any plastic materials.

4.3. Sulfur will interfere and can be removed using procedures described in SOP CORP-OP-0001.

4.4. Interferences co-extracted from samples will vary considerably from source to source. The presence of interferences may raise quantitation limits for individual samples. Specific cleanups may be performed on the sample extracts, including florisil cleanup (Method 3620), Gel Permeation Chromatography (Method 3640), and Sulfur cleanup (Method 3660). These cleanup procedures are included in SOP # CORP-OP-0001. Use or hexane / acetone as the extraction solvent (rather than hexane / methylene chloride) will reduce the amount of interferences extracted.

5. SAFETY

5.1. Refer to section 5 of the Method 8000B SOP for general safety requirements.

5.2. Aroclors have been classified as a potential carcinogen under OSHA. Concentrated solutions of Aroclors must be handled with extreme care to avoid excess exposure. Contaminated gloves and clothing must be removed immediately. Contaminated skin surfaces must be washed thoroughly.

5.3. All ^{63}Ni sources shall be leak tested every six months, or in accordance with the manufacturer's general radioactive material license.

5.4. All ^{63}Ni sources shall be inventoried every six months. If a detector is missing, the Director, EH&S shall be immediately notified and a letter sent to the NRC or local state agency.

6. EQUIPMENT AND SUPPLIES

6.1. Refer to Section 6 of the 8000B section of this SOP. A ^{63}Ni electron capture detector is required.

6.2. Refer to Table B-2 for analytical columns.

6.3. Microsyringes, various sizes, for standards preparation, sample injection, and extract dilution.

7. REAGENTS AND STANDARDS

7.1. Refer to the method 8000B section of this SOP for general requirements for reagents and supplies.

7.2. Refer to Table B-3 for details of calibration standards.

7.3. Surrogate Standards

Tetrachloro-m-xylene and decachlorobiphenyl are the surrogate standards. Refer to tables B-5 and B-6 for details of surrogate standards.

7.4. Column Degradation Evaluation Mix

A mid-level standard containing 4,4'-DDT and Endrin and not containing any of their breakdown products must be prepared for evaluation of degradation of these compounds by the GC column and injection port. This mix must be replaced after one year, or whenever corrective action to columns fails to eliminate the breakdown of the compounds, whichever is shorter. This solution also contains the surrogates. Refer to Table B-4 for details of the column degradation evaluation mix.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

Refer to Section 8 of the 8000B section of this SOP.

9. QUALITY CONTROL

Refer to Section 9 of the 8000B section of this SOP.

10. CALIBRATION AND STANDARDIZATION

10.1. Refer to Section 10 of the 8000B section of this SOP for general calibration requirements.

10.2. Refer to Table B-2 for details of GC operating conditions. The conditions listed should result in resolution of all analytes listed in Table B-1 on both columns. Closely eluting pairs are DDE and Dieldrin on the Rtx-5 or DB-5 column and Endosulfan II and DDD on the 1701 column.

10.3. Column Degradation Evaluation

Before any calibration runs, either initial or 12 hour, The column evaluation mix must be injected before each initial or daily calibration. The degradation of DDT and endrin must be calculated (see equations 9 and 10) and each shown to be less than 15% before calibration can proceed. This is only necessary if the target compound list includes DDT, Endrin, or any of their degradation products.

If the breakdown of DDT and/or endrin exceeds the limits given above, corrective action must be taken. This action may include:

- Replacement of the injection port liner or the glass wool.
- Cutting off a portion of the injection end of a capillary column.

- Replacing the GC column.

10.4. Initial Calibration

Refer to Section 10 of the 8000B section of this SOP for details of calibration procedures.

10.4.1. Refer to Table B-8 for the initial calibration analytical sequence.

10.4.2. The response for each single-peak analyte will be calculated by the procedures described in the general method for GC analysis.

10.4.3. The surrogate calibration curve is calculated from the Individual AB mix. Surrogates in the other calibration standards are used only as retention time markers. If there are resolution problems, then the A and B mixes may be analyzed separately.

10.4.4. For multi-component pesticides:

Single point calibration is used for multicomponent pesticides (typically toxaphene and technical chlordane). Two options are possible; the same quantitation option must be used for standards and samples. Refer to section 12.3 for guidance on which option to use.

10.4.5. For multicomponent analytes, the mid level standard must be analyzed as part of the initial calibration. This single point calibration is used to quantitate multicomponent analytes.

10.4.6. The analyst may include a full 5 point calibration for any of the multicomponent analytes with the initial calibration.

10.5. 12 hour Calibration Verification

The 12 hour calibration verification sequence must be analyzed within 12 hours of the start of the initial calibration and at least once every 12 hours thereafter if samples are being analyzed. If more than 12 hours have elapsed since the injection of the last sample in the analytical sequence, a new analytical sequence must be started with a 12 hour calibration. A mid level calibration standard is used for the 12 hour calibration. Refer to the 8000B section of this SOP for acceptance criteria.

10.5.1. At a minimum, the 12 hour calibration includes analysis of the breakdown mix followed by mid level standards of any single and multicomponent analytes.

10.5.2. The retention time windows for any analytes included in the 12 hour calibration are updated.

10.6. Continuing Calibration

The AB calibration mix is analyzed as the continuing calibration standard. At a minimum, this is analyzed after every 20 samples, including matrix spikes, LCS, and method blanks. If 12 hours elapse analyze the 12 hour standard sequence instead. The continuing calibration standard need not include multicomponent analytes. If instrument drift is expected due to sample matrix or other factors, it may be advisable to analyze the continuing calibration standard more frequently.

10.6.1. A mid level calibration standard is used for the continuing calibration.

11. PROCEDURE

11.1. Refer to the method 8000B section of this SOP for general procedural requirements.

11.2. Extraction

The extraction procedure is described in SOP No. CORP-OP-0001.

11.3. Cleanup

Cleanup procedures are described in SOP No. CORP-OP-0001.

11.4. Suggested gas chromatographic conditions are given in Table B-2.

11.5. Allow extracts to warm to ambient temperature before injection.

11.6. The suggested analytical sequence is given in Table B-8.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Refer to the 8000B section of this SOP for identification and quantitation of single component analytes.

12.2. Identification of Multicomponent Analytes

Retention time windows are also used for identification of multi-component analytes, but the "fingerprint" produced by major peaks of those compounds in the standard is used in tandem with the retention times to identify the compounds. The ratios of the areas of the major peaks are also taken into consideration. Identification of these compounds may be made even if the retention times of the peaks in the sample fall outside of the retention time windows of the standard, if in the analyst's judgment the fingerprint (retention time and peak ratios) resembles the standard chromatogram.

12.3. Quantitation of Multicomponent Analytes

Use 3-10 major peaks or total area for quantitation as described in section 10.4.4, initial calibration of multicomponent analytes.

12.3.1. If there are no interfering peaks within the envelope of the multicomponent analyte, the total area of the standards and samples may be used for quantitation. Any surrogate or extraneous peaks within the envelope must be subtracted from the total area.

12.3.1.1. Multiple peak option

This option is particularly valuable if toxaphene is identified but interferences make quantitation based on total area difficult. Select 3-10 major peaks in the analyte pattern. Calculate the response using the total area or total height of these peaks. Alternatively, find the response of each of the 3-10 peaks per multi-peak pesticide, and use these responses independently, averaging the resultant concentrations found in samples for a final concentration result. When using this option, it is appropriate to remove peaks that appear to be coeluting with contaminant peaks from the quantitation. (i.e. peaks which are significantly larger than would be expected from the rest of the pattern.)

Chlordane may be quantitated either using the multiple peak option (12.3.1.1) total area option (12.3.1.2.) or by quantitation of the major components, α-chlordane, γ-chlordane and heptachlor.

12.3.1.2. Total area option

The total area of the standards and samples may be used for quantitation of multicomponent analytes. Any surrogate or extraneous peaks within the envelope must be subtracted from the total area. This option should not be used if there are significant interference peaks within the multicomponent pattern in the samples. The retention time window for total area measurement must contain at least 90% of the area of the analyte.

12.4. Second column confirmation multi-component analytes will only be performed when requested by the client, because the appearance of the multiple peaks in the sample usually serves as a confirmation of analyte presence.

12.5. Surrogate recovery results are calculated and reported for decachlorobiphenyl (DCB) unless it is determined that sample interference has adversely affected the quantitation of that surrogate. Tetrachloro-m-xylene (TCMX) recovery is reported in lieu of DCB in samples having the interference, and also may be used in samples in which DCB recovery is low. Corrective action is only necessary if DCB and TCMX are both outside of acceptance limits.

12.6. Calculation of Column Degradation/% Breakdown (%B)

$$DDT\ \%B = \frac{A_{DDD} + A_{DDE}}{A_{DDD} + A_{DDE} + A_{DDT}} x\ 100$$

where:
A_{DDD}, A_{DDE}, and A_{DDT} = the response of the peaks for 4,4'-DDD, 4,4'-DDE, and 4,4'-DDT in the column degradation evaluation mix.

$$Endrin\ \%B = \frac{A_{EK} + A_{EA}}{A_{EK} + A_{EA} + A_{E}} x\ 100$$

where:
A_{EK}, A_{EA}, and A_{E} = the response of endrin ketone, endrin aldehyde, and endrin in the column degradation evaluation mix.

13. METHOD PERFORMANCE

13.1. Performance limits for the four replicate initial demonstration of capability required under Section 13.1 of the main body of this SOP are presented in Table B-7. The spiking level should be equivalent to a mid level calibration.

14. POLLUTION PREVENTION

Refer to section 14 of the 8000B section of this SOP.

15. WASTE MANAGEMENT

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

16. REFERENCES

SW846, Update III, December 1996, Method 8081A

17. MISCELLANEOUS

17.1. Modifications from Reference Method

None

17.2. Modifications from Previous Revisions

17.2.1. No revisions were made to this appendix.

17.3. Tables

Table B-1
Standard Analyte list and Reporting Limits

Compound	Reporting Limit, µg/L or µg/kg		
	water	soil	waste
Aldrin	0.05	1.7	50
α-BHC	0.05	1.7	50
β-BHC	0.05	1.7	50
δ-BHC	0.05	1.7	50
γ-BHC (Lindane)	0.05	1.7	50
α-Chlordane	0.05	1.7	50
γ-Chlordane	0.05	1.7	50
Chlordane (technical)	0.5	17	500
4,4'-DDD	0.05	1.7	50
4,4'-DDE	0.05	1.7	50
4,4'-DDT	0.05	1.7	50
Dieldrin	0.05	1.7	50
Endosulfan I	0.05	1.7	50
Endosulfan II	0.05	1.7	50
Endosulfan Sulfate	0.05	1.7	50
Endrin	0.05	1.7	50
Endrin Aldehyde	0.05	1.7	50
Heptachlor	0.05	1.7	50
Heptachlor Epoxide	0.05	1.7	50
Methoxychlor	0.1	3.3	100
Toxaphene	2.0	67	2000
APPENDIX IX ADD ONs			
Diallate	1.0	33	1000
Isodrin	0.1	3.3	100
Chlorobenzillate	0.1	3.3	100
Kepone[1]	1.0	33	1000

[1] Kepone is sometimes requested for analysis by method 8081A. However kepone may produce peaks with broad tails that elute later than the standard by up to a minute (presumably due to hemi-acetal formation). As a result kepone analysis by 8081A is unreliable and not recommended. Analysis by method 8270C is a possible alternative. Note: alpha chlordane, gamma chlordane, and endrin ketone are not required for some projects.

The following concentration factors are assumed in calculating the Reporting Limits:

	Extraction Vol.	Final Vol.
Ground water	1000 mL	10 mL
Low-level Soil	30 g	10 mL
High-level soil / waste	1 g	10 mL

Table B-2	
Parameter	**Recommended Conditions**
Injection port temp	220°C
Detector temp	325°C
Temperature program	120°C for 1 min, 8.5°C/min to 285°C, , 6 min hold
Column 1	Rtx-CLPesticides 30m x 0.32mm id, 0.5µm
Column 2	Rtx-35 30m x 0.32 mm id, 0.5µm
Column 3	DB-608, 30m X 0.32 mm, 0.25µm
Injection	2µL
Carrier gas	Helium or Hydrogen
Make up gas	Nitrogen
Y splitter	Restek or J&W or Supelco glass tee

Table B-3

Calibration Levels ng/mL

	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6[2]
Individual Mix AB[1]						
Aldrin	5	10	25	50	100	200
g-BHC (Lindane)	5	10	25	50	100	200
Heptachlor	5	10	25	50	100	200
Methoxychlor	10	20	50	100	200	400
Dieldrin	5	10	25	50	100	200
Endosulfan I	5	10	25	50	100	200
Endosulfan II	5	10	25	50	100	200
4,4'-DDT	5	10	25	50	100	200
Endrin Aldehyde	5	10	25	50	100	200
Endrin Ketone	5	10	25	50	100	200
β-BHC	5	10	25	50	100	200
δ-BHC	5	10	25	50	100	200
α-BHC	5	10	25	50	100	200
4,4'-DDD	5	10	25	50	100	200
4,4'-DDE	5	10	25	50	100	200
Endosulfan Sulfate	5	10	25	50	100	200
Endrin	5	10	25	50	100	200
α-Chlordane [3]	5	10	25	50	100	200
γ-Chlordane [3]	5	10	25	50	100	200
Multicomponent Standards						
Chlordane (Technical)			250[4]			
Toxaphene			1000[5]			
Surrogates are included with all the calibration mixes at the following levels:						
Tetrachloro-m-xylene	5	10	25	50	100	200
Decachlorobiphenyl	5	10	25	50	100	200

[1] Standards may be split into an A and B mix if resolution of all compounds on both columns is not obtained.
[2] Level 6 is optional and should only be used if linearity can be maintained on the instrument to this level.
[3] Compounds may be used in lieu of running a daily technical Chlordane standard for samples that are non-detect for technical Chlordane.
[4] This standard may be used for quantitation of technical chlordane between 50 and 1000 ng/mL. If the chlordane is more concentrated, the extract must be diluted and reanalyzed.
[5] This standard may be used for quantitation of toxaphene between 200 and 4000 ng/mL. If the toxaphene is more concentrated, the extract must be diluted and reanalyzed.

Table B-4	
Column Degradation Evaluation Mix ng/mL	
Component	Concentration
4,4'-DDT	25
Endrin	25
Tetrachloro-m-xylene (Surrogate)	20
Decachlorobiphenyl (Surrogate)	20

Table B-5			
LCS/Matrix Spike and Surrogate Spike levels µg/L or µg/kg			
	Aqueous	Soil	Waste
gamma BHC (Lindane)	0.20	6.67	200
Aldrin	0.20	6.67	200
Heptachlor	0.20	6.67	200
Dieldrin	0.50	16.7	500
Endrin	0.50	16.7	500
4,4'DDT	0.50	16.7	500
Tetrachloro-m-xylene (Surrogate)	0.20	6.67	200
Decachlorobiphenyl (Surrogate)	0.20	6.67	200

Table B-6		
LCS/Matrix Spike and Surrogate Spike levels for TCLP µg/L or µg/kg		
	Aqueous	Waste
Heptachlor	5	500
Heptachlor epoxide	5	500
Lindane	5	500
Endrin	5	500
Methoxychlor	10	1000

Table B-7
Suggested Analytical Sequence

Initial Calibration

Solvent blank (optional)	
Breakdown Mix	
Individual mix AB	All levels
Technical Chlordane	Level 3[1]
Toxaphene	Level 3[1]
Solvent blank	
Up to 20 samples unless 12 hours comes first)	
Solvent blank (optional)	
Individual mix AB	Mid level (Continuing calibration)
Samples	
After 12 hours:	
Breakdown mix	
Individual mix AB	
Any other single component analytes	
Any multicomponent analytes	

[1] A five point curve for any of the multicomponent analytes may be included
If Arochlors are included, a 5 point calibration for Arochlor 1016/1260 should be included with the initial calibration and a single point for the other Arochlors. The mid point 1016/1260 mix is included with the daily calibration (every 12 hours).

12 hour Calibration

At least every 12 hours, counting from the start of the initial calibration, or from the start of the last daily calibration, the retention time windows must be updated using the Individual mix AB, and the breakdown mix must be run before the continuing calibration.

Table B-8		
Performance limits, four replicate initial demonstration of capability		
Compound	Initial demonstration, mean recovery limits	Initial demonstration, RSD limits
Aldrin	46-112	21
alpha-BHC	51-122	24
beta-BHC	61-120	32
delta-BHC	49.5-118.5	36
gamma-BHC	57-116	23
Chlordane	44.8-108.6	20
4,4'-DDD	52-126	28
4,4'-DDE	46-120	27.5
4,4'-DDT	54-137	36
Dieldrin	42.5-124.5	38
Endosulfan I	43-141	24.5
Endosulfan II	78-171	61
Endosulfan Sulfate	62-132	27
Endrin	49-126	37
Heptachlor	57-100	20
Heptachlor Epoxide	43.5-131.5	25.4
Toxaphene	44.4-111.2	20

1. SCOPE AND APPLICATION

1.1. This SOP Appendix describes procedures to be used when SW-846 Method 8000B is applied to the analysis of polychlorinated biphenyls (PCB) by GC/ECD. This Appendix is to be applied when SW-846 Method 8082 is requested, and is applicable to extracts derived from any matrix which are prepared according to the appropriate STL sample extraction SOPs. (CORP-OP-0001). The PCBs are determined and quantitated as Arochlor mixes.

Table C-1 lists compounds which are routinely determined by this method and gives the Reporting Limits (RL) for each matrix. RLs given are based on the low level standard and the sample preparation concentration factors. Matrix interferences may result in higher RLs than those listed.

Note: SW-846 method 8082 provides incomplete guidance for determination of individual PCB congeners. This SOP does not include directions for congener specific analysis.

2. SUMMARY OF METHOD

This method presents conditions for the analysis of prepared extracts of PCBs. The PCBs are injected onto the column and separated and detected by electron capture detection. Quantitation is by the external standard method.

3. DEFINITIONS

Refer to the QAMP for definitions of terms used in this document.

4. INTERFERENCES

4.1. Refer to the method 8000B section of this SOP for information regarding chromatographic interferences.

4.2. Interferences in the GC analysis arise from many compounds amenable to gas chromatography that give a measurable response on the electron capture detector. Phthalate esters, which are common plasticizers, can pose a major problem in the determinations. Interferences from phthalates are minimized by avoiding contact with any plastic materials.

4.3. Sulfur will interfere and can be removed using procedures described in SOP CORP-OP-0001.

4.4. Interferences co-extracted from samples will vary considerably from source to source. The presence of interferences may raise quantitation limits for individual samples. Specific cleanups may be performed on the sample extracts, including florisil cleanup (Method 3620), Gel Permeation Chromatography (Method 3640), and Sulfur cleanup (Method 3660). These cleanup procedures are included in SOP # CORP-OP-0001.

5. SAFETY

5.1. Refer to section 5 of the Method 8000B SOP for general safety requirements.

5.2. Aroclors have been classified as a potential carcinogen under OSHA. Concentrated solutions of Aroclors must be handled with extreme care to avoid excess exposure. Contaminated gloves and clothing must be removed immediately. Contaminated skin surfaces must be washed thoroughly.

5.3. All ^{63}Ni sources shall be leak tested every six months, or in accordance with the manufacturer's general radioactive material license.

5.4. All ^{63}Ni sources shall be inventoried every six months. If a detector is missing, the Director, EH&S shall be immediately notified and a letter sent to the NRC or local state agency.

6. EQUIPMENT AND SUPPLIES

6.1. Refer to Section 6 of the 8000B section of this SOP. A ^{63}Ni electron capture detector is required.

6.2. Refer to Table C-2 for analytical columns.

6.3. Microsyringes, various sizes, for standards preparation, sample injection, and extract dilution.

7. REAGENTS AND STANDARDS

7.1. Refer to the method 8000B section of this SOP for general requirements for reagents and supplies. All standards for this method must be replaced

7.2. Refer to Table C-3 for details of calibration standards.

7.3. Surrogate Standards

Tetrachloro-m-xylene and decachlorobiphenyl are the surrogate standards. Other surrogates may be used at client request. Refer to Table C-4 for details of surrogate standards.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

Refer to Section 8 of the 8000B section of this SOP.

9. QUALITY CONTROL

Refer to Section 9 of the 8000B section of this SOP.

10. CALIBRATION AND STANDARDIZATION

10.1. Refer to Section 10 of the 8000B section of this SOP for general calibration requirements.

10.2. Initial Calibration

10.2.1. Refer to Table C-5 for the initial calibration analytical sequence.

10.2.2. The response for each Arochlor will be calculated by the procedures described in the general method for GC analysis, with the following modifications.

10.2.3. A five point calibration of the Arochlor 1016/1260 mix is generated with at least mid level single points for the other Aroclor mixes. The average response factor is used to quantitate Arochlors 1260 and 1016, other Arochlors are quantitated from the mid level single point.

10.2.4. The analyst may include a full 5 point calibration for any of the Arochlors with the initial calibration.

10.2.5. The high and low standards for the initial 5 point calibration of 1016 / 1260 define the acceptable quantitation range for the other Arochlors. If any Arochlor is determined above this concentration the extract must be diluted and reanalyzed.

10.2.6. If the analyst knows that a specific Arochlor is of interest for a particular project, that Arochlor may be used for the five point calibration rather than the 1016 / 1260 mix.

10.2.7. The surrogate calibration curve is calculated from the Aroclor 1016/1260 mix. Surrogates in the other calibration standards are used only as retention time markers.

10.2.8. Two options are possible for quantitation of Aroclors. The same quantitation option must be used for standards and samples.

10.2.8.1. Multiple peak option

Select 3-10 major peaks in the analyte pattern. Calculate the response using the total area or total height of these peaks. Alternatively, find the response of each of the 3-10 peaks per Aroclor, and use these responses independently, averaging the resultant concentrations found in samples for a final concentration result. When using this option, it is appropriate to remove peaks that appear to be coeluting with contaminant peaks from the quantitation. (i.e. peaks which are significantly larger than would be expected from the rest of the pattern.)

10.2.8.2. Total area option

The total area of the standards and samples may be used for quantitation of multicomponent analytes. Any surrogate or extraneous peaks within the envelope must be subtracted from the total area. This option should not be used if there are significant interference peaks within the multicomponent pattern in the samples. The retention time window for total area measurement must contain at least 90% of the area of the analyte.

10.3. 12 hour Calibration

The 12 hour calibration verification must be analyzed within 12 hours of the start of the initial calibration and at least once every 12 hours thereafter if samples are being analyzed. If there is a break in the analytical sequence of greater than 12 hours, then a new continuing calibration run must be analyzed before proceeding with the sequence. If more than 12 hours have elapsed since the injection of the last sample in the analytical sequence, a new analytical sequence must be started with a 12 hour calibration.

10.3.1. At a minimum, the 12 hour calibration includes analysis of the Arochlor 1260 / 1016 mix.

10.3.2. It is adequate to verify calibration with a mixture of Aroclors 1016 and 1260. If a specific Aroclor is expected, it should be included in the daily calibration check.

10.3.3. The retention time windows for any analytes included in the daily calibration are updated.

10.3.4. For this method samples must be bracketed with successful calibration verification runs.

10.4. Calibration verification

The Arochlor 1260/1016 calibration mix is analyzed as the calibration verification standard. This is analyzed after every 20 samples, including matrix spikes, LCS, and method blanks. (Depending on the type of samples, it may be advisable to analyze verifications more frequently in order to minimize reruns.).

10.4.1. A mid level standard is used for the calibration verification.

11. PROCEDURE

11.1. Refer to the method 8000B section of this SOP for general procedural requirements.

11.2. Extraction

The extraction procedure is described in SOP No. CORP-OP-0001.

11.3. Cleanup

Cleanup procedures are described in SOP No. CORP-OP-0001.

11.4. Suggested gas chromatographic conditions are given in Table C-2.

11.5. Allow extracts to warm to ambient temperature before injection.

11.6. The suggested analytical sequence is given in Table C-5.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Identification of Arochlors

Retention time windows are used for identification of Arochlors, but the "fingerprint" produced by major peaks of those analytes in the standard is used in tandem with the retention times for identification. The ratios of the areas of the major peaks are also taken into consideration. Identification may be made even if the retention times of the peaks in the sample fall outside of the retention time windows of the standard, if in the analyst's judgment the fingerprint (retention time and peak ratios) resembles the standard chromatogram.

A clearly identifiable Arochlor pattern serves as confirmation of single column GC analysis. However, if the pattern is not clear, or if no historical data for the site is available, then second column confirmation must be performed.

12.2. Quantitation of Arochlors

Use 3-10 major peaks or total area for quantitation

If the analyst believes that a combination of Aroclor 1254 and 1260, or a combination of 1242, 1248 and 1232 is present, then only the predominant Arochlor is quantitated and reported, but the suspicion of multiple Aroclors is discussed in the narrative. If well separated Aroclor patterns are present, then both Aroclors are quantitated and reported.

12.3. If there are no interfering peaks within the envelope of the Arochlor, the total area of the standards and samples may be used for quantitation. Any surrogate or extraneous peaks within the envelope must be subtracted from the total area.

12.4. Second column confirmation of Aroclors will only be performed when requested by the client, or if the pattern is not clear or there is no historical data leading to a suspicion that Arochlors may be present. The appearance of the multiple peaks in the sample usually serves as a confirmation of Aroclor presence.

12.5. Surrogate recovery results are calculated and reported for decachlorobiphenyl (DCB) unless it is determined that sample interference has adversely affected the quantitation of that surrogate. Tetrachloro-m-xylene (TCMX) recovery is reported in lieu of DCB in samples having the interference, and also may be used in samples in which DCB recovery is low. Corrective action is only necessary if DCB and TCMX are both outside of acceptance limits.

13. METHOD PERFORMANCE

13.1. Performance limits for the four replicate initial demonstration of capability required under Section 13.1 of the main body of this SOP are recovery of 70-130%. The spiking level should be equivalent to a mid level calibration.

13.2. Method detection limits (MDL) are determined for Arochlor 1016 and 1260. Arochlor 1016 represents an Arochlor consisting primarily of low chlorinated congeners while Arochlor 1260 represents an Arochlor consisting primarily of high chlorinated congeners. The same reporting limit is applied to all Arochlors, and must be supported by both MDLs.

14. POLLUTION PREVENTION

Refer to section 14 of the 8000B section of this SOP.

15. WASTE MANAGEMENT

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

16. REFERENCES

SW846, Update III, December 1996, Method 8082

17. MISCELLANEOUS

17.1. Modifications from Reference Method

17.1.1. Method 8082 includes limited direction for congener specific quantitation. This is outside the scope of this SOP.

17.2. Modifications from Previous Revisions

No changes were made to this Appendix

17.3. Tables

Table C-1
Standard Analyte list and Reporting Limits

Compound	Reporting Limit, µg/L or µg/kg		
	water	soil	waste
Aroclor-1016	1.0	33	1000
Aroclor-1221	1.0	33	1000
Aroclor-1232	1.0	33	1000
Aroclor 1242	1.0	33	1000
Aroclor-1248	1.0	33	1000
Aroclor-1254	1.0	33	1000
Aroclor-1260	1.0	33	1000

The following concentration factors are assumed in calculating the Reporting Limits:

	Extraction Vol.	Final Vol.
Ground water	1000 mL	10 mL
Low-level Soil	30 g	10 mL
High-level soil / waste	1 g	10 mL

Table C-2

Parameter	Recommended Conditions
Injection port temp	220°C
Detector temp	325°C
Temperature program	70°C for 0.5min, 30°C/min to 190°C, 2.5°C/min to 225, 18°C/min to 280°C, 3 min hold
Column 1	DB-5 or Rtx-5 30m x 0.32mm id, 0.5µm
Column 2	DB-1701 or Rtx 1701 30m x 0.32 mm id, 0.25µm
Column 3	DB-608, 30m X 0.32 mm, 0.25µm
Injection	1-2µL
Carrier gas	Helium or Hydrogen
Make up gas	Nitrogen
Y splitter	Restek or J&W or Supelco glass tee

Table C-3						
Calibration Levels ng/mL						
	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6[1]
Aroclor 1016/1260	100	200	500	1000	2000	4000
Aroclor 1242[2]			500			
Aroclor 1221 +1254[2]			500			
Aroclor 1232[2]			500			
Aroclor 1248[2]			500			
Surrogates are included with all the calibration mixes at the following levels:						
Tetrachloro-m-xylene	5	10	25	50	100	200
Decachlorobiphenyl	5	10	25	50	100	200

[1] Level 6 is optional and should only be used if linearity can be maintained on the instrument to this level.
[2] Aroclors may be quantitated within the range 100 to 2000 ng/mL (4000ng/mL if the level 6 1016/1260 standard is included). If the Aroclor is more concentrated, it must be reanalyzed at a dilution.

Table C-4			
LCS/Matrix Spike and Surrogate Spike levels for Aroclor analysis with Acid Cleanup µg/L or µg/kg			
	Aqueous	Soil	Waste
Aroclor 1016/1260	10	333	10,000
Tetrachloro-m-xylene (Surrogate)	0.20	6.67	200
Decachlorobiphenyl (Surrogate)	0.20	6.67	200

Table C-5
Suggested Analytical Sequence

Initial Calibration

Injection #		
1	Solvent blank (optional)	
2	Aroclor 1016/1260	Level 1
3	Aroclor 1016/1260	Level 2
4	Aroclor 1016/1260	Level 3
5	Aroclor 1016/1260	Level 4
6	Aroclor 1016/1260	Level 5
7	Aroclor 1232	Level 3
8	Aroclor 1242	Level 3
9	Aroclor 1248	Level 3
10	Aroclor 1221/1254	Level 3
11	Solvent blank	
12-31	Sample 1-20 (or as many samples as can be analyzed in 12 hours	
	Solvent blank (optional)	
32	Aroclor 1016/1260	Level 3

etc

12 hour Calibration

At least every 12 hours, counting from the start of the initial calibration, or from the start of the last daily calibration, the retention time windows must be updated using the Aroclor 1260 / 1016 mix. Mid level standards of any other Aroclors expected to be present in the samples are also injected.

1. SCOPE AND APPLICATION

This method is applicable to the gas chromatographic determination of Chlorinated phenoxy acid herbicides in extracts prepared by SOP CORP-OP-0001. The herbicides listed in Table D1 are routinely analyzed. Other chlorinated acids may be analyzed by this method if the quality control criteria in section 9 and the initial demonstration of method performance in section 13 are met.

2. SUMMARY OF METHOD

This method presents conditions for the analysis of prepared extracts of phenoxy acid herbicides by gas chromatography. The herbicides, as their methyl esters, are injected onto the column, separated, and detected by electron capture detectors. Quantitation is by the external standard method.

3. DEFINITIONS

Refer to the QAMP for definitions of terms used in this document.

4. INTERFERENCES

4.1. Refer to the method 8000B section of this SOP for general information regarding chromatographic interferences.

4.2. Chlorinated acids and phenols cause the most direct interference with this method.

4.3. Sulfur may interfere and may be removed by the procedure described in SOP#CORP-OP-0001.

5. SAFETY

5.1. Refer to section 5 of the Method 8000B SOP for general safety requirements.

6. EQUIPMENT AND SUPPLIES

6.1. Refer to Section 6 of the 8000B section of this SOP. A Ni_{63} electron capture detector is required.

6.2. Refer to Table D2 for analytical columns.

6.3. Microsyringes, various sizes, for standards preparation, sample injection, and extract dilution.

7. REAGENTS AND STANDARDS

7.1. Refer to section 7 of the 8000B section of this SOP for general information on reagents and standards.

7.2. Refer to Table D-3 and D-4 for details of calibration and other standards.

8. SAMPLE PREPARATION, PRESERVATION AND STORAGE

Refer to section 8 of the 8000B section of this SOP.

9. QUALITY CONTROL

9.1. Refer to Section 9 of the 8000B section of this SOP for quality control requirements, including the initial demonstration of capability, definition of a batch, surrogate limits, method blanks, laboratory control samples (LCS), and matrix spikes (MS).

9.2. Refer to Table D-5 for minimum performance criteria for the initial demonstration of capability.

9.3. Refer to Table D-4 for the components and levels of the LCS and MS mixes.

10. CALIBRATION AND STANDARDIZATION

10.1. Refer to Section 10 of the 8000B section of this SOP for general calibration requirements.

10.2. Calibration standards are made up from the free acids, and then esterified using the same process as for samples (See SOP Corp-OP-0001)

10.3. The low level standard must be at or below the laboratory reporting limit. Other standards are chosen to bracket the expected range of concentrations found in samples, without saturating the detector or leading to excessive carryover.

10.4. Refer to Table D-2, for details of GC operating conditions.

11. PROCEDURE

11.1. Refer to the method 8000B section of this SOP for procedural requirements.

11.2. Extraction

The extraction procedure is described in SOP #CORP-OP-0001.

11.3. Cleanup

The alkaline hydrolysis and subsequent extraction of the basic solution described in the extraction procedure provides an effective cleanup.

11.4. Analytical Sequence

The analytical sequence starts with an initial calibration of at least five points, or a daily calibration that meets % difference criteria from an existing initial calibration.

11.4.1. The daily calibration must be analyzed at least once every 24 hours when samples are being analyzed. If there is a break in the analytical sequence of greater than 12 hours, then a new continuing calibration run must be analyzed before proceeding with the sequence. If more than 24 hours have elapsed since the injection of the last sample in the analytical sequence, a new analytical sequence must be started with a daily calibration.

11.4.2. The daily calibration consists of mid level standards of all analytes of interest. Retention time windows must be updated with the daily calibration.

11.4.3. After every 12 hours a continuing calibration is analyzed. The continuing calibration consists of mid level standards of all analytes of interest. Retention time windows are updated with continuing calibrations.

11.5. Gas Chromatography

Chromatographic conditions are listed in Table D-2.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Refer to the 8000B section of this SOP for identification and quantitation of single component analytes.

12.2. The herbicides are analyzed as their methyl esters, but reported as the free acid. For this reason it is necessary to correct the results for the molecular weight of the ester versus the free acid. This is achieved through the concentrations of the calibration standards. For example the 20µg/L calibration standard for 2,4-D contains 21.3 µg/L of the methyl ester. No further correction is necessary.

Standard Analyte list Weight Corrections			
Compound	*CAS Number*	*Molecular weight(g/mol)*	
		Acid	*Methyl Ester*
2,4-D	*94-75-7*	*221.0*	*235.1*
2,4-DB	*94-82-6*	*249.1*	*263.1*
2,4,5-TP (Silvex)	*93-72-1*	*269.5*	*283.5*
2,4,5-T	*93-76-5*	*255.5*	*269.5*
Dalapon	*75-99-0*	*143.0*	*157.0*
Dicamba	*1918-00-9*	*221.0*	*235.1*
Dichloroprop	*120-36-5*	*235.1*	*249.1*
Dinoseb	*88-85-7*	*240.2*	*254.2*
MCPA	*94-74-6*	*200.6*	*214.6*
MCPP	*7085-19-0*	*214.6*	*228.6*

13. METHOD PERFORMANCE

13.1. Multiple laboratory performance data has not been published by the EPA for this method. Table D-5 lists minimum performance standards required by STL for the four replicate initial demonstration or capability (required by Section 13.2 of the 8000B part of this SOP) for this method. The spiking level should be equivalent to a mid level calibration.

14. POLLUTION PREVENTION

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

15. WASTE MANAGEMENT

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

16. REFERENCES

Method 8151A, SW-846, Update III, December 1996

17. MISCELLANEOUS

17.1. Modifications from Reference Method

Refer to the method 8000B section of this SOP for modifications from the reference method.

17.2. Modifications from Previous Revision

The calibration procedure has been changed to require esterification of the calibration standards

17.3. Tables

Table D-1					
Standard Analyte list					
Compound	CAS Number	Reporting Limit, µg/L or µg/kg			
		Aqueous	Soil	Waste	TCLP
2,4-D	94-75-7	4	80	4000	500
2,4-DB	94-82-6	4	80	4000	---
2,4,5-TP (Silvex)	93-72-1	1	20	1000	500
2,4,5-T	93-76-5	1	20	1000	---
Dalapon	75-99-0	2	40	2000	---
Dicamba	1918-00-9	2	40	2000	---
Dichloroprop	120-36-5	4	80	4000	---
Dinoseb	88-85-7	0.6	12	600	---
MCPA	94-74-6	400	8000	400,000	---
MCPP	93-65-2	400	8000	400,000	---

The following concentration factors are assumed in calculating the Reporting Limits:

	Extraction Vol.	Final Vol.	Dilution Factor
Ground water	1000 mL	10 mL	20
Low-level Soil without GPC	50 g	10 mL	20
High-level soil / waste	1 g	10 mL	20

Specific reporting limits are highly matrix dependent. The reporting limits listed above are provided for guidance only and may not always be achievable. For special projects, the extracts may be analyzed without any dilution, resulting in reporting limits 20 times lower than those in Table D-1.

Table D-2	
Instrumental Conditions	
PARAMETER	Recommended conditions
Injection port temp	220°C
Detector temp	325°C
Temperature program	80,2/30/170,0/1/180,1
Column 1	DB-5MS or RTX 5 30x0.32, 0.5um
Column 2	DB-1701 or Rtx-1701
Injection	1-2µL
Carrier gas	Helium / Hydrogen
Make up gas	Nitrogen

Recommended conditions should result in resolution of all analytes listed in Table D-1.

The reporting limits listed in Table D-1 will be achieved with these calibration levels and a 20 fold dilution of the sample extract. Lower reporting limits can be achieved with lesser dilutions of the sample extract.

Table D-3				
LCS/Matrix Spike and Surrogate Spike levels µg/L or µg/kg[1]				
	Aqueous	Soil	Waste	TCLP
2,4-D	16	800	16000	6ug/L ; 120ug/kg
Silvex	4	200	4000	6ug/L ; 120ug/kg
2,4,5-T	4	200	4000	6ug/L ; 120ug/kg
2,4-DB	16	800	16000	---
Dalapon	8	400	8000	---
DCAA (surrogate)	16	800	16000	10ug/L;500ug/kg

[1] LCS, MS and SS spikes are as the free acid.

Table D-4		
Performance limits, four replicate initial demonstration of capability		
Compound	Initial demonstration, mean recovery limits	Initial demonstration, RSD limits
2,4-D	50-150	25
2,4-DB	50-150	25
2,4,5-TP (Silvex)	50-150	25
2,4,5-T	50-150	25
Dalapon	50-150	25
Dicamba	50-150	25
Dichloroprop	50-150	25
Dinoseb	25-120	40
MCPA	50-150	25
MCPP	50-150	25

PITTSBURGH SPECIFIC APPENDIX FOR THE ANALYSIS OF PAHs by HPLC SW-846 METHOD 8310

Prepared by: _____

Reviewed by: _____
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Approved by: _____
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Approved by: _____
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Approved by: _____
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1. SCOPE AND APPLICATION

This SOP Appendix describes procedures to be used when SW-846 Method 8310 is applied to the analysis of Polynuclear Aromatic Hydrocarbons by HPLC. This Appendix is applicable to extracts derived from any matrix which are prepared according to the appropriate STL sample extraction SOPs. (CORP-OP-0001)

Table B-1 lists compounds which are routinely determined by this method and gives the Reporting Limits (RL) for each matrix. RLs given are based on the low level standard and the sample preparation concentration factors. Matrix interferences may result in higher RLs than those listed.

2. SUMMARY OF METHOD

This method presents conditions for the analysis of prepared extracts of Polynuclear Aromatic Hydrocarbons. The extracts are injected onto the column and separated and detected by ultraviolet(UV) and fluorescence detection. Quantitation may be by internal or external standard methods.

3. DEFINITIONS

Refer to the QAMP for definitions of terms used in this document.

4. INTERFERENCES

4.1. Refer to the method 8000B section of this SOP for information regarding chromatographic interferences.

4.2. Interferences in the HPLC analysis arise from many compounds amenable to HPLC that give a measurable response on the UV and fluorescence detector. Phthalate esters, which are common plasticizers, can pose a major problem in the determinations. Interferences from phthalates are minimized by avoiding contact with any plastic materials.

4.3. Interferences co-extracted from samples will vary considerably from source to source. The presence of interferences may raise quantitation limits for individual samples. Specific cleanups have not been determined for this method.

5. SAFETY

5.1. Refer to section 5 of the Method 8000B SOP for general safety requirements.

5.2.

6. EQUIPMENT AND SUPPLIES

6.1. Refer to Section 6 of the 8000B section of this SOP. UV and fluororescence detectors are required.

6.2. Refer to Table B-2 for analytical columns.

6.3. Microsyringes, various sizes, for standards preparation, sample injection, and extract dilution.

7. REAGENTS AND STANDARDS

7.1. Refer to the method 8000B section of this SOP for general requirements for reagents and supplies.

7.2. Refer to Table B-3 for details of calibration standards.

7.3. Surrogate Standards

Benzo(e)pyrene and p-terphenyl are the surrogate standards. Refer to tables B-5 for details of surrogate standards.

.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

Refer to Section 8 of the 8000B section of this SOP.

9. QUALITY CONTROL

Refer to Section 9 of the 8000B section of this SOP.

10. CALIBRATION AND STANDARDIZATION

10.1. Refer to Section 10 of the 8000B section of this SOP for general calibration requirements.

10.2. Refer to Table B-2 for details of HPLC operating conditions. The conditions listed should result in resolution of all analytes listed in Table B-1 on both detectors.

10.3. Initial Calibration

Refer to Section 10 of the 8000B section of this SOP for details of calibration procedures.

10.3.1. Refer to Table B-8 for the initial calibration analytical sequence.

10.3.2. The response for each single-peak analyte will be calculated by the procedures described in the general method for GC analysis.

10.4. 12 hour Calibration Verification

The 12 hour calibration verification sequence must be analyzed within 12 hours of the start of the initial calibration and at least once every 12 hours thereafter if samples are being analyzed. If more than 12 hours have elapsed since the injection of the last sample in the analytical sequence, a new analytical sequence must be started with a 12 hour calibration. A mid level calibration standard is used for the 12 hour calibration. Refer to the 8000B section of this SOP for acceptance criteria.

10.4.1. .

10.4.2. The retention time windows for any analytes included in the 12 hour calibration are updated.

10.5. Continuing Calibration

The mid-level calibration mix is analyzed as the continuing calibration standard. At a minimum, this is analyzed after every 20 samples, including matrix spikes, LCS, and method blanks. If 12 hours elapse analyze the 12 hour standard sequence instead. If instrument drift is expected due to sample matrix or other factors, it may be advisable to analyze the continuing calibration standard more frequently.

10.5.1. A mid level calibration standard is used for the continuing calibration.

11. PROCEDURE

11.1. Refer to the method 8000B section of this SOP for general procedural requirements.

11.2. Extraction

The extraction procedure is described in SOP No. CORP-OP-0001.

11.3. Cleanup

No cleanup procedure has been determined.

11.4. Suggested HPLC conditions are given in Table B-2.

11.5. Allow extracts to warm to ambient temperature before injection.

11.6. The suggested analytical sequence is given in Table B-8.

12. DATA ANALYSIS AND CALCULATIONS

Both the fluorescence detector and the UV detector are used for qualitative determination and confirmation of the presence of target compounds, however each target compound is quantitated using only one detector. Table B-1 presents the detectors used for quantitating each compound.The MDL studies are performed on both detectors. The highest MDL will be used for reporting "J"-Values. In the instance where there is no detection of any compounds on the UV detector, the Flourescence Detector results will not be submitted.

12.1. Surrogate recovery results are calculated and reported for Benzo(e)pyrene and p-terphenyl. Corrective action is only necessary if Benzo(e)pyrene and p-terphenyl are both outside of acceptance limits.

13. METHOD PERFORMANCE

13.1. Performance limits for the four replicate initial demonstration of capability required under Section 13.1 of the main body of this SOP are presented in Table B-7. The spiking level should be equivalent to a mid level calibration.

14. POLLUTION PREVENTION

Refer to section 14 of the 8000B section of this SOP.

15. WASTE MANAGEMENT

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

16. REFERENCES

SW846, Update III, December 1996, Method 8310

17. MISCELLANEOUS

17.1. Modifications from Reference Method

None

17.2. Modifications from Previous Revisions

17.2.1. No revisions were made to this appendix.

17.3. Tables

Table B-1
Standard Analyte list and Reporting Limits and Detectors

Compound	Reporting Limit, µg/L or µg/kg		
	water	soil	Detectors
Carbazole	1.0	33	UV/Flourescence
Naphthalene	1.0	33	UV/Flourescence
Acenaphthene	1.0	33	UV/Flourescence
Acenaphthylene	1.0	33	UV
Anthracene	.2	6.7	UV/Flourescence
Benzo(a)anthracene	.2	6.7	UV/Flourescence
Benzo(b)fluoranthene	.2	6.7	UV/Flourescence
Benzo(k)fluoranthene	.2	6.7	UV/Flourescence
Benzo(g,h,i)perylene	.2	6.7	UV/Flourescence
Benzo(a)pyrene	.2	6.7	UV/Flourescence
Chrysene	.2	6.7	UV/Flourescence
Fluoranthene	.2	6.7	UV/Flourescence
Fluorene	.2	6.7	UV/Flourescence
Indeno(1,2,3-cd)pyrene	.2	6.7	UV/Flourescence
Pyrene	.2	6.7	UV/Flourescence
Phenanthrene	.2	6.7	UV/Flourescence
Dibenzo(a,h)anthracene	.2	6.7	UV/Flourescence
1-methylnaphthalene	1.0	33	UV/Flourescence
2-methylnaphthalene	1.0	33	UV/Flourescence

The following concentration factors are assumed in calculating the Reporting Limits:

	Extraction Vol.	Final Vol.
Ground water	1000 mL	1.0 mL
Low-level Soil	30 g	1.0 mL
High-level soil / waste	1 g	1.0 mL

Table B-2	
Parameter	**Recommended Conditions**
Mobile phase program	Time 0min:solvent A 50% solvent B 50% flow 1.5 ml/min Time 7min:solvent A 65% solvent B 35% flow 1.5 ml/min Time 10min:solvent A 75% solvent B 25% flow 1.5 ml/min Time 15min:solvent A 85% solvent B 15% flow 1.5 ml/min Time 20min:solvent A 95% solvent B 5% flow 1.5 ml/min
Column 1	Hypersil PAH 150mm x 4.6mm ID
Injection	20µL
Solvent A	CH3CN
Solvent B	H2O

Table B-3						
Calibration Levels ng/mL						
	Level 1	Level 2	Level 3	Level 4	Level 5	
Individual Mix						
Carbazole	1	4	7.5	10	20	
Naphthalene	1	4	7.5	10	20	
Acenaphthene	1	4	7.5	10	20	
Acenaphthylene	1	4	7.5	10	20	
Anthracene	.2	.8	1.5	2	4	
Benzo(a)anthracene	.2	.8	1.5	2	4	
Benzo(b)fluoranthene	.2	.8	1.5	2	4	
Benzo(k)fluoranthene	.2	.8	1.5	2	4	
Benzo(g,h,i)perylene	.2	.8	1.5	2	4	
Benzo(a)pyrene	.2	.8	1.5	2	4	
Chrysene	.2	.8	1.5	2	4	
Fluoranthene	.2	.8	1.5	2	4	
Fluorene	.2	.8	1.5	2	4	
Indeno(1,2,3-cd)pyrene	.2	.8	1.5	2	4	
Pyrene	.2	.8	1.5	2	4	
Phenanthrene	.2	.8	1.5	2	4	
Dibenzo(a,h)anthracene	.2	.8	1.5	2	4	
1-methylnaphthalene	1	4	7.5	10	20	
2-methylnaphthalene	1	4	7.5	10	20	
p-terphenyl	1	4	7.5	10	20	
Benzo(e)pyrene	1	4	7.5	10	20	

Table B-5		
LCS/Matrix Spike and Surrogate Spike levels µg/L or µg/kg		
	Aqueous	Soil
Carbazole	6.25	208
Naphthalene	6.25	208
Acenaphthene	6.25	208
Acenaphthylene	6.25	208
Anthracene	1.25	41.7
Benzo(a)anthracene	1.25	41.7
Benzo(b)fluoranthene	1.25	41.7
Benzo(k)fluoranthene	1.25	41.7
Benzo(g,h,i)perylene	1.25	41.7
Benzo(a)pyrene	1.25	41.7
Chrysene	1.25	41.7
Fluoranthene	1.25	41.7
Fluorene	1.25	41.7
Indeno(1,2,3-cd)pyrene	1.25	41.7
Pyrene	1.25	41.7
Phenanthrene	1.25	41.7
Dibenzo(a,h)anthracene	1.25	41.7
1-methylnaphthalene	6.25	208
2-methylnaphthalene	6.25	208
p-terphenyl	10	333
Benzo(e)pyrene	10	333

Table B-7
Suggested Analytical Sequence

Initial Calibration

Solvent blank (optional)

Individual mix All levels

Solvent blank
Up to 20 samples unless 12 hours comes first)
Solvent blank (optional)
Individual mix Mid level (Continuing calibration)
Samples
After 12 hours:

Individual mix [1]

12 hour Calibration

At least every 12 hours, counting from the start of the initial calibration, or from the start of the last daily calibration, the retention time windows must be updated using the Individual mix ..

Tables B8 & B9 Laboratory Control Limits and Control Compound List (STL Reference Data Summary) See Attachements: current print outs from LIMS system.

CORP-MT-0001

Inductively Coupled Plasma-Atomic Emission Spectroscopy,
Spectrometric Method for Trace Element Analyses,
SW846 Method 6010B and EPA Method 200.7

Controlled Copy
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Implementation Date: _____

STL STANDARD OPERATING PROCEDURE

TITLE: INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROSCOPY, SPECTROMETRIC METHOD FOR TRACE ELEMENT ANALYSES, SW-846 METHOD 6010B AND EPA METHOD 200.7

(SUPERSEDES: REVISION 2)

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1. SCOPE AND APPLICATION

1.1. This procedure describes the analysis of trace elements including metals in solution by Inductively Coupled Plasma -Atomic Emission Spectroscopy (ICP-AES) using SW-846 Method 6010B and EPA Method 200.7 . Table I of Appendix A lists the elements appropriate for analysis by Methods 6010B and 200.7. Additional elements may be analyzed under Methods 6010B and 200.7 provided that the method performance criteria presented in Section 13.0 are met.

1.2. ICP analysis provides for the determination of metal concentrations over several orders of magnitude. Detection limits, sensitivity and optimum concentration ranges of the metals will vary with the matrices and instrumentation used. For instance, in comparison to conventional ICP technique, ICP-Trace can achieve detection levels comparable to those determined using the graphite furnace atomic absorption spectroscopy (GFAAS) technique.

1.3. Method 6010B is applicable to the determination of dissolved, suspended, total recoverable and total elements in ground water, aqueous samples, soils, sludges, wastes, sediments, and TCLP, EP and other leachates/extracts. All matrices require digestion prior to analysis with the exception of analyses for dissolved metals in filtered and acidified aqueous samples. Although digestion is not specifically required by the method, some clients and regulators may require digestion of **dissolved samples** and this must be clarified and documented before project initiation. Silver concentrations must be below 2.0 mg/L in aqueous samples and 100 mg/kg in solid matrix samples. Precipitation may occur in samples where silver concentrations exceed these levels and lead to the generation of erroneous data.

1.4. Method 200.7 is applicable to the determination of dissolved, suspended, total recoverable, and total elements in water, waste water, and solid wastes. All matrices require digestion prior to analysis with the exception of analyses for dissolved metals in filtered and acidified aqueous samples if the criteria in Section 11.1 are met. Silver concentrations must be below 0.1 mg/L in aqueous samples and 50 mg/kg in solid matrix samples.

1.5. State-specific requirements may take precedence over this SOP for drinking water sample analyses

2. SUMMARY OF METHOD

2.1. This method describes a technique for the determination of multi elements in solution using sequential or simultaneous optical systems and axial or radial viewing of the plasma. The basis of the method is the measurement of atomic emission by an optical spectroscopic technique. Samples are nebulized and the aerosol that is produced is

transported to the plasma torch where excitation occurs. Characteristic atomic-line emission spectra are produced by a radio frequency inductively coupled plasma (ICP). The spectra are dispersed by a grating spectrometer and the intensities of the emission lines are monitored by photomultiplier tubes. The photocurrents from the photomultiplier tubes are processed and controlled by a computer system. A background correction technique is required to compensate for variable background contribution to the determination of trace elements. Background must be measured adjacent to analyte lines during analysis. The position selected for the background intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used must be free of spectral interferences and reflect the same change in background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result. The possibility of additional interferences should also be recognized and appropriate actions taken. Alternatively, multivariate calibration methods may be chosen for which point selection for background correction is superfluous since whole spectral regions are processed.

2.2. Refer to the appropriate SOPs for details on sample preparation methods.

3. DEFINITIONS

3.1. Dissolved Metals: Those elements which pass through a 0.45 um membrane. (Sample is acidified <u>after</u> filtration).

3.2. Suspended Metals: Those elements which are retained by a 0.45 um membrane.

3.3. Total Metals: The concentration determined on an unfiltered sample following vigorous digestion.

3.4. Total Recoverable Metals: The concentration determined on an unfiltered sample following treatment with hot, dilute mineral acid.

4. INTERFERENCES

4.1. Spectral, physical and chemical interference effects may contribute to inaccuracies in the determinations of trace elements by ICP. Spectral interferences are caused by:

- Overlap of a spectral line from another element.
- Unresolved overlap of molecular band spectra.
- Background contribution from continuous or recombination phenomena.

- Stray light from the line emission of high concentration elements.

4.1.1. A background correction technique is required to compensate for variable background contribution to the determination of trace elements. Background correction is not required in cases where a background corrective measurement would actually degrade the analytical result.

4.1.2. Inter-element correction factors (IECs) are necessary to compensate for spectral overlap. Inter-element interferences occur when elements in the sample emit radiation at wavelengths so close to that of the analyte that they contribute significant intensity to the analyte channel. If such conditions exist, the intensity contributed by the matrix elements will cause an excessively high (or sometimes low) concentration to be reported for the analyte. Inter-element corrections IECs must be applied to the analyte to remove the effects of these unwanted emissions.

4.1.3. Physical interferences are generally considered to be effects associated with sample transport, nebulization and conversion within the plasma. These interferences may result in differences between instrument responses for the sample and the calibration standards. Physical interferences may occur in the transfer of solution to the nebulizer (e.g., viscosity effects), at the point of aerosol formation and transport to the plasma (e.g., surface tension) or during excitation and ionization processes within the plasma itself. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples containing high dissolved solids or high acid concentrations. If physical interferences are present, dilution of the sample, use of a peristaltic pump, mass flow controller, use of an internal standard and/or use of a high solids nebulizer can reduce the effect.

4.1.4. Chemical interferences are characterized by molecular compound formation, ionization effects and solute vaporization effects. Normally these effects are not significant with the ICP technique but if observed can be minimized by buffering the sample, matrix matching or standard addition procedures.

5. SAFETY

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

5.2. Eye protection that satisfies ANSI Z87.1 (as per the Chemical Hygiene Plan), laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

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

5.3.1. The following materials are known to be **corrosive**:

sulfuric acid, hydrochloric acid, nitric acid and hydrofluoric acid. (NOTE: sulfuric and hydrofluoric acids are used in cleaning the ICP torch and hydrofluoric acid is also commonly used in air toxics preparations.)

5.3.2. The following materials are known to be **oxidizing agents**:

nitric acid and hydrogen peroxide.

5.3.3. The plasma emits strong UV light and is harmful to vision. **NOTE: AVOID looking directly at the plasma.**

5.3.4. The RF generator produces strong radio frequency waves, most of which are unshielded. People with pacemakers should not go near the instrument while in operation.

5.4. Exposure to chemicals must be maintained **as low as reasonably achievable**, therefore, unless they are known to be non-hazardous, all samples should be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Metals digestates can be processed outside of a fume hood. Solvent and waste containers will be kept closed unless transfers are being made.

5.5. The preparation of standards and reagents will be conducted in a fume hood or well ventilated area.

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

5.7. The use of hydrofluoric acid requires special safety precautions. Consult the facility EH&S Manager and laboratory supervisor for guidance.

6. EQUIPMENT AND SUPPLIES

6.1. Inductively Coupled Plasma Atomic Emission Spectrometer equipped with autosampler and background correction.

6.2. Radio Frequency Generator.

6.3. Argon gas supply, welding grade or equivalent.

6.4. Coolflow or appropriate water cooling device.

6.5. Peristaltic Pump.

6.6. Calibrated automatic pipettes or Class A glass volumetric pipettes.

6.7. Class A volumetric flasks.

6.8. Autosampler tubes.

7. REAGENTS AND STANDARDS

7.1. Intermediate standards are purchased as custom STL multi-element mixes or as single-element solutions. All standards must be stored in FEP fluorocarbon or unused polyethylene or polypropylene bottles. Intermediate standard solutions must be replaced prior to the expiration date provided by the manufacturer. If no expiration date is provided, the intermediate solutions may be used for up to one year and must be replaced sooner if verification from an independent source indicates a problem. Expiration dates can be extended provided that the acceptance criteria described in laboratory-specific SOPs are met.

7.2. Working calibration and calibration verification solutions may be used for up to 3 months and must be replaced sooner if verification from an independent source indicates a problem. Standards should be prepared in a matrix of 5% hydrochloric and 5% nitric acids. An exception to this is in the event the Trace ICP is utilized without the internal standard. In this case, the standard acid matrix must be matched to the final preparation matrix as listed in Section 11.10.

7.3. Refer to Tables III, IV, IVA, V and VI (Appendix A) for details regarding the working standard concentrations for calibration, calibration verification, interference correction and spiking solutions.

7.4. Concentrated nitric acid (HNO_3), trace metal grade or better.

7.5. Concentrated hydrochloric acid (HCl), trace metal grade or better.

7.6. Reagent water must be produced by a Millipore DI system or equivalent. Reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Sample holding times for metals are six months from time of collection to the time of analysis.

8.2. Aqueous samples are preserved with nitric acid to a pH of <2 and may be stored in either plastic or glass. If boron or silica are to be determined, plastic containers are preferred. Refrigeration is not required. Preservation must be verified prior to analysis. For samples that will be analyzed by Method 200.7 for compliance with Safe Drinking Water regulations, the samples must be held for a minimum of 16 hours prior to verifying the pH.

8.3. Soil samples do not require preservation but must be stored at 4°C ± 2° until the time of preparation .

9. QUALITY CONTROL

Table VII (Appendix A) provides a summary of quality control requirements including type, frequency, acceptance criteria and corrective action.

9.1. Initial Demonstration of Capability

Prior to analysis of any analyte using either Method 200.7 or Method 6010B, the following requirements must be met.

9.1.1. Instrument Detection Limit (IDL) - The IDL for each analyte must be determined for each analyte wavelength used on each instrument. The IDL must be determined annually. If the instrument is adjusted in anyway that may affect the IDL, the IDL for that instrument must be redetermined. The IDL shall be determined by multiplying by 3, the standard deviation obtained from the analysis of a standard solution (each analyte in reagent water) at a concentration 3x - 5x the previously determined IDL, with seven consecutive measurements. Each measurement must be performed as though it were a separate analytical sample (i.e., each measurement must be followed by a rinse and/or any other procedure performed between the analysis of separate samples). The result of the IDL determination must be below the STL reporting limit. The CLP IDL procedure can be used for this method.

9.1.2. Method Detection Limit (MDL) - An MDL must be determined for each analyte prior to the analysis of any client samples. The MDL is determined using seven replicates of reagent water, spiked with all the analytes of interest, that have been carried through the entire analytical procedure. MDLs must be redetermined on an annual basis in accordance with 40 CFR Part 136 Appendix B requirements as detailed in STL QA Policy QA-005. The spike level must be between the calculated MDL and 10X the MDL to be considered valid. The result of the MDL determination must be below the STL reporting limit (RL). MDL studies for the determination of metals in soil need not be performed; an appropriate soil MDL may be computed from the experimentally determined MDL for metals in aqueous solution.

9.1.3. Linear Range Verification (LR) - The linear range must be determined on an

annual basis for each analyte wavelength used on each instrument. The linear range is the concentration above which results cannot be reported without dilution of the sample. The standards used to define the linear range limit must be analyzed during a routine analytical run. For the **initial** determination of the upper limit of the linear dynamic range (LDR) for each wavelength, determine the signal responses from a minimum of three to five different concentration standards across the estimated range. One standard should be near the upper limit of the estimated range. The concentration measured at the LDR must be no more than 10% less than the expected level extrapolated from lower standards. If the instrument is adjusted in any way that may affect the LRs, new dynamic ranges must be determined. The LR data must be documented and kept on file.

9.1.4. Background Correction Points - To determine the appropriate location for off-line background correction when establishing methods, the user must scan the area on either side adjacent to the wavelength and record the apparent emission intensity from all other method analytes. This spectral information must be documented and kept on file. The location selected for background correction must be either free of off-line interelement spectral interference or a computer routine must be used for automatic correction on all determinations. Tests to determine spectral interference must be done using analyte concentrations that will adequately describe the interference. Background correction points must be set prior to determining IECs. Refer to the facility-specific instrument operation SOP and ICP instrument manual for specific procedures to be used in setting background correction points.

9.1.5. Inter-element Corrections (IECs) - ICP interelement correction factors must be determined prior to the analysis of samples and every six months thereafter. If the instrument is adjusted in any way that may affect the IECs, the IECs must be redetermined. When initially determining IECs for an instrument, wavelength scans must be performed to ensure that solutions in use are free from contaminants. If an IEC varies significantly from the previously determined IEC then the possibility of contamination should be investigated. The purity of the IEC check solution can be verified by using a standard from a second source or an alternate method (i.e., GFAA or ICP-MS). Published wavelength tables (e.g. MIT tables, Inductively Coupled Plasma-Atomic Spectroscopy: Prominent Lines) can also be consulted to evaluate the validity of the IECs. Refer to the facility specific instrument operation SOP and instrument manufacturer's recommendations for specific procedures to be used in setting IECs. An IEC must be established to compensate for any interelement interference which results in a false analyte signal greater than ± the RL as defined in Tables I, IA or II. To determine IECs, run a single element standard at the established linear range. To calculate an IEC, divide the observed concentration of the analyte by the observed concentration of the "interfering element."

Note: Trace ICP IECs are more sensitive to small changes in the plasma and instrument setup conditions. Adjustments in the IECs will be required on a more frequent basis for the Trace as reflected by the ICSA response.

9.1.6. Rinse Time Determination - Rinse times must be determined annually. To determine the appropriate rinse time for a particular ICP system, the linear range verification standard (see 9.1.3) should be aspirated as a regular sample followed by the analysis of a series of rinse blanks. The length of time required to reduce the analyte signals to < RL will define the rinse time for a particular ICP system. For some analytes it may be impractical to set the rinse time based on the linear range standard result (i.e., analyte not typically detected in environmental samples at that level and an excessive rinse time would be required at the linear range level). Until the required rinse time is established, the method recommends a rinse period of at least 60 seconds between samples and standards. If a memory effect is suspected, the sample must be reanalyzed after a rinse period of sufficient length. Rinse time studies can be conducted at additional concentration levels. These additional studies must be documented and kept on file, if a concentration other than the linear range level is used to set the rinse time. The concentration levels used to establish the rinse time must be taken into consideration when reviewing the data.

9.2. Method Blank (MB) - One method blank must be processed with each preparation batch. The method blank consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. The method blank should not contain any analyte of interest at or above the reporting limit (exception: common laboratory contaminants, see below) or at or above 5% of the measured concentration of that analyte in associated samples, whichever is higher (sample result must be a minimum of 20x higher than the blank contamination level).

- If the analyte is a common laboratory contaminant (copper, iron, lead (Trace only) or zinc) the data may be reported with qualifiers if the concentration of the analyte in the method blank is less than two times the RL. **Such action must be taken in consultation with the client and must be addressed in the project narrative.**

- Repreparation and reanalysis of all samples associated with an unacceptable method blank is required when reportable concentrations are determined in the samples (see exception noted above).

- If there is no analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. **Such**

action must be taken in consultation with the client and must be addressed in the project narrative.

- If the above criteria are not met and reanalysis is not possible, then the sample data must be qualified. **This anomaly must be addressed in the project narrative and the client must be notified.**

- For dissolved metals samples which have not been digested, a CCB result is reported as the method blank. The CCB run immediately prior to the start of the dissolved sample analyses must be used for this purpose. No more than 20 samples can be associated with one CCB.

9.3. Laboratory Control Sample (LCS) - One aqueous LCS must be processed with each preparation batch. The LCS must contain all analytes of interest and must be carried through the entire analytical procedure. Aqueous LCS spike levels are provided in Table III (Appendix A). The LCS is used to monitor the accuracy of the analytical process. On-going monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines.

- If any analyte is outside established control limits the system is out of control and corrective action must occur. Until in-house control limits are established, for method 6010B, a control limit of 80 - 120% (85-115% for 200.7) recovery must be applied.

- In the event that an MS/MSD analysis is not possible a Laboratory Control Sample Duplicate (LCSD) must be analyzed. The RPD of the LCS and LCSD must be compared to the matrix spike RPD limits.

- In the instance where the LCS recovery is greater than 120% (115% for 200.7) and the sample results are < RL, the data may be reported with qualifiers. **Such action must be taken in consultation with the client and must be addressed in the report narrative.**

- Corrective action will be repreparation and reanalysis of the batch unless the client agrees that other corrective action is acceptable.

- For dissolved metals samples which have not been digested, a CCV result is reported as the LCS. The CCV run immediately prior to the start of the dissolved sample analyses must be used for this purpose. No more than 20 samples can be associated with one CCV.

9.4. Matrix Spike/Matrix Spike Duplicate (MS/MSD) - One MS/MSD pair must be processed for each preparation batch. A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added. A matrix spike duplicate

(MSD) is a second aliquot of the same sample (spiked identically as the MS) prepared and analyzed along with the sample and matrix spike. Some client specific data quality objectives (DQO's) may require the use of sample duplicates in place of or in addition to MS/MSDs. The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Due to the potential variability of the matrix of each sample, these results may have immediate bearing only on the specific sample spiked. Samples identified as field blanks cannot be used for MS/MSD analysis. Spiking levels are provided in Tables III and VI (Appendix A).

- If any analyte recovery or RPD falls outside the acceptance range, the recovery of that analyte must be in control for the LCS. For both methods 200.7 and 6010B, control limits of 75 - 125% recovery and 20% RPD or historical acceptance criteria must be applied to the MS/MSD. If the LCS recovery is within limits, then the laboratory operation is in control and the results may be accepted. If the recovery of the LCS is outside limits corrective action must be taken. Corrective action will include repreparation and reanalysis of the batch. MS/MSD results which fall outside the control limits must be addressed in the narrative.

- If the native analyte concentration in the MS/MSD exceeds 4x the spike level for that analyte, the recovery data are reported as NC (i.e., not calculated). If the reporting software does not have the ability to report NC then the actual recovery must be reported and narrated as follows: "Results outside of limits do not necessarily reflect poor method performance in the matrix due to high analyte concentrations in the sample relative to the spike level."

- If an MS/MSD is not possible due to limited sample volume then a laboratory control sample duplicate (LCSD) should be analyzed. The RPD of the LCS and LCSD must be compared to the matrix spike RPD limits.

- For dissolved metals samples which have not been digested, a MS/MSD must be performed per batch of up to 20 samples by spiking two aliquots of the sample at the levels specified in Table III (Appendix A).

9.5. Dilution test – A dilution test is performed to determine whether significant physical or chemical interferences exist due to the sample matrix. One sample per preparation batch must be processed as a dilution test. The test is performed by running a sample at a 5x (1:4) dilution. Samples identified as field blanks cannot be used for dilution tests. The results of the diluted sample, after correction for dilution, should agree within 10% of the original sample determination when the original sample concentration is greater than 50x the IDL. If the results are not within 10%, the possibility of chemical or physical interference exists.

9.6. Initial Calibration Verification (ICV/ICB) - Calibration accuracy is verified by analyzing a second source standard (ICV). For analyses conducted under Method

200.7, the ICV result must fall within 5% of the true value for that solution with relative standard deviation <3% from replicate (minimum of two) exposures. For Method 6010B, the ICV must fall within 10% of the true value for that solution with relative standard deviation <5% from replicate (minimum of two) exposures. An ICB is analyzed immediately following the ICV to monitor low level accuracy and system cleanliness. The ICB result must fall within +/- the RL from zero. If either the ICV or ICB fail to meet criteria, the analysis should be terminated, the problem corrected, the instrument recalibrated and the calibration reverified. (See Section 11.11 or 11.12 for required run sequence).

9.7. Continuing Calibration Verification (CCV/CCB) - Calibration accuracy is monitored throughout the analytical run through the analysis of a known standard after every 10 samples. The CCV is be a mid-range standard made from a dilution of the calibration standard. The CCV for both methods must fall within 10% of the true value for that solution with relative standard deviation <5% from replicate (minimum of two) exposures. A CCB is analyzed immediately following each CCV. (See Section 11.11 or 11.12 for required run sequence.) The CCB result must fall within +/- RL from zero. If the blank is less than 1/10 the concentration of the action level of interest, and no sample is within 10% of the action limit, reanalysis and recalibration are not required before continuation of the run. Sample results may only be reported when bracketed by valid CCV/CCB pairs. If a mid-run CCV or CCB fails, the analysis for the affected element must be terminated, the problem corrected, the instrument recalibrated, the calibration verified and the affected samples reanalyzed. (Refer to Section 11.13 for an illustration of the appropriate rerun sequence).

9.8. Interference Check Analysis (ICSA/ICSAB) - The validity of the interelement correction factors is demonstrated through the successful analysis of interference check solutions. The ICSA contains only interfering elements, the ICSAB contains analytes and interferents. Refer to Table V (Appendix A) for the details of ICSA and ICSAB composition. Custom STL multielement ICS solutions must be used. All analytes should be spiked into the ICSAB solution, therefore, if a non-routine analyte is required then it should be manually spiked into the ICSAB using a certified ultra high purity single element solution or custom lab-specific mix. If the ICP will display overcorrection as a negative number then the non-routine elements can be controlled from the ICSA as described in section 9.8.3. Elements known to be interferents on a required analyte must be included in the ICP run when that analyte is determined. Aluminum, iron, calcium and magnesium must always be included in all ICP runs.

9.8.1. The ICSA and ICSAB solutions must be run at the beginning of the run. (See Section 11.11 or 11.12 for required run sequence.)

9.8.2. The ICSAB results for the interferents must fall within 80 - 120% of the true value. If any ICSAB interferent result fails criteria, the analysis should be terminated, the problem corrected, the instrument recalibrated and the samples

rerun.

9.8.3. ICSA results for the non-interfering elements with reporting limits ≤ 10 ug/L must fall within the STL guidelines of ± 2x RL from zero. ICSA results for the non-interfering elements with RLs> 10 µg/L must fall within the STL guidelines of ± 1x RL from zero. If the ICSA results for the non-interfering elements do not fall within +/- 2x RL (RL ≤10) or ± 1xRL (RL>10) from zero the field sample data must be evaluated as follows:

- If the non-interfering element concentration in the ICSA is the result of contamination versus a spectral interference, and this reason is documented, the field sample data can be accepted.
- If the affected element was not required then the sample data can be accepted.
- If the interfering elements are not present in the field sample at a concentration which would result in a false positive or negative result greater than +/- 2x RL from zero then the field sample data can be accepted.
- If the interfering element is present in the field sample at a level which would result in a false analyte signal greater than ± 2x RL from zero, the data can be accepted only if the concentration of the affected analyte in the field sample is more than 10x the analyte signal in the ICSA.
- If the data does not meet the above conditions then the IECs must be re-evaluated and corrected if necessary and the affected samples reanalyzed or the sample results manually corrected through application of the new IEC to the raw results. If the results are recalculated manually the calculations must be clearly documented on the raw data.

9.9. Method of Standard Addition (MSA) -This technique involves adding known amounts of standard to one or more aliquots of the processed sample solution. This technique compensates for a sample interferent that may enhance or depress the analyte signal, thus producing a different slope from that of the calibration standards. It will not correct for additive interferences which cause a baseline shift. Refer to Section 11.17 for additional information on when MSA is required as well as Appendix D for specific MSA requirements.

9.10. Quality Assurance/Project Summaries - Certain clients may require project- or program-specific QC which may supersede this SOP requirements. Quality Assurance Summaries (QASs) or equivalent documents providing project-specific requirements should be developed so that project staff clearly understand the special project requirements.

10. CALIBRATION AND STANDARDIZATION

10.1. Set up the instrument with the operating parameters recommended by the manufacturer. Allow the instrument to become thermally stable before beginning calibration (approximately 30 minutes of warm-up is required).

10.2. Profile and calibrate the instrument according to the instrument manufacturer's recommended procedures. Flush the system with the calibration blank between each standard or as the manufacturer recommends. The calibration curve must consist of a minimum of a blank and a standard. Refer to the facility-specific instrument SOP or ICP instrument manual for a detailed set up and operation protocols.

10.3. Calibration must be performed daily and each time the instrument is set up. Instrument runs may be continued over periods exceeding 24 hours as long as all calibration verification (CCV) and interference check QC criteria are met. The instrument standardization date and time must be included in the raw data.

10.4. Refer to Section 9.0 for calibration verification procedures, acceptance criteria and corresponding corrective actions.

11. PROCEDURE

11.1. For 200.7 analyses, dissolved (preserved) samples must be digested unless it can be documented that the sample meets all of the following criteria:

A. Visibly transparent with a turbidity measurement of 1 NTU or less.

B. Is of one liquid phase and free of particulate or suspended matter following acidification.

C. Is NOT being analyzed for silver.

11.2. A minimum of <u>two</u> <u>exposures</u> for each standard, field sample and QC sample is required. The average of the exposures is reported. For Trace ICP analyses, the results of the sum channel must be used for reporting.

11.3. Prior to calibration and between each sample/standard the system is rinsed with the calibration blank solution. The minimum rinse time between analytical samples is 60 seconds unless following the protocol outlined in 9.1.6 it can be demonstrated that a shorter rinse time may be used. Triton-X can be added to the rinse solution to facilitate the rinse process.

11.4. The use of an autosampler for all runs is strongly recommended.

11.5. The use of automated QC checks through the instrument software is highly recommended for all calibration verification samples (ICV,CCV), blanks

(ICB,CCB,PB), interference checks (ICSA,ICSAB) and field samples (linear range) to improve the data review process.

11.6. To facilitate the early identification of QC failures and samples requiring rerun it is strongly recommended that sample data be reviewed periodically throughout the run.

11.7. To facilitate the data review and reporting processes it is strongly recommended that all necessary dilutions be performed before closing out the instrument run.

11.8. For unattended overnight auto-runs it is strongly recommended that the frequency of ICSA/ICSAB analysis be increased to every 4 hours.

11.9. The use of an internal standard is recommended on the conventional, non-Trace ICPs as an alternative to using the method of standard additions. This technique is useful in overcoming matrix interferences especially in high solids matrices. However, for conventional ICP techniques, internal standards may not be necessary provided that one of the following is performed to minimize physical interferences: (1) peristaltic pump is used, (2) high solids nebulizer is used, or (3) high solids samples are diluted and reanalyzed.

11.10. The use of an internal standard is **required** on the Trace ICP unless the calibration and QC standards are matrix matched to each digestion procedure used as follows:

Preparation Method	% HNO_3	% HCl
CLP Aqueous	1	5
CLP Soil	5	2.5
SW846 3050	5	10
SW846 3005	2	5
SW846 3010	3	5

The following procedural guidelines must be followed when using an internal standard:

11.10.1. Typically used internal standards are: yttrium or scandium. (Note: Any element can be used that is not typically found in environmental samples at a high rate of occurrence.)

11.10.2. The internal standard (IS) must be added to every sample and standard at the

same concentration. It is recommended that the IS be added to each analytical sample automatically through use of a third pump channel and mixing coil. Internal standards should be added to blanks, samples and standards in a like manner, so that dilution effects resulting from the addition may be disregarded.

11.10.3. The concentration of the internal standard should be sufficiently high to obtain good precision in the measurement of the IS analyte used for data correction and to minimize the possibility of correction errors if the IS analyte is naturally present in the sample.

11.10.4. The internal standard raw intensity counts must be printed on the raw data.

11.10.5. The analyst must monitor the response of the internal standard throughout the sample analysis run. This information is used to detect potential problems and identify possible background contributions from the sample (i.e., natural occurrence of IS analyte).

11.10.5.1. If the internal standard counts fall within ±30% of the counts observed in the ICB then the data is acceptable.

11.10.5.2. If the internal standard counts in the field samples are more than ±30% higher than the expected level, the field samples must then be:

(1) Diluted and reanalyzed;

(2) The IS concentrations must be raised; or

(3) A different internal standard must be used.

11.11. The following analytical sequence must be used for Methods 6010B and 200.7:

Instrument Calibration
ICV
ICB
ICSA
ICSAB
8 samples
CCV
CCB
10 samples
CCV
CCB

Repeat sequence of up to 10 samples between CCV/CCB pairs as required to complete run
CCV
CCB

Refer to Quality Control Section 9.0 and Table VII (Appendix A) for Method 6010B and 200.7 quality control criteria.

11.12. Additional quality control analyses are necessary for analysis under the Contract Laboratory Program (CLP). If these are included then CLP, 6010 and 200.7 samples can be included in the same sequence. Refer to CORP-MT-002 for details.

11.13. Full method required QC must be available for each wavelength used in determining reported analyte results.

11.14. Guidelines are provided in the appendices on procedures to minimize contamination of samples and standards, preventive maintenance and troubleshooting.

11.15. All measurements must fall within the defined linear range where spectral interference correction factors are valid. Dilute and reanalyze all samples for required analytes that exceed the linear range or use an alternate wavelength for which QC data are established. If an interelement correction exists for an analyte which exceeds the linear range, the IEC may be inaccurately applied. Therefore, even if an overrange analyte may not be required to be reported for a sample, if that analyte is a interferent for any requested analyte in that sample, the sample must be diluted. Acid strength must be maintained in the dilution of samples.

11.16. For TCLP samples, full four-point MSA will be required if all of the following conditions are met:

1) recovery of the analyte in the matrix spike is not at least 50%,

2) the concentration of the analyte does not exceed the regulatory level, and,

3) the concentration of the analyte is within 20% of the regulatory level.

The reporting and regulatory limits for TCLP analyses as well as matrix spike levels are detailed in Table VI (Appendix A). Appendix E provides guidance on performing MSA analyses.

11.17. Any variation in procedure shall be completely documented using instrument run logs, maintenance logs, report narratives, a Nonconformance Memo, or an anomaly report and is approved by a Supervisor/Group Leader and QA Manager. If contractually required, the client shall be notified by the Project Manager.

11.18. Nonconformance documentation shall be filed in the project file.

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

12. DATA ANALYSIS AND CALCULATIONS

12.1. ICV percent recoveries are calculated according to the equation:

$$\%R = 100\left(\frac{Found(ICV)}{True(ICV)}\right)$$

12.2. CCV percent recoveries are calculated according to the equation:

$$\%R = 100\left(\frac{Found(CCV)}{True(CCV)}\right)$$

12.3. Matrix Spike Recoveries are calculated according to the following equation:

$$\%R = 100\left(\frac{SSR - SR}{SA}\right)$$

Where:
SSR = Spike Sample Result
SR = Sample Result
SA = Spike Added

12.4. The relative percent difference (RPD) of matrix spike/matrix spike duplicates are calculated according to the following equations:

$$RPD = 100\left[\frac{|MSD - MS|}{\left(\frac{MSD + MS}{2}\right)}\right]$$

Where:
MS = determined spiked sample concentration
MSD = determined matrix spike duplicate concentration

12.5. The final concentration for a digested aqueous sample is calculated as follows:

$$mg/L = \frac{C \times V1 \times D}{V2}$$

Where:
C = Concentration (mg/L) from instrument readout
D = Instrument dilution factor
V1 = Final volume in liters after sample preparation
V2 = Initial volume of sample digested in liters

12.6. The final concentration determined in digested solid samples when reported on a dry weight basis is calculated as follows:

$$mg/Kg, dry\ weight = \frac{C \times V \times D}{W \times S}$$

Where:
C = Concentration (mg/L) from instrument readout
D = Instrument dilution factor
V = Final volume in liters after sample preparation
W = Weight in Kg of wet sample digested
S = Percent solids/100

Note: A Percent Solids determination must be performed on a separate aliquot when dry weight concentrations are to be reported. If the results are to be reported on wet weight basis the "S" factor should be omitted from the above equation.

12.7. The LCS percent recovery is calculated according to the following equation:

$$\%R = 100\left(\frac{Found(LCS)}{True(LCS)}\right)$$

12.8. The dilution test percent difference for each component is calculated as follows:

$$\%Difference = \frac{|I - S|}{I} \times 100$$

Where:
I = Sample result (Instrument reading)
S = Dilution test result (Instrument reading × 5)

12.9. Appropriate factors must be applied to sample values if dilutions are performed.

12.10. Sample results should be reported with up to three significant figures in accordance with the STL significant figure policy.

13. METHOD PERFORMANCE

13.1. Each laboratory must have initial demonstration of performance data on file for each analyte of interest as described in Section 9.0.

13.2. Refer to Tables I, IA & II in Appendix A for the list of Method 6010B and 200.7 analytes as well as additional analytes that may be analyzed using this SOP.

13.3. Method performance is determined by the analysis of MS and MSD samples as well as method blanks and laboratory control samples. The MS or MSD recovery should fall within +/- 25 % and the MS/MSD should compare within 20% RPD or within the laboratory's historical acceptance limits. These criteria apply to analyte concentrations greater than or equal to 10xIDL. Method blanks must meet the criteria specified in Section 9.2. The laboratory control samples should recover within 20% (15% for 200.7) of the true value or within the laboratory's historical acceptance limits.

13.4. Training Qualification:

The group/team leader or the supervisor has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience.

14. POLLUTION PREVENTION

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

15. WASTE MANAGEMENT

15.1. Waste generated in the procedure must be segregated and disposed of according to the facility hazardous waste procedures and per the local, state, and federal regulations. The Environmental Health and Safety Director should be contacted, if additional information is required.

15.2. Standards should be purchased and prepared in volumes consistent with laboratory use to minimize the volume of expired standards to be disposed.

16. REFERENCES

16.1. 40 CFR Part 136, Appendix B, 7-5-95, Determination of Method Detection Limits.

16.2. Test Methods for Evaluating Solid Waste , Physical/Chemical Methods, SW-846, 3rd Edition, Final Update III, Revision 2, December 1996. Method 6010B.

16.3. Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma-Atomic Emission Spectrometry, Revision 4.4, May 1994. Method 200.7.

16.4. CORP-MT-0002, Inductively Coupled Plasma-Atomic Emission Spectroscopy, Method 200.7 & CLP-M, SOW ILMO3.0.

16.5. QA-003, STL QC Program.

16.6. QA-004, Rounding and Significant Figures.

16.7. QA-005, Method Detection Limits.

17. MISCELLANEOUS (TABLES, APPENDICES, ETC.)

17.1. Modifications/Interpretations from reference method

17.1.1. Modifications/interpretations from both Methods 6010B and 200.7.

17.1.1.1. STL laboratories use mixed calibration standard solutions purchased from approved vendors instead of using individual mixes prepared in house as recommended by the subject methods.

17.1.1.2. The alternate run sequence presented in Section 11.12 is consistent with method requirements. Additional QC (i.e., ICSA) analyses were added to accommodate the CLP protocol requirements.

17.1.1.3. Methods 200.7 and 6010B state that if the correction routine is operating properly, the determined apparent analyte(s) concentration from analysis of each interference solution should fall within a specific concentration range around the calibration blank. In determining IECs, because of lack of definition clarification for "concentration range around the calibration blank," STL has adopted the procedure in EPA CLP ILMO4.0.

17.1.1.4. Section 8.5 of Method 6010B and Section 9.5 of Method 200.7 recommend that whenever a new or unusual matrix is encountered, a

series of tests be performed prior to reporting concentration data for that analyte. The dilution test helps determine if a chemical or physical interference exists. Because STL laboratories receive no prior information from clients regarding when to expect a new or unusual matrix, STL may select to perform a dilution test on one sample in each prep batch. According to the method, the post digestion spike (PDS) determines any potential matrix interferences. At STL labs, matrix interference is determined by evaluating data for the LCS and MS/MSD. STL requires documented, clear guidance when a new or unusual matrix will be received for a project and a request to perform the dilution test or PDS on a client-identified sample.

17.1.2. Modifications from Method 200.7.

17.1.2.1. Method 200.7 defines the IDL as the concentration equivalent to a signal, due to the analyte, which is equal to three times the standard deviation of a series of ten replicate measurements of the calibration blank signal at the same wavelength. STL labs utilize the CLP IDL definition as defined in Section 9.1.1 of this SOP.

17.1.2.2. The calibration blank is prepared in an acid matrix of 5% HNO_3/5% HCl instead of the specified 2% HNO_3/10% HCl matrix as the former matrix provides for improved performance relative to the wide variety of digestate acid matrices which result from the various EPA preparation protocols applied.

17.1.2.3. Method section 9.3.4 specifies that "Analysis of the IPC (ICSA/AB) solution immediately following calibration must verify that the instrument is within ± 5% of calibration with a relative standard deviation <3% from replicate integrations ≥ 4." STL uses a minimum of two exposures.

17.1.2.4. Section 7.12 of 200.7 indicates that the QCS (ICV) should be prepared at a concentration near 1 ppm. The ICV specified in this SOP accommodates the 1 ppm criteria for the majority of analytes. For the remaining analytes, this SOP specifies ICV concentrations which are appropriate to the range of calibration. The intent of the ICV, verification of calibration standard accuracy, is independent of the ICV concentration used.

17.1.2.5. The ICS criteria applied by this SOP differ from those stated in the method. Method 200.7 section 10.4 states that results should fall within the established control limits of 3 times the standard deviation

of the calibration blank for that analyte. The control limits listed in this SOP are those applicable to the EPA designed solution.

17.1.2.6. Method 200.7 section 9.3.4 states the CCB should be less than the IDL, but > the lower 3-sigma control limit of the calibration blank. The intent of this requirement is to ensure that the calibration is not drifting at the low end. STL has adopted an absolute control limit of +/- RL from zero for calibration blank criteria. SOP section 9.7 provides the detailed corrective action criteria that must be followed.

17.1.3. Modifications from Method 6010B.

17.1.3.1. Chapter 1 of SW-846 states that the method blank should not contain any analyte of interest at or above the MDL. This SOP states that the method blank must not contain any analyte of interest at or above the reporting limit. Common lab contaminants are allowed up to two times the reporting limit in the blank following consultation with the client.

17.1.3.2. Method 6010B section 8.6.1.3 states that the results of the calibration blank are to agree within 3x the IDLIf not, repeat the analysis two or more times and average the results. If the average is not within three standard deviation of the background mean, terminate the analysis, correct the problem, recalibrate, and reanalyze the previous 10 samples. The intent of this requirement is to ensure that the calibration is not drifting at the low end. STL has adopted an absolute control limit of +/- RL from zero for calibration blank criteria. See SOP Section 9.7 for a detailed description of the required corrective action procedures.

17.2. Modifications from previous SOP

Refer to revision 1 of this SOP.

17.3. Facility-Specific SOPs

Each facility shall review and revise as appropriate this SOP to reflect any facility-specific requirementsIf no facility-specific amendments are required, the SOP can be adopted as is.

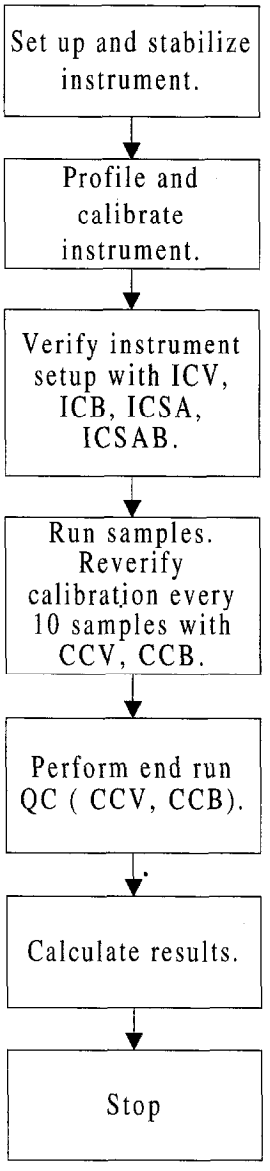
17.4. Documentation and Record Management

The following documentation comprises a complete ICP raw data package:

- Raw data (direct instrument printout).

- Relevant sample preparation benchsheets.
- Run log printout from instrument software where this option is available (TJA) or manually generated run log (i.e., Ward WSL printout).
- Data review checklist - See Appendix B.
- Standards documentation (including prep and expiration dates, source, and lot #).
- Nonconformance/anomaly documentation (if applicable).

17.5. Flow Diagram



APPENDIX A

TABLES

TABLE I. Method 200.7 and 6010B Target Analyte List

ELEMENT	Symbol	CAS #	6010B analyte	200.7 analyte	Reporting Limit (ug/L) Water	Reporting Limit (mg/kg) Soil
Aluminum	Al	7429-90-5	X	X	200	20
Antimony	Sb	7440-36-0	X	X	60	6
Arsenic	As	7440-38-2	X	X	300	30
Barium	Ba	7440-39-3	X	X	200	20
Beryllium	Be	7440-41-7	X	X	5.0	0.5
Boron	B	7440-42-8		X	200	20
Cadmium	Cd	7440-43-9	X	X	5.0	0.5
Calcium	Ca	7440-70-2	X	X	5000	500
Chromium	Cr	7440-47-3	X	X	10	1
Cobalt	Co	7440-48-4	X	X	50	5
Copper	Cu	7440-50-8	X	X	25	2.5
Iron	Fe	7439-89-6	X	X	100	10
Lead	Pb	7439-92-1	X	X	100	10
Lithium	Li	7439-93-2	X	X	50	5
Magnesium	Mg	7439-95-4	X	X	5000	500
Manganese	Mn	7439-96-5	X	X	15	1.5
Molybdenum	Mo	7439-98-7	X	X	40	4
Nickel	Ni	7440-02-0	X	X	40	4
Phosphorus	P	7723-14-0	X	X	300	30
Potassium	K	7440-09-7	X	X	5000	500
Selenium	Se	7782-49-2	X	X	250	25
Silicon	Si	7631-86-9		X	500	N/A
Silver	Ag	7440-22-4	X	X	10	1
Sodium	Na	7440-23-5	X	X	5000	500
Strontium	Sr	7440-24-6	X		50	5
Thallium	Tl	7440-28-0	X	X	2000	200
Vanadium	V	7440-62-2	X	X	50	5
Zinc	Zn	7440-66-6	X	X	20	2

TABLE IA. Method 200.7 and 6010B Trace ICP Target Analyte List

ELEMENT	Symbol	CAS #	Reporting Limit (ug/L) Water	Reporting Limit (mg/kg) Soil
Arsenic	As	7440-38-2	10	1.0
Lead	Pb	7439-92-1	3.0	0.3
Selenium	Se	7782-49-2	5.0	0.5
Thallium	Tl	7440-28-0	10	1.0
Antimony	Sb	7440-36-0	10	1.0
Cadmium	Cd	7440-43-9	2.0	0.2
Silver	Ag	7440-22-4	5.0	0.5
Chromium	Cr	7440-47-3	5.0	0.5

TABLE II. Non-Routine Analyte List

ELEMENT	Symbol	CAS #	Reporting Limit (ug/L) Water	Reporting Limit (mg/kg) Soil
Tin	Sn	7440-31-5	100	10
Titanium	Ti	7440-32-6	50	5
Bismuth	Bi	7440-06-99	200	20
Zirconium	Zr	7440-06-77	100	10
Tungsten	W	7440-03-37	500	50
Tellurium	Te	1349-48-09	500	50
Thorium	Th	7440-02-91	500	50
Uranium	U	7440-06-11	500	50
Palladium	Pd	7440-00-53	100	10

NOTE: Analysis of all elements listed may not be available at all STL facilities.

TABLE III. Matrix Spike and Aqueous Laboratory Control Sample Levels

ELEMENT	LCS Level (ug/L)	Matrix Spike Level (ug/L)
Aluminum	2000	2000
Antimony	500	500
Arsenic	2000	2000
Barium	2000	2000
Beryllium	50	50
Cadmium	50	50
Calcium	50000	50000
Chromium	200	200
Cobalt	500	500
Copper	250	250
Iron	1000	1000
Lead	500	500
Lithium	1000	1000
Magnesium	50000	50000
Manganese	500	500
Molybdenum	1000	1000
Nickel	500	500
Phosphorous	10000	10000
Potassium	50000	50000
Selenium	2000	2000
Silver	50	50
Sodium	50000	50000
Strontium	1000	1000
Thallium	2000	2000
Vanadium	500	500
Zinc	500	500
Boron	1000	1000
Silicon	10000	10000
Tin	2000	2000
Titanium	1000	1000
Bismuth	1000	1000
Zirconium	1000	1000
Tellurium	1000	1000
Thorium	1000	1000
Uranium	1000	1000
Tungsten	1000	1000
Palladium	1000	1000

TABLE IV. ICP Calibration and Calibration Verification Standards

Element	Calibration Level	RL (ug/L)	ICV (ug/L)	CCV (ug/L)
Aluminum	100000	200	25000	50000
Antimony	10000	60	1000	5000
Arsenic	10000	300	1000	5000
Barium	10000	200	1000	5000
Beryllium	10000	5	1000	5000
Cadmium	10000	5	1000	5000
Calcium	100000	5000	25000	50000
Chromium	10000	10	1000	5000
Cobalt	10000	50	1000	5000
Copper	10000	25	1000	5000
Iron	100000	100	25000	50000
Lead	10000	100	1000	5000
Lithium	10000	50	1000	5000
Magnesium	100000	5000	25000	50000
Manganese	10000	15	1000	5000
Molybdenum	10000	40	1000	5000
Nickel	10000	40	1000	5000
Phosphorous	10000	300	1000	5000
Potassium	100000	5000	25000	50000
Selenium	10000	250	1000	5000
Silver	2000	10	500	1000
Sodium	100000	5000	25000	50000
Strontium	10000	50	1000	5000
Thallium	20000	2000	5000	10000
Vanadium	10000	50	1000	5000
Zinc	10000	20	1000	5000
Boron	10000	200	1000	5000
Silicon	10000	500	1000	5000
Tin	10000	100	1000	5000
Titanium	10000	50	1000	5000
Bismuth	10000	200	1000	5000
Zirconium	10000	100	1000	5000
Tellurium	10000	500	1000	5000
Thorium	10000	500	1000	5000
Uranium	10000	500	1000	5000
Tungsten	10000	500	1000	5000
Palladium	10000	100	1000	5000

TABLE IVA. Trace ICP Calibration and Calibration Verification Standards

Element	Calibration Level	RL (ug/L)	ICV (ug/L)	CCV (ug/L)
Aluminum	50000	200	12500	25000
Antimony	1000	10	250	500
Arsenic	1000	10	250	500
Barium	4000	10	1000	2000
Beryllium	4000	5	1000	2000
Cadmium	1000	2	250	500
Calcium	100000	5000	25000	50000
Chromium	4000	5	1000	2000
Cobalt	4000	50	1000	2000
Copper	4000	25	1000	2000
Iron	50000	100	12500	25000
Lead	1000	3	250	500
Magnesium	100000	5000	25000	50000
Manganese	4000	15	1000	2000
Molybdenum	4000	40	1000	2000
Nickel	4000	40	1000	2000
Potassium	100000	5000	25000	50000
Selenium	1000	5	250	500
Silver	2000	5	500	1000
Sodium	100000	5000	25000	50000
Thallium	2000	10	500	1000
Vanadium	4000	50	1000	2000
Zinc	4000	20	1000	2000

TABLE V. Interference Check Sample Concentrations*

Element	ICSA (ug/L)	ICSAB (ug/L)
Aluminum	500000	500000
Antimony	-	1000
Arsenic	-	1000
Barium	-	500
Beryllium	-	500
Cadmium	-	1000
Calcium	500000	500000
Chromium	-	500
Cobalt	-	500
Copper	-	500
Iron	200000	200000
Lead	-	1000
Magnesium	500000	500000
Manganese	-	500
Molybdenum	-	1000
Nickel	-	1000
Potassium	-	10000
Selenium	-	1000
Silver	-	1000
Sodium	-	10000
Thallium	-	10000**
Vanadium	-	500
Zinc	-	1000
Tin	-	1000

* Custom STL solutions contain analytes common to all STL facilities. Non-routine elements not listed above should be spiked into the ICSAB at 1000 ug/L.

** Thallium level for Trace ICP should be at 1000 ug/L.

TABLE VI. TCLP Reporting Limits, Regulatory Limits and Matrix Spike Levels

ELEMENT	Reporting Level (ug/L)	Regulatory Limit (ug/L)	Spike Level (ug/L)
Arsenic	500	5000	5000
Barium	10000	100000	50000
Cadmium	100	1000	1000
Chromium	500	5000	5000
Lead	500	5000	5000
Selenium	250	1000	1000
Silver	500	5000	1000

TABLE VII. Summary Of Quality Control Requirements

QC PARAMETER	FREQUENCY *	ACCEPTANCE CRITERIA	CORRECTIVE ACTION
Two-point Initial Calibration	Beginning of every analytical run, every 24 hours, whenever instrument is modified, or CCV criterion is not met	RSD between duplicate exposures ≤5%	Terminate analysis; Correct the problem; Prepare new standards; Recalibrate following system performance.
ICV	Beginning of every analytical run.	Method 200.7: 95 - 105 % recovery. Method 6010B: 90 - 110 % recovery.	Terminate analysis; Correct the problem; Recalibrate.
ICB	Beginning of every analytical run, immediately following the ICV.	The result must be within +/- RL from zero.	Terminate analysis; Correct the problem; Recalibrate.
CCV	Every 10 samples and at the end of the run.	Method 200.7 & 6010B: 90 - 110 % recovery.	Terminate analysis; Correct the problem; Recalibrate and rerun all samples not bracketed by acceptable CCV.
CCB	Immediately following each CCV.	The result must be within +/- RL from zero.	Terminate analysis; Correct the problem; Recalibrate and rerun all samples not bracketed by acceptable CCB.
ICSA	Beginning of every run	See Section 9.8.3	See Section 9.8.3.
ICSAB	Immediately following each ICSA.	Results must be within 80 - 120% recovery.	See Section 9.8.2.

* See Sections 11.11 and 11.12 for exact run sequence to be followed.

TABLE VII. Summary of Quality Control Requirements (Continued)

QC PARAMETER	FREQUENCY	ACCEPTANCE CRITERIA	CORRECTIVE ACTION
Dilution Test	One per prep batch.	For samples > 50x IDL, dilutions must agree within 10%.	Narrate the possibility of physical or chemical interference per client request.
Method Blank	One per sample preparation batch of up to 20 samples.	The result must be less than or equal to the RL. Common lab contaminants may be accepted up to 2x the RL after consultation with the client (See 9.2). Sample results greater than 10x the blank concentration are acceptable. Samples for which the contaminant is < RL may not require redigestion or reanalysis (see Section 9.2).	Redigest and reanalyze samples. Note exceptions under criteria section. See Section 9.2 for additional requirements.
Laboratory Control Sample (LCS)	One per sample preparation batch of up to 20 samples.	Aqueous LCS must be within 80 - 120% recovery or in-house control limits. (85-115% for 200.7) Samples for which the contaminant is < RL and the LCS results are > 120% (115% for 200.7) may not require redigestion or reanalysis (see Section 9.3)	Terminate analysis; Correct the problem; Redigest and reanalyze all samples associated with the LCS.

TABLE VII. Summary of Quality Control Requirements (Continued)

QC PARAMETER	FREQUENCY	ACCEPTANCE CRITERIA	CORRECTIVE ACTION
Matrix Spike	One per sample preparation batch of up to 20 samples.	75 - 125 % recovery or in-house control limits. I For TCLP See Section 11.17.	In the absence of client specific requirements, flag the data; no flag required if the sample level is > 4x the spike added. For TCLP see Section 11.17.
Matrix Spike Duplicate	See Matrix Spike	75 - 125 % recovery; RPD ≤ 20% .	See Corrective Action for Matrix Spike.

APPENDIX B

STL ICP DATA REVIEW CHECKLIST

STL ICP Data Review Checklist

Run/Project Information:

Run Date: _____ **Analyst:**_____ **Instrument:**_____
Prep Batches Run:_____

Circle Methods used: 6010B / 200.7: CORP-MT-0001 Rev 2
CLP ILMO3.0/4.0 : CORP-MT-0002 Rev 1

Review Items

A. Calibration/Instrument Run QC	Yes	No	N/A	2nd Level
1. Instrument calibrated per manufacturer's instructions and at SOP specified levels ?				
2. ICV/CCV analyzed at appropriate frequency and within control limits ? (6010B, CLP = 90 - 110%, 200.7 = 95 -105%[ICV])				
3. ICB/CCB analyzed at appropriate frequency and within +/- RL or +/- CRDL (CLP) ?				
4. CRI analyzed? (for CLP only)				
5. ICSA/ICSAB run at required frequency and within SOP limits ?				
B. Sample Results				
1. Were samples with concentrations > the linear range for any parameter diluted and reanalyzed ?				
2. All reported results bracketed by in control QC ?				
3. Sample analyses done within holding time ?				
C. Preparation/Matrix QC				
1. LCS done per prep batch and within QC limits ?				
2. Method blank done per prep batch and < RL or CRDL (CLP) ?				
3. MS run at required frequency and within limits ?				
4. MSD or DU run at required frequency and RPD within SOP limits ?				
5. Dilution Test done per prep batch (or per SDG for CLP) ?				
6. Post digest spike analyzed if required (CLP only) ?				
D. Other				
1. Are all nonconformances documented appropriately ?				
2. Current IDL/LR/IEC data on file ?				
3. Calculations checked for error ?				
4. Transcriptions checked for error ?				
5. All client/project specific requirements met ?				
6. Date/time of analysis verified as correct ?				

Analyst: _____ **Date:** _____
Comments:_____

2nd Level Reviewer : _____ **Date:** _____
Comments:_____

APPENDIX C

CROSS REFERENCE OF TERMS USED IN METHODS 6010B, 200.7, AND BY STL

CROSS REFERENCE OF TERMS COMMONLY USED IN METHODS EPA 200.7, SW6010B, AND STL INC. SOP

EPA 200.7	SW6010B	STL Inc. SOP
Calibration blank (CB)	Calibration blank	Initial and continuing calibration blanks (ICB/CCB)
Dilution test	Dilution test	Dilution Test
Instrument detection limit (IDL)	Instrument detection limit (IDL)	Instrument detection limit (IDL)
Instrument performance check (IPC)	Continuing calibration verification (CCV)	Continuing calibration verification (CCV)
Internal standard	Internal standard	Internal standard (IS)
Laboratory duplicates	n/a	n/a
Laboratory fortified blank (LFB)	n/a	Laboratory control sample (LCS)
Laboratory fortified sample matrix (LFM)	Matrix spike and matrix spike duplicate (MS/MSD)	Matrix spike and matrix spike duplicate (MS/MSD)
Laboratory reagent blank (LRB)	Method blank	Method or Prep blank (MB)
Linear dynamic range (LDR)	Linear dynamic range (LDR)	Linear dynamic range (LDR)
Method detection limit (MDL)	Method detection limit (MDL)	Method detection limit (MDL)
Quality control sample (QCS)	Check standard or Initial calibration verification (ICV)	Initial calibration verification (ICV)
Spectral interference check solution (SIC)	Interference check solution (ICS)	Interference check solution (ICSA/ICSAB)

APPENDIX D

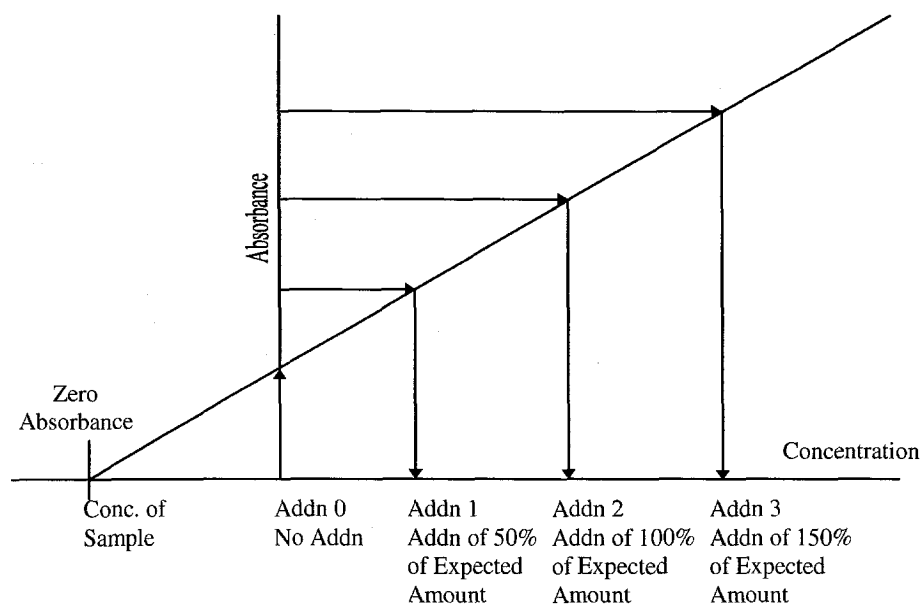
MSA GUIDANCE

Appendix D. MSA Guidance

Method of Standard Addition

Four equal volume aliquots of sample are measured and known amounts of standards are added to three aliquots. The fourth aliquot is the unknown and no standard is added to it. The concentration of standard added to the first aliquot should be 50% of the expected concentration. The concentration of standard added to the second aliquot should be 100% of the expected concentration and the concentration of standard added to the third aliquot should be 150% of the expected concentration. The volume of the unspiked and spiked standard should be the same.

In order to determine the concentration of analyte in the sample, the analytical value of each solution is determined and a plot or linear regression performed. On the vertical axis the analytical value is plotted versus the concentrations of the standards on the horizontal axis. An example plot is shown in Figure 1. When the resulting line is extrapolated back to zero absorbance, the point of interception of the horizontal axis is the concentration of the unknown.



For the method of standard additions to be correctly applied, the following limitations must be taken into consideration:

- The plot of the sample and standards must be linear over the concentration range of concern. For best results, the slope of the curve should be similar to that of a plot of the aqueous standard curve.

- The effect of the interference should not vary as the ratio of the standard added to the sample matrix changes.

APPENDIX E

TROUBLESHOOTING GUIDE

APPENDIX E. TROUBLESHOOTING GUIDE

Problem	Possible Cause/ Solution
High Blanks	Increase rinse time Clean or replace tip Clean or replace torch Clean or replace sample tubing Clean or replace nebulizer Clean or replace mixing chamber Lower Torch
Instrument Drift	RF not cooling properly Vacuum level is too low Replace torch (Crack) Clean or replace nebulizer (blockage) Check room temperature (changing) Replace pump tubing Room humidity too high Clean torch tip (salt buildup) Check for argon leaks Adjust sample carrier gas Reprofile Horizontal Mirror Replace PA tube
Erratic Readings, Flickering Torch or High RSD	Check for argon leaks Adjust sample carrier gas Replace tubing (clogged) Check drainage(back pressure changing) Increase uptake time (too short) Increase flush time (too short) Clean nebulizer, torch or spray chamber Increase sample volume introduced Check that autosampler tubes are full Sample or dilution of sample not mixed Increase integration time (too short) Realign torch Reduce amount of tubing connectors
Cu/Mn Ratio Outside Limits or Low Sensitivity	Plasma conditions changed Clean nebulizer, torch or spray chamber Replace tubing (clogged) Realign torch Check IECs
Standards reading twice normal absorbance or concentration	Incorrect standard used Incorrect dilution performed

APPENDIX F

CONTAMINATION CONTROL GUIDELINES

APPENDIX F. CONTAMINATION CONTROL GUIDELINES

The following procedures are strongly recommended to prevent contamination:

All work areas used to prepare standards and spikes should be cleaned before and after each use.

All glassware should be washed with detergent and tap water and rinsed with 1:1 nitric acid followed by deionized water.

Proper laboratory housekeeping is essential in the reduction of contamination in the metals laboratory. All work areas must be kept scrupulously clean.

Powdered or Latex Gloves must not be used in the metals laboratory since the powder contains silica and zinc as well as other metallic analytes. Only vinyl or nitrile gloves should be used in the metals laboratory.

Glassware should be periodically checked for cracks and etches and discarded if found. Etched glassware can cause cross contamination of any metallic analytes.

Autosampler trays should be covered to reduce the possibility of contamination. Trace levels of elements being analyzed in the samples can be easily contaminated by dust particles in the laboratory.

The following are helpful hints in the identification of the source of contaminants:

Yellow pipet tips and volumetric caps can sometimes contain cadmium.

Some sample cups have been found to contain lead.

The markings on glass beakers have been found to contain lead. If acid baths are in use for glassware cleaning, they should be periodically checked for contaminants since contaminant concentrations will increase over time.

New glassware especially beakers can be a source of silica and boron.

Reagents or standards can contain contaminants or be contaminated with the improper use of a pipette.

Improper cleaning of glassware can cause contamination.

Latex gloves contain over 500 ppb of zinc.

APPENDIX G

PREVENTIVE MAINTENANCE

APPENDIX G. PREVENTIVE MAINTENANCE

A maintenance log is used to record when maintenance is performed on instruments. When an instrument problem occurs indicate the date, time and instrument number, then identify the problem and corrective action in the maintenance log.

The following procedures are required to ensure that that the instrument is fully operational.

Daily	Change sample pump tubing and pump windings Check argon gas supply level Check rinse solution and fill if needed Check waste containers and empty if needed Check sample capillary tubing is clean and in good condition Check droplet size to verify nebulizer is not clogged. Check sample flow for cross flow nebulizer Check Cu/Mn ratio-should be 30% of value at date that IECs were performed Check pressure for vacuum systems
As Needed	Clean plasma torch assembly to remove accumulated deposits Clean nebulizer and drain chamber; keep free-flowing to maintain optimum performance Replace peristaltic pump tubing, sample capillary tubing and autosampler sipper probe
Weekly	Apply silicon spray on autosampler tracks Check water level in coolflow
Monthly	Clean air filters on back of power unit to remove dust Check D mirror for air instruments
Bi-yearly	Change oil for vacuum systems Replace coolant water filter (may require more or less frequently depending on quality of cooling water)

CORP-MT-0005PT

Preparation and Analysis of Mercury in Aqueous Samples by Cold Vapor Atomic Absorption, SW 846-7470A and MCAWW 245.1

Controlled Copy
Copy No._____

LABORATORY-SPECIFIC

STL STANDARD OPERATING PROCEDURE

TITLE: PREPARATION AND ANALYSIS OF MERCURY IN AQUEOUS SAMPLES BY COLD VAPOR ATOMIC ABSORPTION, SW846 7470A AND MCAWW 245.1

(SUPERSEDES: CORP-MT-0005, REVISION 1)

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Approved by: _____
Laboratory Director

Approved by: _____
Corporate Technology and/or Corporate Quality Assurance

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1. SCOPE AND APPLICATION

1.1. This procedure describes the preparation and analysis of mercury (Hg, CAS # 7439-97-6) by Cold Vapor Atomic Absorption Spectroscopy (CVAA) using SW-846 Method 7470A and MCAWW Method 245.1.

1.2. CVAA analysis provides for the determination of total mercury (organic and inorganic). The combination of the oxidants, potassium permanganate and potassium persulfate, has been found to give 100% recovery with both types of compounds. Detection limits, sensitivity and optimum concentration ranges for mercury analysis will vary with the matrices, instrumentation and volume of sample used.

1.3. Method 7470A is applicable to the preparation and analysis of mercury in ground water, aqueous samples, wastes, wipes, TCLP, EP and other leachates/extracts. Certain solid and sludge type wastes may also be analyzed, however Method 7471A (see CORP-MT-0007) is usually the method of choice. All matrices require sample preparation prior to analysis.

1.4. Method 245.1 is applicable to the determination of mercury in drinking, surface and saline waters, domestic and industrial wastes. All matrices require sample preparation prior to analysis.

1.5. The STL reporting limit for mercury in aqueous matrices is 0.0002 mg/L except for TCLP, SPLP or EPTOX leachates for which the reporting limit is 0.002 mg/L.

2. SUMMARY OF METHOD

2.1. This SOP describes a technique for the determination of mercury in solution. The procedure is a physical method based on the absorption of radiation at 253.7 nm by mercury vapor. A representative portion of the sample is digested in sulfuric and nitric acids. Organic mercury compounds are oxidized with potassium permanganate and potassium persulfate and the mercury reduced to its elemental state with stannous chloride and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance is measured as a function of mercury concentration. Concentration of the analyte in the sample is determined by comparison of the sample absorbance to the calibration curve (absorbance vs. concentration).

3. DEFINITIONS

3.1. Dissolved Metals: Those elements which pass through a 0.45 um membrane. (Sample is acidified after filtration).

3.2. Suspended Metals: Those elements which are retained by a 0.45 um membrane.

3.3. Total Metals: The concentration determined on an unfiltered sample following digestion.

4. INTERFERENCES

Chemical and physical interferences may be encountered when analyzing samples using this method.

4.1. Potassium permanganate which is used to breakdown organic mercury compounds also eliminates possible interferences from sulfide. Concentrations as high as 20 mg/L of sulfide as sodium sulfide do not interfere with the recovery of inorganic mercury from reagent water.

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

4.3. Chlorides can cause a positive interference. Seawaters, brines and industrial effluents high in chlorides require additional permanganate (as much as 25 mL) because, during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation at 253.7 nm. Care must be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. This is accomplished by adding excess hydroxylamine reagent (25 mL) and purging the sample head space before stannous chloride is added. Both inorganic and organic mercury spikes have been quantitatively recovered from seawater using this technique.

Note: Sufficient addition of permanganate is apparent when the purple color persists at least 15 minutes. Some samples may require dilution prior to digestion due to extremely high concentrations of chloride.

4.4. Interference from certain volatile organic materials that absorb at this wavelength may also occur. If suspected, a preliminary run without stannous chloride can determine if this type of interference is present. While the possibility of absorption from certain organic substances present in the sample does exist, this problem is not routinely encountered. This is mentioned only to caution the analyst of the possibility. If this condition is found to exist, the mercury concentration in the sample can be determined

by subtracting the result of the sample run without the reducing reagent (stannous chloride) from that obtained with the reducing reagent.

4.5. Samples containing high concentrations of oxidizable organic materials, as evidenced by high COD levels, may not be completely oxidized by this procedure. When this occurs the recovery of mercury will be low. The problem can be eliminated by reducing the volume of original sample used.

4.6. The most common interference is laboratory contamination which may arise from impure reagents, dirty glassware, improper sample transfers, dirty work areas, etc. Be aware of potential sources of contamination and take appropriate measures to minimize or avoid them.

5. SAFETY

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

5.2. Eye protection that satisfies ANSI Z87.1 (as per the Chemical Hygiene Plan), laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

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

5.3.1. The following materials are known to be **corrosive:**

hydrochloric acid, nitric acid and sulfuric acid.

5.3.2. The following materials are known to be **oxidizing agents**:

nitric acid, potassium permanganate, potassium persulfate and magnesium perchlorate.

5.3.3. Mercury is a highly toxic element that must be handled with care. The analyst must be aware of the handling and clean-up techniques before working with mercury. Since mercury vapor is toxic, precaution must be taken to avoid its inhalation, ingestion or absorption through skin. All lines should be checked for

leakage and the mercury vapor must be vented into a hood or passed through a mercury absorbing media such as:

5.3.3.1. Equal volumes of 0.1 M $KMnO_4$ and 10% H_2SO_4, or

5.3.3.2. Iodine, 0.25%, in a 3% KI solution.

5.3.4. Magnesium sulfate is known to be a reproductive toxin (mutagen).

5.4. Exposure to chemicals must be maintained **as low as reasonably achievable.** Therefore, unless they are known to be non-hazardous, all samples should be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

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

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

5.7. Do not look directly into the beam of the Hg lamp. The UV light that these lamps radiate is harmful to the eyes.

5.8. Cylinders of compressed gas must be handled with caution, in accordance with local regulations. It is recommended that, wherever possible, cylinders be located outside the laboratory and the gas led to the instrument through approved lines.

5.9. The CVAA apparatus must be properly vented to remove potentially harmful fumes generated during sample analysis.

6. EQUIPMENT AND SUPPLIES

6.1. Temperature controlled water bath (capable of maintaining a temperature of 90-95 °C) or autoclave that is able to obtain conditions of 15 lbs., 120 °C for 15 minutes.

6.2. Atomic Absorption Spectrophotometer equipped with:

6.2.1. Absorption Cell with quartz end windows perpendicular to the longitudinal axis. Dimensions of the cell must result in sufficient sensitivity to meet the SOP defined reporting limit. The quartz windows must be maintained to provide

accurate measurements. Any scratches or fingerprints can alter the absorption of UV radiation.

6.2.2. Mercury specific hollow cathode lamp (HCL) or electrodeless discharge lamp (EDL).

6.2.3. Peristaltic pump which can deliver 1 L/min air.

6.2.4. Flowmeter capable of measuring an airflow of 1 L/min.

6.2.5. Recorder or Printer.

6.2.6. Aeration Tubing: A straight glass frit having a course porosity and Tygon tubing is used for the transfer of mercury vapor from the sample bottle to the absorption cell and return.

6.2.7. Drying device (a drying tube containing magnesium perchlorate or magnesium sulfate and/or a lamp with a 60 W bulb) to prevent condensation in cell. The lamp is positioned to shine on the absorption cell maintaining the air temperature in the cell about 10 °C above room temperature. Other drying devices that achieve the same purpose are also acceptable (i.e., Gortex filter).

NOTE: Instruments designed specifically for the measurement of mercury using the cold vapor technique may be substituted for the atomic absorption spectrophotometer.

6.3. BOD bottles or equivalent.

6.4. Nitrogen or argon gas supply, welding grade or equivalent.

6.5. Calibrated automatic pipettes or Class A glass volumetric pipettes.

6.6. Class A volumetric flasks.

6.7. Thermometer (capable of accurate readings at 95 °C).

6.8. Disposable cups or tubes.

7. REAGENTS AND STANDARDS

7.1. Reagent water must be produced by a Millipore DI system or equivalent. Reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks.

7.2. Stock (1000 ppm) mercury standards (in 10% HNO_3) are purchased as custom STL solutions. All standards must be stored in FEP fluorocarbon or previously unused polyethylene or polypropylene bottles. Stock standard solutions must be replaced prior to the expiration date provided by the manufacturer. If no expiration date is provided, the stock solutions may be used for up to one year and must be replaced sooner if verification from an independent source indicates a problem.

7.3. Intermediate mercury standard (10 ppm): Take 1 mL of the stock mercury standard (7.2) and dilute to 100 mL with reagent water. The intermediate standard must be made monthly and must be prepared in a matrix of 2% HNO_3 . This acid (2 mL of concentrated HNO_3) must be added to the flask/bottle before the addition of the stock standard aliquot.

7.4. Working mercury standard (0.1 ppm): Take 1 mL of the intermediate mercury standard (7.3) and dilute to 100 mL with reagent water. The working mercury standard must be made daily and must be prepared in a matrix of 0.15% HNO_3. This acid (150 uL of concentrated HNO_3) must be added to the flask/bottle before the addition of the stock standard aliquot.

7.5. The calibration standards listed in Table I must be prepared fresh daily from the working standard (7.4) by transferring 0, 0.2, 0.5, 1.0, 2.0, 5.0 and 10.0 mL aliquots of the working mercury standard into 100 mL flasks and diluting to volume with reagent water.

Note: Alternate approaches to standard preparation may be taken and alternate volumes of standard may be prepared as long as the accuracy and final standard concentrations as detailed in Table I are maintained. For example, automated mercury systems do not require 100 mL of standard and therefore smaller volumes may be generated to reduce waste generation.

7.6. The initial calibration verification standard must be made from a different stock solution than that of the calibration standards.

7.7. Refer to Table I (Appendix A) for details regarding the working standard concentrations for calibration, calibration verification and spiking solutions. All standards must be processed through the entire analytical procedure including sample preparation.

7.8. Nitric acid (HNO_3), concentrated, trace metal grade or better.

Note: If a high reagent blank is obtained, it may be necessary to distill the nitric acid.

7.9. Sulfuric acid (H_2SO_4), concentrated, trace metal grade or better.

7.9.1. Sulfuric acid, 0.5 N: Dilute 14.0 mL of concentrated H_2SO_4 to 1 liter with reagent water.

7.10. Stannous sulfate solution: Add 25 g of stannous sulfate to 250 mL of 0.5 N sulfuric acid. This mixture is a suspension and should appear cloudy. This solution should be made daily and should be stirred continuously during use.

Note: Stannous chloride may be used in place of stannous sulfate. Prepare the stannous chloride solution according to the recommendations provided by the instrument manufacturer.

7.11. Sodium chloride-hydroxylamine hydrochloride solution: Add 12 g of sodium chloride and 12 g of hydroxylamine hydrochloride to every 100 mL of reagent water.

Note: Hydroxylamine sulfate may be used in place of hydroxylamine hydrochloride.

7.12. Potassium permanganate, 5% solution (w/v): Dissolve 5 g of potassium permanganate for every 100 mL of reagent water.

7.13. Potassium persulfate, 5% solution (w/v): Dissolve 5 g of potassium persulfate for every 100 mL of reagent water.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Sample holding time for mercury is 28 days from time of collection to the time of analysis.

8.2. Aqueous samples are preserved with nitric acid to a pH of <2 and may be stored in either plastic or glass. Refrigeration is not required. Preservation must be verified prior to analysis.

9. QUALITY CONTROL

Table II (Appendix A) provides a summary of quality control requirements including type, frequency, acceptance criteria and corrective action.

9.1. Initial Demonstration of Capability

Prior to the analysis of any analyte using 7470A or the 245.1, the following requirements must be met.

9.1.1. Method Detection Limit (MDL) - An MDL must be determined for each analyte/matrix prior to the analysis of any samples. The MDL is determined using seven replicates of reagent water, spiked with all the analytes of interest, that have been carried through the entire analytical procedure. MDLs must be redetermined on an annual basis in accordance with 40 CFR Part 136 Appendix B requirements. The spike level must be between the calculated MDL and 10X the MDL to be valid. The result of the MDL determination must be below the STL reporting limit.

9.1.2. Initial Demonstration Study - This requires the analysis of four QC check samples. The QC check sample is a well characterized laboratory generated sample used to monitor method performance. The results of the initial demonstration study must be acceptable before analysis of samples may begin.

9.1.2.1. Four aliquots of the check sample (LCS) are prepared and analyzed using the procedures detailed in this SOP and the determinative SOPs.

9.2. Preparation Batch - A group of up to 20 samples that are of the same matrix and are processed together using the same procedures and reagents. The preparation batch must contain a method blank, a LCS and a matrix spike/matrix spike duplicate. In some cases, at client request, it may be appropriate to process a matrix spike and sample duplicate in place of the MS/MSD. If clients specify specific samples for MS/MSD, the batch may contain multiple MS/MSD pairs.

9.3. Sample Count - Laboratory generated QC samples (method blanks, LCS) are not included in the sample count for determining the size of a preparation batch. MS/MSD are not included in the sample count unless there are multiple sets of MS/MSD per batch. In other words, the first MS/MSD are not counted; all additional MS and MSDs are counted as samples.

9.4. Method Blank (MB) - One method blank must be processed with each preparation batch. The method blank consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. The method blank should not contain any analyte of interest at or above the reporting limit or at or above 5% of the measured concentration of that analyte in associated samples, whichever is higher (sample result must be a minimum of 20 times higher than the blank contamination level).

- Repreparation and reanalysis of all samples associated with an unacceptable method blank is required when reportable concentrations are determined in the samples (see exception noted above).

- If there is no analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. **Such action must be taken in consultation with the client and must be addressed in the project narrative.**

- If the above criteria are not met and reanalysis is not possible, then the sample data must be qualified. **This anomaly must be addressed in the project narrative and the client must be notified.**

9.5. Laboratory Control Sample (LCS) - One aqueous LCS must be processed with each preparation batch. The LCS is used to monitor the accuracy of the analytical process. On-going monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines. The LCS must be carried through the entire analytical procedure. The CCV results can be reported as LCS results since all CCVs (as well as all other standards) are processed through the sample preparation step with the field samples. No more than 20 samples can be associated with one CCV used for the purpose of reporting LCS data.

- If the LCS is outside established control limits the system is out of control and corrective action must occur. Until in-house control limits are established, a control limit of 80 - 120% recovery must be applied.

- In the instance where the LCS recovery is > 120% and the sample results are < RL, the data may be reported with qualifiers. Such action must be taken in consultation with the client and must be addressed in the case narrative.

- In the event that an MS/MSD analysis is not possible, a Laboratory Control Sample Duplicate (LCSD) must be analyzed. The RPD of the LCS and LCSD must be compared to the matrix spike RPD limits.

- Corrective action will be repreparation and reanalysis of the batch unless the client agrees that other corrective action is acceptable.

9.6. Matrix Spike/Matrix Spike Duplicate (MS/MSD) - One MS/MSD pair must be processed for each preparation batch. A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added. A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked identically as the MS) prepared and analyzed along with the sample and matrix spike. Some client specific data quality objectives (DQO's) may require the use of sample duplicates in place of or in addition to

MS/MSD's. The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Due to the potential variability of the matrix of each sample, these results may have immediate bearing only on the specific sample spiked. Samples identified as field blanks cannot be used for MS/MSD analysis. Spiking levels are provided in Table I (Appendix A).

- If analyte recovery or RPD falls outside the acceptance range, the recovery of that analyte must be in control for the LCS. Until in-house control limits are established, a control limit of 75 - 125 % recovery and 20% RPD must be applied to the MS/MSD. If the LCS recovery is within limits, then the laboratory operation is in control and the results may be accepted. If the recovery of the LCS is outside limits, corrective action must be taken. Corrective action will include repreparation and reanalysis of the batch. MS/MSD results which fall outside the control limits must be addressed in the narrative.

- If the native analyte concentration in the MS/MSD exceeds 4 times the spike level for that analyte, the recovery data are reported as NC (i.e., not calculated). If the reporting software does not have the ability to report NC then the actual recovery must be reported and narrated as follows: "Results outside of limits do not necessarily reflect poor method performance in the matrix due to high analyte concentrations in the sample relative to the spike level."

- If an MS/MSD is not possible due to limited sample volume, then a laboratory control sample duplicate (LCSD) should be analyzed. The RPD of the LCS and LCSD must be compared to the matrix spike RPD limits.

9.7. Initial Calibration Verification (ICV/ICB) - Calibration accuracy is verified by analyzing a second source standard (ICV). The ICV result must fall within 20% of the true value for that solution. An ICB is analyzed immediately following the ICV to monitor low level accuracy and system cleanliness. The ICB result must fall within +/- the reporting limit (RL) from zero. If either the ICV or ICB fail to meet criteria, the analysis should be terminated, the problem corrected and the instrument recalibrated. (See Section 11.2.11 and Section 11.2.12 for required run sequence). If the cause of the ICV or ICB failure was not directly instrument related the corrective action will include repreparation of the associated samples.

9.8. Continuing Calibration Verification (CCV/CCB) - Calibration accuracy is monitored throughout the analytical run through the analysis of a known standard after every 10 samples. The CCV must be a mid-range standard at a concentration other than that of the ICV. The CCV result must fall within 20% of the true value for that solution. A CCB is analyzed immediately following each CCV. (See Section 11.2.11 and 11.2.12 for required run sequence.) The CCB result must fall within +/- RL from zero. Each CCV and CCB analyzed must reflect the conditions of analysis of all associated samples.

Sample results may only be reported when bracketed by valid ICV/CCV and ICB/CCB pairs. If a mid-run CCV or CCB fails, the analysis must be terminated, the problem corrected, the instrument recalibrated, the calibration verified and the affected samples reanalyzed. If the cause of the CCV or CCB failure was not directly instrument related the corrective action will include repreparation of the associated samples.

9.9. Method of Standard Addition (MSA) -This technique involves adding known amounts of standard to one or more aliquots of the sample prior to preparation. This technique compensates for a sample interferent that may enhance or depress the analyte signal, thus producing a different slope from that of the calibration standards. It will not correct for additive interferences which cause a baseline shift. Refer to Section 11.2.13 for additional information on when full 4 point MSA is required as well as Appendix C for specific MSA requirements.

10. CALIBRATION AND STANDARDIZATION

10.1. Calibration standards must be processed through the preparation procedure as described in Section 11.1.

10.2. Due to the differences in preparation protocols separate calibration and calibration verification standards must be prepared for aqueous and solid matrices.

10.3. Calibration must be performed daily (every 24 hours) and each time the instrument is set up . The instrument calibration date and time must be included in the raw data.

10.4. Set up the instrument with the operating parameters recommended by the manufacturer. Allow the instrument to become thermally stable before beginning calibration (approximately 30 minutes of warm-up is required). Refer to the facility specific instrument SOP and CVAA instrument manual for detailed setup and operation protocols.

10.5. Calibrate the instrument according to instrument manufacturer's instructions, using a minimum of five standards and a blank. One standard must be at the STL reporting limit. Analyze standards in ascending order beginning with the blank. Refer to Section 7.5 and Table I for additional information on preparing calibration standards and calibration levels.

10.6. The calibration curve must have a correlation coefficient of ≥0.995 or the instrument shall be stopped and recalibrated prior to running samples. Sample results can not be reported from a curve with an unacceptable correlation coefficient.

10.7. Refer to Section 9.0 for calibration verification procedures, acceptance criteria and corrective actions.

11. PROCEDURE

11.1. Sample Preparation:

11.1.1. All calibration and calibration verification standards (ICV, ICB, CCV, CCB) are processed through the digestion procedure as well as the field samples. *An exception to this is for Method 245.1 samples. The calibration curve samples are* ***not*** *heated.*

11.1.2. Transfer 100 mL of well mixed sample or standard to a clean sample digestion bottle.

Note: Reduced sample volumes can be used as long as a representative sample can be obtained and the reagent levels are adjusted to maintain the same sample to reagent ratio. All samples and standards must be processed similarly.

11.1.3. Add 5 mL of concentrated H_2SO_4 and 2.5 mL of concentrated HNO_3 mixing after each addition.

Note: All spiking should be done after the initial addition of acids.

11.1.4. Add 15 mL of potassium permanganate solution. For samples high in organic materials or chlorides, additional permanganate may be added. Shake and add additional portions of permanganate solution until a purple color persists for at least 15 minutes. If after the addition of up to 25 mL additional permanganate the color does not persist, sample dilution prior to reanalysis may be required.

Note: When performing analyses using automated vs. manual techniques the sample dilution resultant from the addition of more than the original aliquot of permanganate solution must be compensated for by the addition of the same volume of permanganate to all associated samples, standards, *and QC samples (e.g. LCS and blank)* in the run. In instances, where this is not feasible, the addition of excess reagent can be addressed through mathematical correction of the results to account for the resultant dilution effect.

11.1.5. Add 8 mL of potassium persulfate solution and heat for two hours in a water bath at 90 - 95 °C.

NOTE: Alternatively, for RCRA analyses using 7470A, samples may be digested using an autoclave for 15 minutes at 120 °C and 15 lbs.

11.1.6. Cool samples.

11.2. Sample Analysis:

11.2.1. Because of differences between various makes and models of CVAA instrumentation, no detailed operating instructions can be provided. Refer to the facility specific instrument operating SOP and the CVAA instrument manual for detailed setup and operation protocols.

11.2.2. All labs are required to detail the conditions/programs utilized for each instrument within the facility specific instrument operation SOP.

11.2.3. When ready to begin analysis, add 6 mL of sodium chloride-hydroxylamine hydrochloride solution to the samples to reduce the excess permanganate (the permanganate has been reduced when no purple color remains). Add this solution in 6 mL increments until the permanganate is completely reduced.

11.2.4. Manual determination:

11.2.4.1. Treating each sample individually, purge the head space of the sample bottle for at least one minute.

11.2.4.2. Add 5 mL of stannous chloride solution and immediately attach the bottle to the aeration apparatus.

11.2.4.3. Allow the sample to stand quietly without manual agitation while the sample is aerated (1 L/min flow). Monitor the sample absorbance during aeration. When the absorbance reaches a maximum and the signal levels off, open the bypass valve and continue aeration until the absorbance returns to its baseline level. Close the bypass valve and remove the aeration device.

11.2.4.4. Place the aeration device into 100 mL of 1% HNO_3 and allow to bubble rinse until the next sample is analyzed.

11.2.5. Automated determination: Follow instructions provided by instrument manufacturer.

11.2.6. Perform a linear regression analysis of the calibration standards by plotting maximum response of the standards vs. concentration of mercury. Determine the mercury concentration in the samples from the linear regression fit of the calibration curve. Calibration using computer or calculation based regression curve fitting techniques on concentration/response data is acceptable.

11.2.7. All measurements must fall within the defined calibration range to be valid. Dilute and reanalyze all samples for analytes that exceed the highest calibration standard.

11.2.8. If the sample results are negative and the absolute value of the negative result is greater than the reporting limit, the sample must be diluted and reanalyzed.

11.2.9. The samples must be allowed to cool to room temperature prior to analysis or a decrease in the response signal can occur.

11.2.10. Baseline correction is acceptable as long as it is performed after every sample or after the CCV and CCB; resloping is acceptable as long as it is immediately preceded and followed by a compliant CCV and CCB.

11.2.11. The following analytical sequence must be used with 7470A and 245.1:

Instrument Calibration
ICV
ICB
Maximum 10 samples
CCV
CCB
Repeat sequence of 10 samples between CCV/CCB pairs as required to complete run
CCV
CCB

Refer to Quality Control Section 9.0 and Table II (Appendix A) for quality control criteria to apply to Methods 7470A and 245.1.

Note: Samples include the method blank, LCS, MS, MSD, duplicate, field samples and sample dilutions.

11.2.12. The following run sequence is consistent with 7470A, CLP and 245.1 and may be used as an alternate to the sequence in 11.2.11. This run sequence is recommended if multiple method requirements must be accommodated in one analytical run:

Instrument Calibration
ICV
ICB
CRA*
CCV
CCB
10 samples
CCV
CCB
Repeat sequence of 10 samples between CCV/CCB pairs as required to complete run.
CCV
CCB

Refer to the appropriate CLP SOP (CORP-MT-0006) for quality control requirements for QC samples.

* Refer to the CLP SOP for information on the CRA.

11.2.13. For TCLP samples, full four point MSA will be required if all of the following conditions are met:

1) recovery of the analyte in the matrix spike is not at least 50%,

2) the concentration of the analyte does not exceed the regulatory level, and,

3) the concentration of the analyte is within 20% of the regulatory level.

The reporting and matrix spike levels for TCLP analyses are detailed in Table I (Appendix A). Appendix E provides guidance on performing MSA analyses. For TCLP mercury determinations, MSA spikes must be added prior to sample preparation.

11.3. To facilitate the early identification of QC failures and samples requiring rerun it is strongly recommended that sample data be reviewed periodically throughout the run.

11.4. Guidelines are provided in the appendices on procedures to minimize contamination of samples and standards, preventive maintenance and troubleshooting.

11.5. One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and is approved by a Technical Specialist and QA Manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file.

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

12. DATA ANALYSIS AND CALCULATIONS

12.1. ICV percent recoveries are calculated according to the equation:

$$\%R = 100\left(\frac{Found(ICV)}{True(ICV)}\right)$$

12.2. CCV percent recoveries are calculated according to the equation:

$$\%R = 100\left(\frac{Found(CCV)}{True(CCV)}\right)$$

12.3. Matrix spike recoveries are calculated according to the following equation:

$$\%R = 100\left(\frac{SSR - SR}{SA}\right)$$

Where:
SSR = Spike Sample Result
SR = Sample Result
SA = Spike Added

12.4. The relative percent difference (RPD) of matrix spike/matrix spike duplicates or sample duplicates are calculated according to the following equations:

$$RPD = 100\left[\frac{|MSD - MS|}{\left(\frac{MSD + MS}{2}\right)}\right]$$

Where:
MS = determined spiked sample concentration
MSD = determined matrix spike duplicate concentration

$$RPD = 100\left[\frac{|DU1 - DU2|}{\left(\frac{DU1 + DU2}{2}\right)}\right]$$

Where:
DU1 = Sample result
DU2 = Sample duplicate result

12.5. The final concentration for an aqueous sample is calculated as follows:

$$mg/L = C \times D$$

Where:
C = Concentration (mg/L) from instrument readout
D = Instrument dilution factor

12.6. The LCS percent recovery is calculated according to the following equation:

$$\%R = 100\left(\frac{Found(LCS)}{True(LCS)}\right)$$

12.7. Appropriate factors must be applied to sample values if dilutions are performed.

12.8. Sample results should be reported with up to three significant figures in accordance with the STL significant figure policy.

13. METHOD PERFORMANCE

13.1. Each laboratory must have initial demonstration of performance data on file for each analyte of interest as described in Section 9.0.

13.2. Method performance is determined by the analysis of method blanks, laboratory control samples, matrix spike and matrix spike duplicate samples. The matrix spike recovery should fall within +/- 25 % and the matrix spike duplicates should compare within 20% RPD. The method blanks must meet the criteria in Section 9.3. The laboratory control sample should recover within 20% of the true value until in house limits are established.

13.3. Training Qualification:

The group/team leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience.

14. POLLUTION PREVENTION

14.1. This method allows for the proportional reduction of sample and reagent volumes to decrease waste generation.

15. WASTE MANAGEMENT

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

16. REFERENCES

16.1. Test Methods for Evaluating Solid Waste , Physical/Chemical Methods, SW-846, 3rd Edition, Final Update II, Revision I, September 1994, Method 7470A (Mercury).

16.2. "Methods for the Chemical Analysis of Water and Wastes", EPA-600/4-79-020, U.S.EPA, August 1983, Method 245.1.

16.3. U.S.EPA Statement of Work for Inorganics Analysis, ILMO3.0.

16.4. QA-003, STL QC Program.

16.5. QA-004, Rounding and Significant Figures.

16.6. QA-005, Method Detection Limits.

17. MISCELLANEOUS (TABLES, APPENDICES, ETC. . .)

17.1. Modifications/Interpretations from reference method.

17.1.1. Modifications from both 7470A and 245.1.

17.1.1.1. The 200 series methods and Chapter 1 of SW846 specify the use of reagent water with a purity equivalent to ASTM Type II water. This SOP specifies the use of a Millipore DI system or equivalent to produce reagent water. This SOP requires that reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks.

17.1.1.2. This SOP allows for the use of reduced sample volumes to decrease waste generation. Reagent levels are adjusted to maintain the same ratios as stated in the source methods. According to a letter from Robert Booth of EPA EMSL-Cinn to David Payne of EPA Region V, "Reduction in sample size and appropriate corresponding reduction in sample volume is not considered a significant change in the methodology."

17.1.1.3. The alternate run sequence presented in Section 11.2.12 is consistent with method requirements. An additional QC analysis (CRA) was added to accommodate the CLP protocol requirements.

17.1.2. Modifications from Method 7470A

17.1.2.1. Chapter 1 of SW-846 states that the method blank should not contain any analyte of interest at or above the MDL. This SOP states that the method blank must not contain any analyte of interest at or above the reporting limit.

17.1.2.2. Documentation is on file from EPA's Office of Solid Waste (Olliver Fordham 11/28/95) regarding the acceptance of the autoclave as an equivalent heating device to the water bath. In his letter, Mr. Fordham cited the CLP water protocol 245.1 CLP-M and therefore the operating parameters from that method were adopted for 7470A (15 minutes at 120 °C and 15 lbs.).

17.1.2.3. Method 7470A does not state control criteria within the text of the method. The QC section of 7470A refers the analyst to Section 8.0 of Method 7000A, the generic atomic absorption method, which discusses flame and furnace methods. The ICV criteria stated in Method 7000A is ± 10%. This SOP requires ICV control limits of ± 20% based on the fact that the mercury ICV, unlike the ICV for the flame and furnace analytes, is digested and therefore is equivalent to a LCS. The CLP protocol 245.1 CLP-M recognizes this factor and requires control limits of ± 20%.

17.1.3. Modifications from 245.1

17.1.3.1. Method 245.1 Section 9.3 states concentrations should be reported as follows: Between 1 and 10 ug/L, one decimal; above 10 ug/L, to the nearest whole number. STL reports all Hg results under this SOP to two significant figures.

17.2. Modifications from previous SOPs

17.2.1. CORP-MT-0005, rev1: Added text to Note in Section 11.1.4: "and QC samples (e.g. LCS and blank)."

17.3. Facility Specific SOPs

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

17.4. Documentation and Record Management

The following documentation comprises a complete CVAA raw data package:

- Raw data (direct instrument printout)

- Run log printout from instrument software where this option is available or manually generated run log. (A bench sheet may be substituted for the run log as long as it contains an accurate representation of the analytical sequence).
- Data review checklist - See Appendix B
- Standards Documentation (source, lot, date).
- Copy of digestion log.
- Non-conformance summary (if applicable).

Figure 1. Aqueous Sample Preparation - Mercury

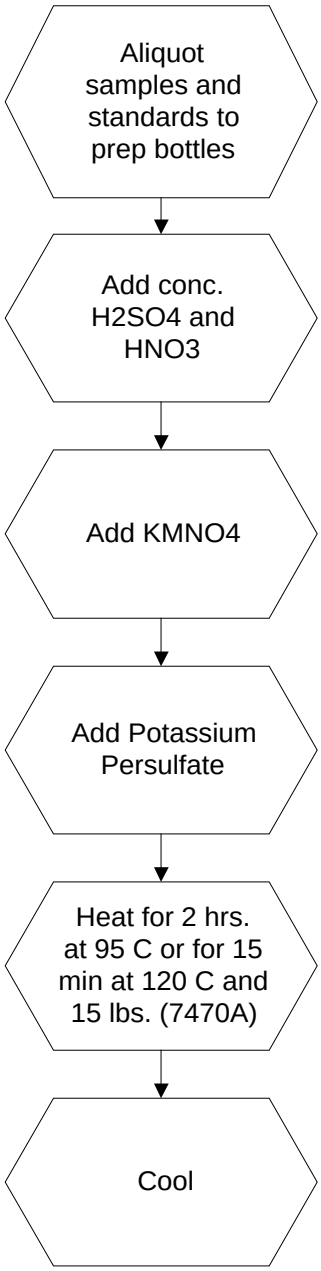
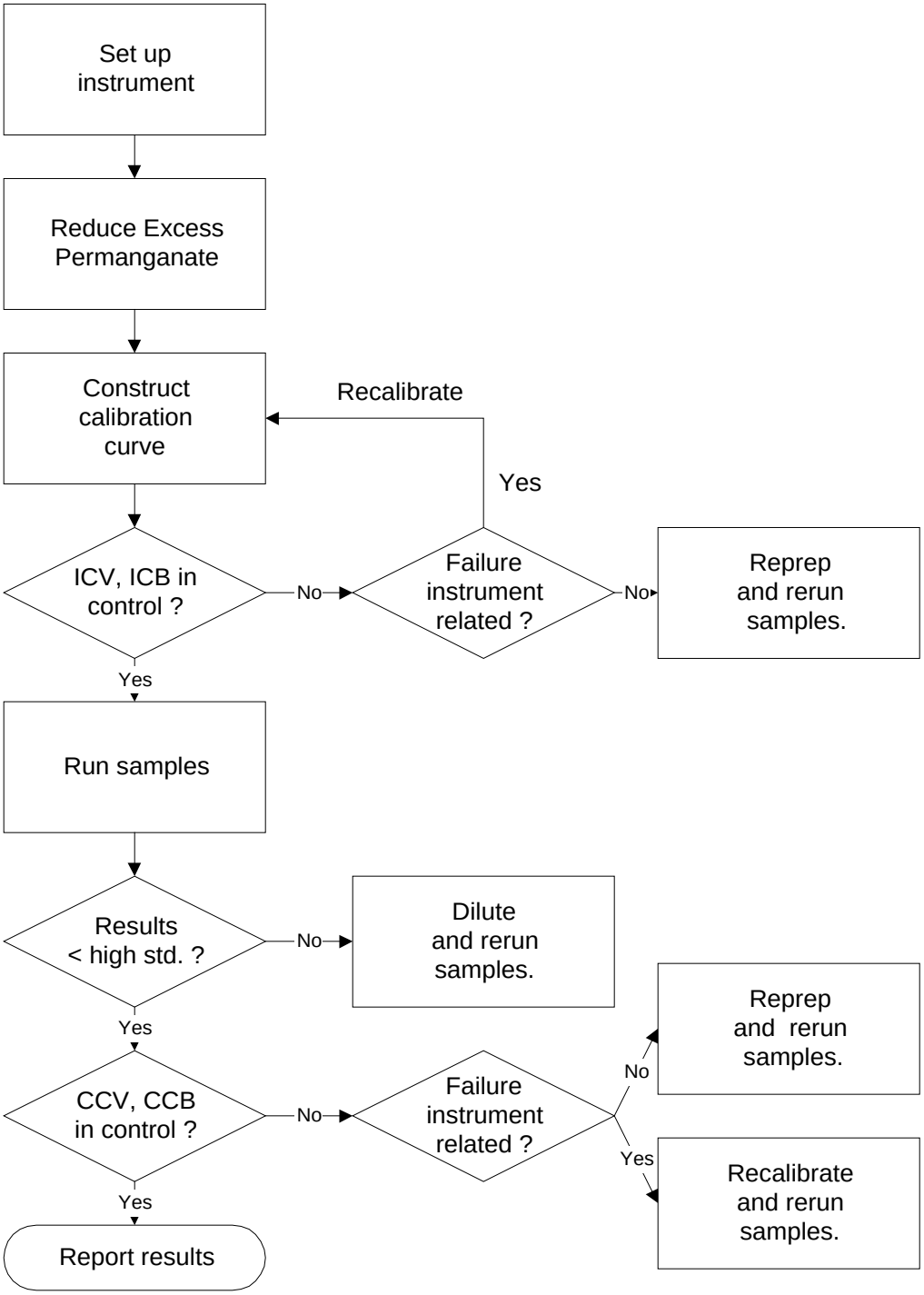


Figure 2. CVAA Mercury Analysis



APPENDIX A

TABLES

TABLE I . MERCURY REPORTING LIMITS, CALIBRATION STANDARD*, QC STANDARD AND SPIKING LEVELS (MG/L)

Standard Aqueous RL	0.0002
TCLP RL	0.002
Std 0	0
Std 1	0.0002
Std 2	0.0005
Std 3	0.001
Std 4	0.002
Std 5	0.005
Std 6 **	0.010
ICV	0.001 or 0.0025 ***
LCS/CCV	0.0025 or 0.005 ***
Aqueous MS	0.001
TCLP MS	0.005

*** SOP specified calibration levels must be used unless prevented by the instrument configuration or client specific requirements. Deviations from specified calibration levels must be documented in the facility specific instrument operation SOP and must be approved by the facility technical manager and Quality Assurance Manager.**

**** Optional standard which may be used to extend the calibration range as allowed by the instrument configuration. If the instrument configuration prevents the use of 6 standards, the 2 ppb standard may be eliminated in favor of the 10 ppb standard.**

***** Concentration level dependent on high calibration standard used. CCV must be 50% of high standard concentration and ICV must be 20-25% of high standard concentration.**

TABLE II. Summary Of Quality Control Requirements

QC PARAMETER	FREQUENCY *	ACCEPTANCE CRITERIA	CORRECTIVE ACTION
ICV	Beginning of every analytical run.	80 - 120 % recovery.	Terminate analysis; Correct the problem; Recalibrate or reprep batch (see Section 9.7).
ICB	Beginning of every analytical run, immediately following the ICV.	The result must be within +/- RL from zero.	Terminate analysis; Correct the problem; Recalibrate or reprep batch (see Section 9.7).
CCV	Every 10 samples and at the end of the run.	80 - 120 % recovery.	Terminate analysis; Correct the problem; Recalibrate and rerun all samples not bracketed by acceptable CCV or reprep batch (see Section 9.8).
CCB	Immediately following each CCV.	The result must be within +/- RL from zero.	Terminate analysis; Correct the problem; Recalibrate and rerun all samples not bracketed by acceptable CCB or reprep batch (see Section 9.8).
Method Blank	One per sample preparation batch of up to 20 samples.	The result must be less than or equal to the RL. Sample results greater than 20x the blank concentration are acceptable. Samples for which the contaminant is < RL do not require redigestion (See Section 9.4).	Redigest and reanalyze samples. Note exceptions under criteria section. See Section 9.4 for additional requirements.

*See Sections 11.2.11 and 11.2.12 for exact run sequence to be followed.

TABLE II. Summary of Quality Control Requirements (Continued)

QC PARAMETER	FREQUENCY	ACCEPTANCE CRITERIA	CORRECTIVE ACTION
Laboratory Control Sample (LCS)	One per sample preparation batch of up to 20 samples.	Aqueous LCS must be within 80 - 120% recovery or in-house control limits.	Terminate analysis; Correct the problem; Redigest and reanalyze all samples associated with the LCS (see Section 9.5).
Matrix Spike	One per sample preparation batch of up to 20 samples.	75 - 125 % recovery or in-house control limits. If the MS/MSD is out for an analyte, it must be in control in the LCS.	In the absence of client specific requirements, flag the data; no flag required if the sample level is > 4x the spike added. (see Section 9.6) For TCLP see Section 11.2.13
Matrix Spike Duplicate	See Matrix Spike	75 - 125 % recovery or in-house control limits; RPD ≤ 20%. (See MS)	See Corrective Action for Matrix Spike.

APPENDIX B
STL Hg DATA REVIEW CHECKLIST

STL Hg Data Review Checklist

Run/Project Information

Run Date: _____ **Analyst:**_____ **Instrument:**_____
Prep Batches Run:_____

Circle Methods used: **7470A / 245.1 :** CORP-MT-0005 Rev 1 **7471 / 245.5 :** CORP-MT-0007 Rev 1
CLP - AQ : CORP-MT-0006 Rev 0 **CLP - SOL :** CORP-MT-0008 Rev 0

Review Items

A. Calibration/Instrument Run QC	Yes	No	N/A	2ndLevel
1. Instrument calibrated per manufacturer's instructions and at SOP specified levels ?				
2. ICV/CCV analyzed at appropriate frequency and within control limits?				
3. ICB/CCB analyzed at appropriate frequency and within +/- RL or +/- CRDL (CLP)?				
4. CRA run (CLP only)?				
B. Sample Results				
1. Were samples with concentrations > the high calibration standard diluted and reanalyzed?				
2. All reported results bracketed by in control QC ?				
3. Sample analyses done within holding time?				
C. Preparation/Matrix QC				
1. LCS done per prep batch and within QC limits ?				
2. Method blank done per prep batch and < RL or CRDL (CLP) ?				
3. MS run at required frequency and within limits ?				
4. MSD or DU run at required frequency and RPD within SOP limits?				
D. Other				
1. Are all nonconformances documented appropriately ?				
2. Current IDL/MDL data on file?				
3. Calculations and Transcriptions checked for error ?				
4. All client/ project specific requirements met?				
5. Date of analysis verified as correct ?				

Analyst: _____ **Date:**_____
Comments:
_____
_____

2nd Level Reviewer : _____ **Date:**_____
_____
_____

APPENDIX C

MSA GUIDANCE

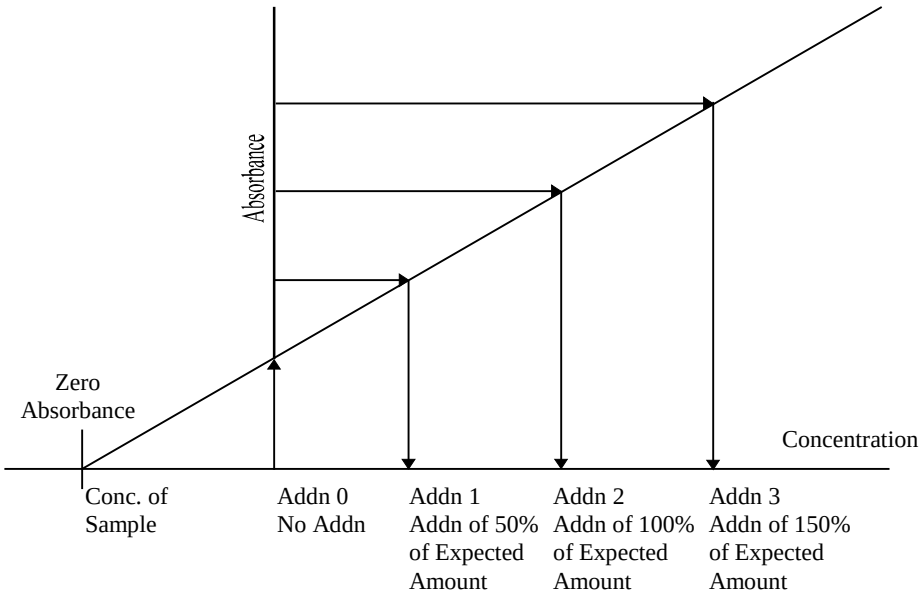
APPENDIX C. MSA GUIDANCE

Method of Standard Addition

Four equal volume aliquots of sample are measured and known amounts of standards are added to three aliquots. The fourth aliquot is the unknown and no standard is added to it. The concentration of standard added to the first aliquot should be 50% of the expected concentration. The concentration of standard added to the second aliquot should be 100% of the expected concentration and the concentration of standard added to the third aliquot should be 150% of the expected concentration. The volume of the unspiked and spiked aliquots should be the same (i.e., the volume of the spike added should be negligible in relation to the volume of sample).

To determine the concentration of analyte in the sample, the absorbance (or response) of each solution is determined and a linear regression performed. On the vertical axis the absorbance (or response) is plotted versus the concentrations of the standards on the horizontal axis using 0 as the concentration of the unspiked aliquot. An example plot is shown in Figure 1. When the resulting line is extrapolated back to zero absorbance, the point of interception of the horizontal axis is the concentration of the unknown. Calculate the correlation coefficient (r) and the x-intercept (where y=0) of the curve. The concentration in the digestate is equal to the negative x-intercept.

Figure 1



- For the method of standard additions to be correctly applied, the following limitations must be taken into consideration.
- The plot of the sample and standards must be linear over the concentration range of concern. For best results, the slope of the curve should be similar to that of a plot of the aqueous standard curve.
- The effect of the interference should not vary as the ratio of the standard added to the sample matrix changes.

APPENDIX D

TROUBLESHOOTING GUIDE

APPENDIX D. TROUBLESHOOTING GUIDE

Problem	**Possible Cause**
Poor or No Absorbance or Sensitivity Check failed	Incorrect wavelength Dirty windows Window loose Etched or dirty optics Wrong lamp Bad lamp Not enough or no sample introduced Empty sample cup Incorrectly made standards Gas leak EDL power supply set on “Continuous”
Erratic Readings	Source lamp not aligned properly Lamp not prewarmed Injection tip partially clogged Contaminated reagents Contaminated glassware Drying tube saturated Bad lamp Injection tip hitting outside of tube Injection tip coated or not set properly Leak in sample tubing Power fluctuations Air bubbles in tubing
EDL Won’t Light	Lamp cable not plugged in Lamp power set at 0 Lamp is dead Power supply fuse is blown Short in cord
Standards reading twice or half normal absorbance or concentration	Incorrect standard used Incorrect dilution performed Dirty cell
Background Correction Light Blinking	Background screen or attenuator faulty

APPENDIX E

CONTAMINATION CONTROL GUIDELINES

APPENDIX E. CONTAMINATION CONTROL GUIDELINES

The following procedures are strongly recommended to prevent contamination:

All work areas used to prepare standards and spikes should be cleaned before and after each use.

All glassware should be washed with detergent and tap water and rinsed with 1:1 nitric acid followed by deionized water.

Proper laboratory housekeeping is essential in the reduction of contamination in the metals laboratory. All work areas must be kept scrupulously clean.

Powdered or Latex Gloves must not be used in the metals laboratory since the powder contains silica and zinc, as well as other metallic analytes. Only vinyl or nitrile gloves should be used in the metals laboratory.

Glassware should be periodically checked for cracks and etches and discarded if found. Etched glassware can cause cross contamination of any metallic analytes.

Autosampler trays should be covered to reduce the possibility of contamination. Trace levels of elements being analyzed in the samples can be easily contaminated by dust particles in the laboratory.

The following are helpful hints in the identification of the source of contaminants:

Reagents or standards can contain contaminants or be contaminated with the improper use of a pipette.

Improper cleaning of glassware can cause contamination.

Separate glassware if an unusually high sample is analyzed and soak with sulfuric acid prior to routine cleaning.

APPENDIX F

PREVENTIVE MAINTENANCE

APPENDIX F. PREVENTIVE MAINTENANCE

A maintenance log is used to record when maintenance is performed on instruments. When an instrument problem occurs indicate the date, time and instrument number, then identify the problem and corrective action in the maintenance log.

The following procedures are required to ensure that that the instrument is fully operational.

Cold Vapor Atomic Absorption (Leeman PS 200) (1)

Daily	Semi-annually	Annually
Clean lens.	Check Hg lamp intensity.	Change Hg lamp.
Check aperture.		Check liquid/gas separator.
Check argon flow.		
Check tubing.		
Check drain.		
Replace drying tube.		

Cold Vapor Atomic Absorption (PE 5000) (1)

Daily	Monthly
Clean aspirator by flushing with DI water.	Clean cell in aqua regia.
Check tubing and replace if needed.	Clean aspirator in aqua regia.
Clean windows with methanol.	
Change silica gel in drying tube.	
Check argon gas supply.	
Adjust lamp.	

CORP-MT-0007

Preparation and Analysis of Mercury in Solid Samples by Cold Vapor Atomic Absorption Spectroscopy, SW 846 7471A and MCAWW 245.5

STL STANDARD OPERATING PROCEDURE

TITLE: PREPARATION AND ANALYSIS OF MERCURY IN SOLID SAMPLES BY COLD VAPOR ATOMIC ABSORPTION SPECTROSCOPY, SW846 7471A AND MCAWW 245.5

(SUPERSEDES: REVISION 1)

Prepared by: Kurt Ill

Reviewed by: _____
Technical Specialist

Approved by: _____
Director, Quality Assurance

Approved by: _____
Director, Environmental Health and Safety

Approved by: _____
Management

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1. SCOPE AND APPLICATION

1.1. This procedure describes the preparation and analysis of mercury (Hg, CAS # 7439-97-6) by Cold Vapor Atomic Absorption Spectroscopy (CVAA) using SW-846 Method 7471A and MCAWW Method 245.5.

1.2. CVAA analysis provides for the determination of total mercury (organic and inorganic). The combination of the oxidants, potassium permanganate and potassium persulfate, has been found to give 100% recovery with both types of compounds. Detection limits, sensitivity and optimum concentration ranges for mercury analysis will vary with the matrices, instrumentation and volume of sample used.

1.3. Methods 7471A and 245.5 are applicable to the preparation and analysis of mercury in soils, sediments, bottom deposits and sludge-type materials. All matrices require sample preparation prior to analysis.

1.4. The STL reporting limit for mercury in solid matrices is 0.033 mg/kg based a 0.6 g sample aliquot (wet weight).

2. SUMMARY OF METHOD

2.1. This SOP describes a technique for the determination of mercury in solution. The procedure is a physical method based on the absorption of radiation at 253.7 nm by mercury vapor. A representative portion of the sample is digested in sulfuric and nitric acids. Organic mercury compounds are oxidized with potassium permanganate and potassium persulfate and the mercury reduced to its elemental state with stannous chloride and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance is measured as a function of mercury concentration. Concentration of the analyte in the sample is determined by comparison of the sample absorbance to the calibration curve (absorbance vs. concentration).

3. DEFINITIONS

3.1. Total Metals: The concentration determined on an unfiltered sample following digestion.

4. INTERFERENCES

Chemical and physical interferences may be encountered when analyzing samples using this method.

4.1. Potassium permanganate which is used to breakdown organic mercury compounds also eliminates possible interferences from sulfide. Concentrations as high as 20 mg/L of sulfide as sodium sulfide do not interfere with the recovery of inorganic mercury from reagent water.

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

4.3. Chlorides can cause a positive interference. Samples high in chlorides require additional permanganate (as much as 25 mL) because, during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation at 253.7 nm. Care must be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. This is accomplished by adding excess hydroxylamine reagent (25 mL) and purging the sample headspace before stannous chloride is added. Both inorganic and organic mercury spikes have been quantitatively recovered from seawater using this technique.

Note: Sufficient addition of permanganate is apparent when the purple color persists at least 15 minutes. Some samples may require dilution prior to digestion due to extremely high concentrations of chloride.

4.4. Interference from certain volatile organic materials that absorb at this wavelength may also occur. If suspected, a preliminary run without stannous chloride can determine if this type of interference is present. While the possibility of absorption from certain organic substances present in the sample does exist, this problem is not routinely encountered. This is mentioned only to caution the analyst of the possibility. If this condition is found to exist, the mercury concentration in the sample can be determined by subtracting the result of the sample run without the reducing reagent (stannous chloride) from that obtained with the reducing reagent.

4.5. Samples containing high concentrations of oxidizable organic materials, as evidenced by high COD levels, may not be completely oxidized by this procedure. When this occurs the recovery of mercury will be low. The problem can be eliminated by reducing the volume of original sample used.

4.6. The most common interference is laboratory contamination which may arise from impure reagents, dirty glassware, improper sample transfers, dirty work areas, etc. Be aware of potential sources of contamination and take appropriate measures to minimize or avoid them.

5. SAFETY

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

5.2. Eye protection that satisfies ANSI Z87.1 (as per the Chemical Hygiene Plan), laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

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

5.3.1. The following materials are known to be **corrosive:**

hydrochloric acid, nitric acid and sulfuric acid.

5.3.2. The following materials are known to be **oxidizing agents**:

nitric acid, potassium permanganate, potassium persulfate and magnesium perchlorate.

5.3.3. Mercury is a highly toxic element that must be handled with care. The analyst must be aware of the handling and clean-up techniques before working with mercury. Since mercury vapor is toxic, precaution must be taken to avoid its inhalation, ingestion or absorption through skin. All lines should be checked for leakage and the mercury vapor must be vented into a hood or passed through a mercury absorbing media such as:

5.3.3.1. Equal volumes of 0.1 M $KMnO_4$ and 10% H_2SO_4, or

5.3.3.2. Iodine, 0.25%, in a 3% KI solution.

5.3.4. Magnesium sulfate is known to be a reproductive toxin (mutagen).

5.4. Exposure to chemicals must be maintained **as low as reasonably achievable.** Therefore, unless they are known to be non-hazardous, all samples should be opened, transferred and prepared in a fume hood, or under other means of mechanical

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

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

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

5.7. Do not look directly into the beam of the Hg lamp. The UV light that these lamps radiate is harmful to the eyes.

5.8. Cylinders of compressed gas must be handled with caution, in accordance with local regulations. It is recommended that, wherever possible, cylinders be located outside the laboratory and the gas led to the instrument through approved lines.

5.9. The CVAA apparatus must be properly vented to remove potentially harmful fumes generated during sample analysis.

6. EQUIPMENT AND SUPPLIES

6.1. Temperature controlled water bath (capable of maintaining temperature of 90- 95 °C) or autoclave capable of obtaining 15 lbs., 120 °C.

6.2. Atomic Absorption Spectrophotometer equipped with:

6.2.1. Absorption Cell with quartz end windows perpendicular to the longitudinal axis. Dimensions of the cell must result in sufficient sensitivity to meet the SOP defined reporting limit. The quartz windows must be maintained to provide accurate measurements. Any scratches or fingerprints can alter the absorption of UV radiation.

6.2.2. Mercury specific hollow cathode lamp (HCL) or electrodeless discharge lamp (EDL).

6.2.3. Peristaltic pump which can deliver 1 L/min air.

6.2.4. Flowmeter capable of measuring an airflow of 1 L/min.

6.2.5. Recorder or Printer.

6.2.6. Aeration Tubing: A straight glass frit having a course porosity and Tygon tubing is used for the transfer of mercury vapor from the sample bottle to the absorption cell and return.

6.2.7. Drying device (a drying tube containing magnesium perchlorate or magnesium sulfate and/or a lamp with a 60 W bulb) to prevent condensation in cell. The lamp is positioned to shine on the absorption cell maintaining the air temperature in the cell about 10 °C above room temperature. Other drying devices that acheive the same purpose are also acceptable (i.e., Gortex filter).

Note: Instruments designed specifically for the measurement of mercury using the cold vapor technique may be substituted for the atomic absorption spectrophotometer.

6.3. BOD bottles or equivalent.

6.4. Nitrogen or argon gas supply, welding grade or equivalent.

6.5. Calibrated automatic pipettes or Class A glass volumetric pipettes.

6.6. Class A volumetric flasks.

6.7. Top-loading balance, capable of reading up to two decimal places.

6.8. Thermometer (capable of accurate readings at 95 °C).

6.9. Disposable cups or tubes.

7. REAGENTS AND STANDARDS

7.1. Reagent water must be produced by a Millipore DI system or equivalent. Reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks.

7.2. Stock (1000 ppm) mercury standards (in 10% HNO_3) are purchased as custom STL solutions. All standards must be stored in FEP fluorocarbon or previously unused polyethylene or polypropylene bottles. Stock standard solutions must be replaced prior to the expiration date provided by the manufacturer. If no expiration date is provided, the stock solutions may be used for up to one year and must be replaced sooner if verification from an independent source indicates a problem.

7.3. Intermediate mercury standard (10 ppm): Take 1 mL of the stock mercury standard (7.2) and dilute to 100 mL with reagent water. The intermediate standard must be made monthly and must be prepared in a matrix of 2% HNO_3 . This acid (2 mL of concentrated HNO_3) must be added to the flask/bottle before the addition of the stock standard aliquot.

7.4. Working mercury standard (0.1 ppm): Take 1 mL of the intermediate mercury standard (7.3) and dilute to 100 mL with reagent water. The working mercury standard must be made daily and must be prepared in a matrix of 0.15% HNO_3. This acid (150 uL of concentrated HNO_3) must be added to the flask/bottle before the addition of the stock standard aliquot.

7.5. The calibration standards must be prepared fresh daily from the working standard (7.4) by transferring 0, 0.2, 0.5, 1.0, 2.0, 5.0 and 10.0 mL aliquots of the working mercury standard into sample prep bottles and proceeding as specified in Section 11.1

Note: Alternate approaches to standard preparation may be taken and alternate volumes of standard may be prepared as long as the accuracy and final standard concentrations as detailed in Table I are maintained. For example, automated mercury systems do not require 100 mL of standard and therefore smaller volumes may be generated to reduce waste generation.

7.6. The initial calibration verification standard must be made from a different stock solution than that of the calibration standards.

7.7. Refer to Table I (Appendix A) for details regarding the working standard concentrations for calibration, calibration verification and spiking solutions. All standards must be processed through the entire analytical procedure including sample preparation.

7.8. Nitric acid (HNO_3), concentrated, trace metal grade or better.

Note: If a high reagent blank is obtained, it may be necessary to distill the nitric acid.

7.9. Sulfuric acid (H_2SO_4), concentrated, trace metal grade or better.

7.9.1. Sulfuric acid, 0.5 N: Dilute 14.0 mL of concentrated H_2SO_4 to 1 liter with reagent water.

7.10. Hydrochloric acid (HCl), concentrated, trace metal grade or better.

7.11. Aqua Regia: Prepare immediately before use by carefully adding three volumes of concentrated HCl to one volume of concentrated HNO_3.

7.12. Stannous sulfate solution: Add 25 g of stannous sulfate to 250 mL of 0.5 N sulfuric acid. This mixture is a suspension and should appear cloudy. This solution should be made daily and should be stirred continuously during use.

Note: Stannous chloride may be used in place of stannous sulfate. Prepare the stannous chloride solution according to the recommendations provided by the instrument manufacturer.

7.13. Sodium chloride-hydroxylamine hydrochloride solution: Add 12 g of sodium chloride and 12 g of hydroxylamine hydrochloride to every 100 mL of reagent water.

Note: Hydroxylamine sulfate may be used in place of hydroxylamine hydrochloride.

7.14. Potassium permanganate, 5% solution (w/v): Dissolve 5 g of potassium permanganate for every 100 mL of reagent water.

7.15. Potassium persulfate, 5% solution (w/v): Dissolve 5 g of potassium persulfate for every 100 mL of reagent water.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Sample holding time for mercury is 28 days from time of collection to the time of sample analysis.

8.2. Soil samples do not require preservation but must be stored at 4° C ± 2° C until the time of analysis.

9. QUALITY CONTROL

Table II (Appendix A) provides a summary of quality control requirements including type, frequency, acceptance criteria and corrective action.

9.1. Initial Demonstration of Capability

Prior to the analysis of any analyte using 7471A or the 245.5, the following requirements must be met.

9.1.1. Method Detection Limit (MDL) - An MDL must be determined for each analyte/matrix prior to the analysis of any samples. The MDL is determined

using seven replicates of reagent water, spiked with all the analytes of interest, that have been carried through the entire analytical procedure. MDLs must be redetermined on an annual basis in accordance with 40 CFR Part 136 Appendix B requirements. The spike level must be between the calculated MDL and 10X the MDL to be valid. The result of the MDL determination must be below the STL reporting limit.

9.1.2. Initial Demonstration Study - This requires the analysis of four QC check samples. The QC check sample is a well characterized laboratory generated sample used to monitor method performance. The results of the initial demonstration study must be acceptable before analysis of samples may begin.

9.1.2.1. Four aliquots of the check sample (LCS) are prepared and analyzed using the procedures detailed in this SOP and the determinative SOPs.

9.2. Preparation Batch - A group of up to 20 samples that are of the same matrix and are processed together using the same procedures and reagents. The preparation batch must contain a method blank, a LCS and a matrix spike/matrix spike duplicate. In some cases, at client request, it may be appropriate to process a matrix spike and sample duplicate in place of the MS/MSD. If clients specify specific samples for MS/MSD, the batch may contain multiple MS/MSD pairs.

9.3. Sample Count - Laboratory generated QC samples (method blanks, LCS and MS/MSDs) are not included in the sample count for determining the size of a preparation batch.

9.4. Method Blank (MB) - One method blank must be processed with each preparation batch. The method blank consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. The method blank should not contain any analyte of interest at or above the reporting or at or above 5% of the measured concentration of that analyte in associated samples, whichever is higher (sample result must be a minimum of 20 times higher than the blank contamination level).

- Repreparation and reanalysis of all samples associated with an unacceptable method blank is required when reportable concentrations are determined in the samples (see exception noted above).

- If there is no analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. **Such action must be taken in consultation with the client and must be addressed in the project narrative.**

- If the above criteria are not met and reanalysis is not possible, then the sample data must be qualified. **This anomaly must be addressed in the project narrative and the client must be notified.**

9.5. Laboratory Control Sample (LCS) - One aqueous LCS must be processed with each preparation batch. The LCS is used to monitor the accuracy of the analytical process. On-going monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines. The LCS must be carried through the entire analytical procedure. The CCV results can be reported as the LCS results since all CCVs (as well as all other standards) are processed through the sample preparation step with the field samples. No more than 20 samples can be associated with one CCV used for the purpose of reporting LCS data.

- If the LCS is outside established control limits the system is out of control and corrective action must occur. Until in-house control limits are established, a control limit of 80 - 120% recovery must be applied.

- In the instance where the LCS recovery is > 120% and the sample results are < RL, the data may be reported with qualifiers. Such action must be taken in consultation with the client and must be addressed in the case narrative."

- In the event that an MS/MSD analysis is not possible, a Laboratory Control Sample Duplicate (LCSD) must be analyzed. The RPD of the LCS and LCSD must be compared to the matrix spike RPD limits.

- Corrective action will be repreparation and reanalysis of the batch unless the client agrees that other corrective action is acceptable.

9.6. Matrix Spike/Matrix Spike Duplicate (MS/MSD) - One MS/MSD pair must be processed for each preparation batch. A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added. A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked identically as the MS) prepared and analyzed along with the sample and matrix spike. Some client specific data quality objectives (DQO's) may require the use of sample duplicates in place of or in addition to MS/MSD's. The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Due to the potential

variability of the matrix of each sample, these results may have immediate bearing only on the specific sample spiked. Samples identified as field blanks cannot be used for MS/MSD analysis. Spiking levels are provided in Table I (Appendix A).

- If analyte recovery or RPD falls outside the acceptance range, the recovery of that analyte must be in control for the LCS. Until in-house control limits are established, a control limit of 75 - 125 % recovery and 20% RPD must be applied to the MS/MSD. If the LCS recovery is within limits, then the laboratory operation is in control and the results may be accepted. If the recovery of the LCS is outside limits, corrective action must be taken. Corrective action will include repreparation and reanalysis of the batch. MS/MSD results which fall outside the control limits must be addressed in the narrative.

- If the native analyte concentration in the MS/MSD exceeds 4 times the spike level for that analyte, the recovery data are reported as NC (i.e., not calculated). If the reporting software does not have the ability to report NC then the actual recovery must be reported and narrated as follows: "Results outside of limits do not necessarily reflect poor method performance in the matrix due to high analyte concentrations in the sample relative to the spike level."

- If an MS/MSD is not possible due to limited sample volume, then a laboratory control sample duplicate (LCSD) should be analyzed. The RPD of the LCS and LCSD must be compared to the matrix spike RPD limits.

9.7. Initial Calibration Verification (ICV/ICB) - Calibration accuracy is verified by analyzing a second source standard (ICV). The ICV result must fall within 20% of the true value for that solution. An ICB is analyzed immediately following the ICV to monitor low level accuracy and system cleanliness. The ICB result must fall within +/- the reporting limit (RL) from zero. If either the ICV or ICB fail to meet criteria, the analysis should be terminated, the problem corrected and the instrument recalibrated. (See Section 11.2.10 and Section 11.2.11 for required run sequence). If the cause of the ICV or ICB failure was not directly instrument related the corrective action will include repreparation of the associated samples.

9.8. Continuing Calibration Verification (CCV/CCB) - Calibration accuracy is monitored throughout the analytical run through the analysis of a known standard after every 10 samples. The CCV must be a mid-range standard at a concentration other than that of the ICV. The CCV result must fall within 20% of the true value for that solution. A CCB is analyzed immediately following each CCV. (See Section 11.2.10 and 11.2.11 for required run sequence.) The CCB result must fall within +/- RL from zero. Each

CCV and CCB analyzed must reflect the conditions of analysis of all associated samples. Sample results may only be reported when bracketed by valid ICV/CCV and ICB/CCB pairs. If a mid-run CCV or CCB fails, the analysis must be terminated, the problem corrected, the instrument recalibrated, the calibration verified and the affected samples reanalyzed. If the cause of the CCV or CCB failure was not directly instrument related the corrective action will include repreparation of the associated samples.

9.9. Method of Standard Addition (MSA) -This technique involves adding known amounts of standard to one or more aliquots of the sample prior to preparation. This technique compensates for a sample interferent that may enhance or depress the analyte signal, thus producing a different slope from that of the calibration standards. It will not correct for additive interferences which cause a baseline shift. Refer to Section 11.2.12 for additional information on when full 4 point MSA is required as well as Appendix C for specific MSA requirements.

10. CALIBRATION AND STANDARDIZATION

10.1. Calibration standards must be processed through the preparation procedure as described in Section 11.1.

10.2. Due to the differences in preparation protocols separate calibration and calibration verification standards must be prepared for aqueous and solid matrices.

10.3. Calibration must be performed daily (every 24 hours) and each time the instrument is set up. The instrument calibration date and time must be included in the raw data.

10.4. Set up the instrument with the operating parameters recommended by the manufacturer. Allow the instrument to become thermally stable before beginning calibration (approximately 30 minutes of warm-up is required). Refer to the facility specific instrument SOP and CVAA instrument manual for detailed setup and operation protocols.

10.5. Calibrate the instrument according to instrument manufacturer's instructions, using a minimum of five standards and a blank. One standard must be at the STL reporting limit. Analyze standards in ascending order beginning with the blank. Refer to Section 7.5 and Table I for additional information on preparing calibration standards and calibration levels.

10.6. The calibration curve must have a correlation coefficient of ≥0.995 or the instrument shall be stopped and recalibrated prior to running samples. Sample results can not be reported from a curve with an unacceptable correlation coefficient.

10.7. Refer to Section 9.0 for calibration verification procedures, acceptance criteria and corrective actions.

11. PROCEDURE

11.1. Standard and Sample Preparation:

11.1.1. All calibration and calibration verification standards (ICV, ICB, CCV, CCB) are processed through the digestion procedure as well as the field samples.

11.1.2. Transfer 0, 0.2, 0.5, 1.0, 2.0, 5.0 and 10.0 mL aliquots of the working standard (7.5) into a series of sample digestion bottles.

Note: Alternate volumes of standard may be prepared as long as the accuracy and final standard concentrations as detailed in Table I are maintained.

11.1.3. Add reagent water to each standard bottle to make a total volume of 10 mL. Continue preparation as described under 11.1.5 or 11.1.6 below.

11.1.4. Transfer triplicate 0.2 g portions of a well mixed sample into a clean sample digestion bottle. Continue preparation as described under 11.2.2 or 11.2.3 below.

11.1.5. Water Bath protocol:

11.1.5.1. To each **standard** bottle: Add 5 mL of aqua regia.
To each **sample** bottle: Add 5 mL of reagent water and 5 mL of aqua regia.

11.1.5.2. Heat for 2 minutes in a water bath at 90 - 95 ° C.

11.1.5.3. Cool.

11.1.5.4. Add 50 mL of distilled water.

11.1.5.5. Add 15 mL of potassium permanganate solution.

11.1.5.6. Add 8 mL of potassium persulfate solution, mix thoroughly.

11.1.5.7. Heat for 30 minutes in the water bath at 90 - 95 °C.

11.1.5.8. Cool.

11.1.5.9. Add 6 mL of sodium chloride-hydroxylamine sulfate solution to reduce the excess permanganate.

11.1.5.10. To each **standard** bottle: Add 50 mL of reagent water.
To each **sample** bottle: Add 55 mL of reagent water.

11.1.5.11. Continue as described under Section 11.2.

11.1.6. Autoclave protocol:

11.1.6.1. Add 5 mL concentrated of H_2SO_4 and 2 mL of concentrated HNO_3.

11.1.6.2. Add 5 mL of saturated potassium permanganate solution.

11.1.6.3. Cover digestion bottle with aluminum foil or screw cap loosely applied.

11.1.6.4. Heat samples at 121 °C and 15 lbs. pressure for 15 minutes.

11.1.6.5. Cool.

11.1.6.6. Add 6 mL of sodium chloride-hydroxylamine sulfate solution to reduce excess permanganate.

Note: Alternate final volumes may be used as long as the standards and sample are treated the same way and reagents are adjusted proportionally.

11.1.6.7. Make up to volume of 100 mL with reagent water.

11.1.6.8. Continue as described under Section 11.2.

11.2. Sample Analysis:

11.2.1. Because of differences between various makes and models of CVAA instrumentation, no detailed operating instructions can be provided. Refer to

the facility specific instrument operating SOP and the CVAA instrument manual for detailed setup and operation protocols.

11.2.2. All labs are required to detail the conditions/programs utilized for each instrument within the facility specific instrument operation SOP.

11.2.3. Manual determination:

11.2.3.1. Treating each sample individually, purge the head space of the sample bottle for at least one minute.

11.2.3.2. Add 5 mL of stannous chloride solution and immediately attach the bottle to the aeration apparatus.

11.2.3.3. Allow the sample to stand quietly without manual agitation while the sample is aerated (1 L/min flow). Monitor the sample absorbance during aeration. When the absorbance reaches a maximum and the signal levels off, open the bypass valve and continue aeration until the absorbance returns to its baseline level. Close the bypass valve and remove the aeration device.

11.2.3.4. Place the aeration device into 100 mLs of 1% HNO_3 and allow to bubble rinse until the next sample is analyzed.

11.2.4. Automated determination: Follow instructions provided by instrument manufacturer.

11.2.5. Perform a linear regression analysis of the calibration standards by plotting maximum response of the standards vs. ug of mercury. Determine the mercury concentration in the samples from the linear regression fit of the calibration curve. Calibration using computer or calculation based regression curve fitting techniques on concentration/response data is acceptable.

11.2.6. All measurements must fall within the defined calibration range to be valid. Dilute and reanalyze all samples for analytes that exceed the highest calibration standard.

11.2.7. If the sample results are negative and the absolute value of the negative result is greater than the reporting limit, the sample must be diluted and reanalyzed.

11.2.8. The samples must be allowed to cool to room temperature prior to analysis or a decrease in the response signal can occur.

11.2.9. Baseline correction is acceptable as long as it is performed after every sample or after the CCV and CCB; resloping is acceptable as long as it is immediately preceded and followed by a compliant CCV and CCB.

11.2.10. The following analytical sequence must be used with 7471A and 245.5:

Instrument Calibration
ICV
ICB
Maximum 10 samples
CCV
CCB
Repeat sequence of 10 samples between CCV/CCB pairs as required to complete run
CCV
CCB

Refer to Quality Control Section 9.0 and Table II (Appendix A) for quality control criteria to apply to Methods 7471A and 245.5.

Note: Samples include the method blank, LCS, MS, MSD, duplicate, field samples and sample dilutions.

11.2.11. The following run sequence is consistent with 7471A, CLP and 245.5 and may be used as an alternate to the sequence in 11.2.10. This run sequence is recommended if multiple method requirements must be accommodated in one analytical run:

Instrument Calibration
ICV
ICB
CRA*
CCV
CCB
10 samples
CCV
CCB
Repeat sequence of 10 samples between CCV/CCB pairs as required to complete run.

CCV
CCB

Refer to the appropriate CLP SOP (CORP-MT-0008) for quality control requirements for QC samples.

* Refer to the CLP SOP for information on the CRA.

11.2.12. For TCLP samples, full four point MSA will be required if all of the following conditions are met:

1) recovery of the analyte in the matrix spike is not at least 50%,

2) the concentration of the analyte does not exceed the regulatory level, and,

3) the concentration of the analyte is within 20% of the regulatory level.

Appendix E provides guidance on performing MSA analyses. For TCLP mercury determinations, MSA spikes must be added prior to sampe preparation.

11.3. To facilitate the early identification of QC failures and samples requiring rerun it is strongly recommended that sample data be reviewed periodically throughout the run.

11.4. Guidelines are provided in the appendices on procedures to minimize contamination of samples and standards, preventive maintenance and troubleshooting.

11.5. One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and is approved by a Technical Specialist and QA Manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file.

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

12. DATA ANALYSIS AND CALCULATIONS

12.1. ICV percent recoveries are calculated according to the equation:

$$\%R = 100\left(\frac{Found(ICV)}{True(ICV)}\right)$$

12.2. CCV percent recoveries are calculated according to the equation:

$$\%R = 100\left(\frac{Found(CCV)}{True(CCV)}\right)$$

12.3. Matrix spike recoveries are calculated according to the following equation:

$$\%R = 100\left(\frac{SSR - SR}{SA}\right)$$

Where:
SSR = Spike Sample Result
SR = Sample Result
SA = Spike Added

12.4. The relative percent difference (RPD) of matrix spike/matrix spike duplicates or sample duplicates are calculated according to the following equations:

$$RPD = 100\left[\frac{|MSD - MS|}{\left(\frac{MSD + MS}{2}\right)}\right]$$

Where:
MS = determined spiked sample concentration
MSD = determined matrix spike duplicate concentration

$$RPD = 100\left[\frac{|DU1 - DU2|}{\left(\frac{DU1 + DU2}{2}\right)}\right]$$

Where:
DU1 = Sample result
DU2 = Sample duplicate result

12.5. For automated determinations, the final concentration determined in solid samples when reported on a dry weight basis is calculated as follows:

mg/kg, dry weight = (C x V x D)/(W x S)

Where:
C = Concentration (ug/L) from instrument readout
V = Volume of digestate (L)
D = Instrument dilution factor
W = Weight in g of wet sample digested
S = Percent solids/100

Note: A Percent Solids determination must be performed on a separate aliquot when dry weight concentrations are to be reported. If the results are to be reported on a wet weight basis, the "S" factor should be omitted from the above equation.

12.6. For manual (total) determinations, the final concentration determined in solid samples when reported on a dry weight basis is calculated as follows:

mg/kg, dry weight = (C)/(W x S)

Where:
C = Concentration (ug) from instrument readout
W = Weight in g of wet sample digested
S = Percent solids/100

Note: A Percent Solids determination must be performed on a separate aliquot when dry weight concentrations are to be reported. If the results are to be reported on a wet weight basis, the "S" factor should be omitted from the above equation.

12.7. The LCS percent recovery is calculated according to the following equation:

$$\%R = 100\left(\frac{Found(LCS)}{True(LCS)}\right)$$

12.8. Sample results should be reported with up to three significant figures in accordance with the STL significant figure policy.

13. METHOD PERFORMANCE

13.1. Each laboratory must have initial demonstration of performance data on file for each analyte of interest as described in Section 9.0.

13.2. Method performance is determined by the analysis of method blank, laboratory control sample, matrix spike and matrix spike duplicate samples. The matrix spike recovery should fall within +/- 25 % and the matrix spike duplicates should compare within 20% RPD. The method blanks must meet the criteria in Section 9.3. The laboratory control sample should recover within 20% of the true value until in house limits are established.

13.3. Training Qualification:

The group/team leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience.

14. POLLUTION PREVENTION

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

15. WASTE MANAGEMENT

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

16. REFERENCES

16.1. Test Methods for Evaluating Solid Waste , Physical/Chemical Methods, SW-846, 3rd Edition, Final Update II, Revision I, September 1994, Method 7471A (Mercury).

16.2. “Methods for the Chemical Analysis of Water and Wastes”, EPA-600/4-79-020, U.S.EPA, August 1983, Method 245.5.

16.3. U.S.EPA Statement of Work for Inorganics Analysis, ILMO3.0.

16.4. QA-003, STL QC Program.

16.5. QA-004, Rounding and Significant Figures.

16.6. QA-005, Method Detection Limits.

17. MISCELLANEOUS (TABLES, APPENDICES, ETC. . .)

17.1. Modifications/Interpretations from reference method.

17.1.1. Modifications from both 7471A and 245.5.

17.1.1.1. A potassium persulfate oxidation step has been included to facilitate the breakdown of organic mercurials which are not completely oxidized by potassium permanganate. Use of potassium persulfate in combination with the permanganate improves the recovery of mercury from organo-mercury compounds. The use of persulfate has been incorporated in several recent EPA mercury protocols.

17.1.1.2. The alternate run sequence presented in Section 11.2.11 is consistent with method requirements. An additional QC analysis (CRA) was added to accommodate the CLP protocol requirements.

17.1.2. Modifications from Method 7471A

17.1.2.1. Chapter 1 of SW846 specify the use of reagent water with a purity equivalent to ASTM Type II water. This SOP specifies the use of a Millipore DI system or equivalent to produce reagent water. This SOP requires that reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks.

17.1.2.2. Chapter 1 of SW-846 states that the method blank should not contain any analyte of interest at or above the MDL. This SOP states that the method blank must not contain any analyte of interest at or above the reporting limit.

17.1.2.3. Method 7471A does not state control criteria within the text of the method. The QC section of 7471A refers the analyst to Section 8.0 of Method 7000A, the generic atomic absorption method, which discusses flame and furnace methods. The ICV criteria stated in Method 7000A is ± 10%. This SOP requires ICV control limits of ± 20% based on the fact that the mercury ICV, unlike the ICV for the flame and furnace analytes, is digested and therefore is equivalent to a LCS. The CLP protocol 245.5 CLP-M recognizes this factor and requires control limits of ± 20%.

17.1.3. Modifications from 245.5

17.1.3.1. Method 245.5 Section 9.3 states concentrations should be reported as follows: Between 0.1 and 1 ug/g, to the nearest 0.01 ug; between 1 and 10 ug/g, to the nearest 0.1ug; above 10 ug/g, to the nearest ug. STL reports all Hg results under this SOP to two significant figures.

17.2. Modifications from previous SOP

17.2.1. Section 1.4 reporting limit changed from 0.1 mg/kg based on a 0.2 g to 0.3mg/kg based on a 0.6 g sample aliquot.

17.2.2. Section 9.3 added MS and MSDs as not counted in determination of preparation batches.

17.3. Facility Specific SOPs

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

17.4. Documentation and Record Management

The following documentation comprises a complete CVAA raw data package:

- Raw data (direct instrument printout)
- Run log printout from instrument software where this option is available or manually generated run log. (A bench sheet may be substituted for the run log as long as it contains an accurate representation of the analytical sequence).
- Data review checklist - See Appendix B
- Standards Documentation (source, lot, date).
- Copy of digestion log.
- Non-conformance summary (if applicable).

Figure 1. Solid Sample Preparation for Mercury - Autoclave Procedure

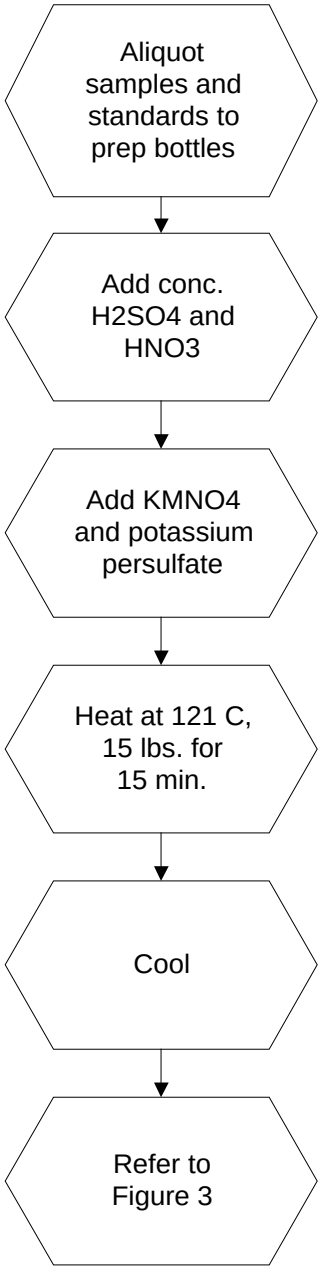


Figure 2. Solid Sample Preparation for Mercury - Water Bath Procedure

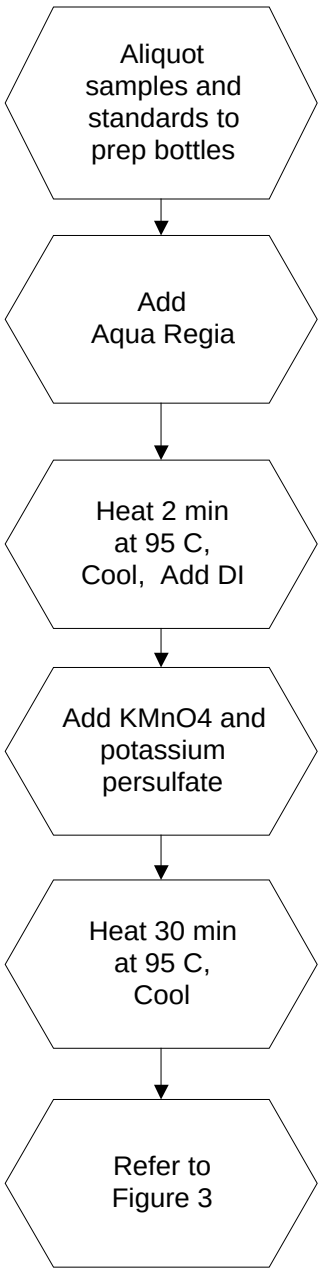
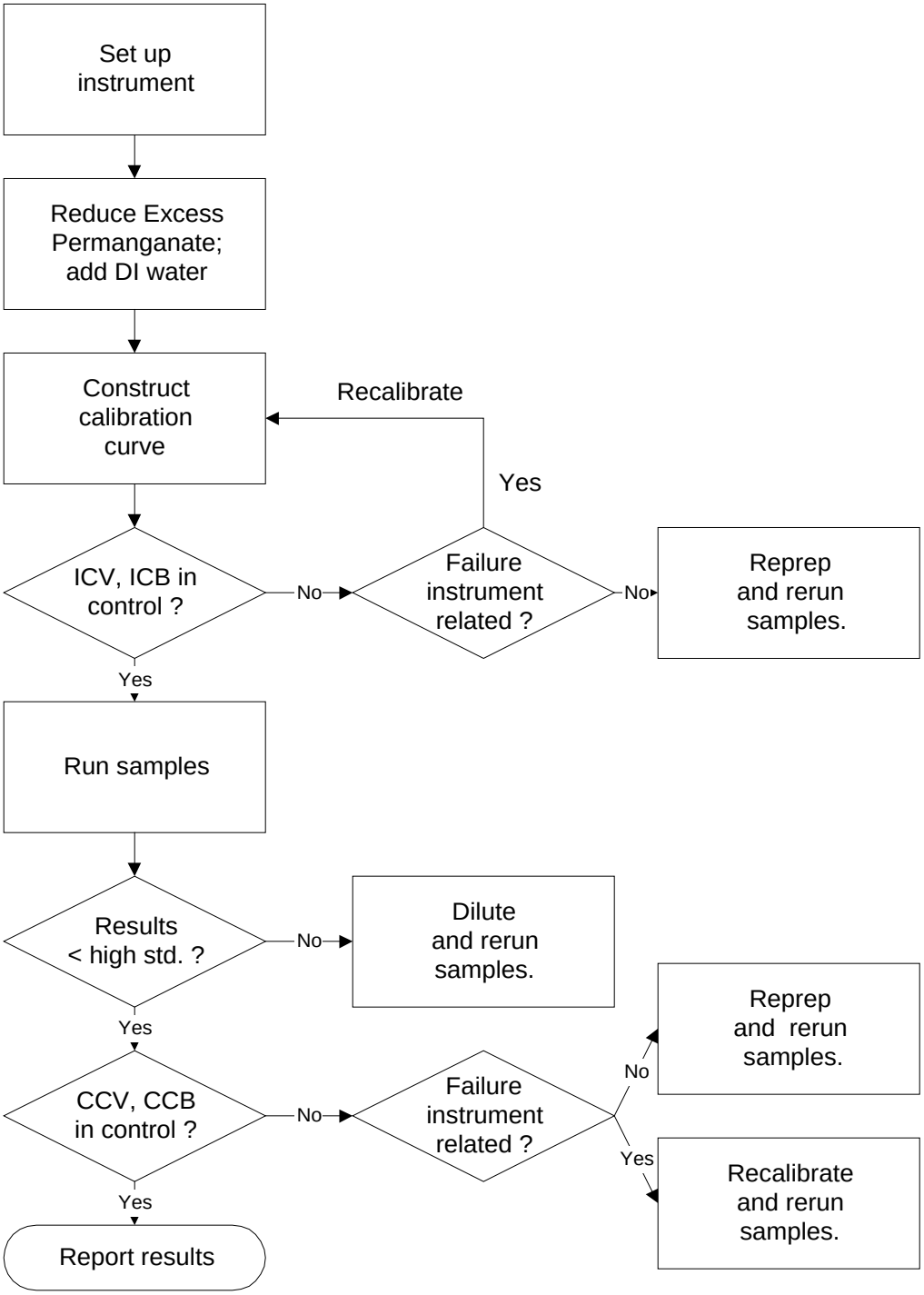


Figure 3. CVAA Mercury Analysis



APPENDIX A

TABLES

TABLE I . MERCURY REPORTING LIMITS, CALIBRATION STANDARD*, QC STANDARD AND SPIKING LEVELS

Soil RL (mg/kg)	0.1
Std 0 (mg/L)	0
Std 1 (mg/L)	0.0002
Std 2 (mg/L)	0.0005
Std 3 (mg/L)	0.001
Std 4 (mg/L)	0.002
Std 5 (mg/L)	0.005
Std 6 (mg/L) **	0.010
ICV (mg/L)	0.001 or 0.0025 ***
CCV/LCS (mg/L)	0.0025 or 0.005 ***
MS (mg/L)	0.001

*** SOP specified calibration levels must be used unless prevented by the instrument configuration or client specific requirements. Deviations from specified calibration levels must be documented in the facility specific instrument operation SOP and must be approved by the facility technical manager and Quality Assurance Manager.**

**** Optional standard which may be used to extend the calibration range as allowed by the instrument configuration. If the instrument configuration prevents the use of 6 standards, the 2 ppb standard may be eliminated in favor of the 10 ppb standard.**

***** Concentration level dependent on high calibration standard used. CCV must be 50% of the high standard concentration and the ICV must be 20-25% of the high standard concentration.**

TABLE II. Summary Of Quality Control Requirements

QC PARAMETER	FREQUENCY *	ACCEPTANCE CRITERIA	CORRECTIVE ACTION
ICV	Beginning of every analytical run.	80 - 120 % recovery.	Terminate analysis; Correct the problem; Recalibrate or reprep batch (see Section 9.7).
ICB	Beginning of every analytical run, immediately following the ICV.	The result must be within +/- RL from zero.	Terminate analysis; Correct the problem; Recalibrate or reprep batch (see Section 9.7).
CCV	Every 10 samples and at the end of the run.	80 - 120 % recovery.	Terminate analysis; Correct the problem; Recalibrate and rerun all samples not bracketed by acceptable CCV or reprep batch (see Section 9.8).
CCB	Immediately following each CCV.	The result must be within +/- RL from zero.	Terminate analysis; Correct the problem; Recalibrate and rerun all samples not bracketed by acceptable CCB or reprep batch (see Section 9.8).
Method Blank	One per sample preparation batch of up to 20 samples.	The result must be less than or equal to the RL. Sample results greater than 20x the blank concentration are acceptable. Samples for which the contaminant is < RL do not require redigestion (See Section 9.4)	Redigest and reanalyze samples. Note exceptions under criteria section. See Section 9.4 for additional requirements.

*See Sections 11.2.10 and 11.2.11 for exact run sequence to be followed.

TABLE II. Summary of Quality Control Requirements (Continued)

QC PARAMETER	FREQUENCY	ACCEPTANCE CRITERIA	CORRECTIVE ACTION
Laboratory Control Sample (LCS)	One per sample preparation batch of up to 20 samples.	Aqueous LCS must be within 80 - 120% recovery or in-house control limits.	Terminate analysis; Correct the problem; Redigest and reanalyze all samples associated with the LCS (see Section 9.5).
Matrix Spike	One per sample preparation batch of up to 20 samples.	75 - 125 % recovery or in-house control limits. If the MS/MSD is out for an analyte, it must be in control in the LCS.	In the absence of client specific requirements, flag the data; no flag required if the sample level is > 4x the spike added. (see Section 9.6) For TCLP see Section 11.3.12
Matrix Spike Duplicate	See Matrix Spike	75 - 125 % recovery or in-house control limits; RPD ≤ 20%. (See MS)	See Corrective Action for Matrix Spike.

APPENDIX B
STL Hg DATA REVIEW CHECKLIST

STL Hg Data Review Checklist

Run/Project Information

Run Date: _____ **Analyst:**_____ **Instrument:**_____
Prep Batches Run:_____

Circle Methods used: **7470A / 245.1 :** CORP-MT-0005 Rev 1 **7471 / 245.5 :** CORP-MT-0007 Rev 1
CLP - AQ : CORP-MT-0006 Rev 0 **CLP - SOL :** CORP-MT-0008 Rev 0

Review Items

A. Calibration/Instrument Run QC	Yes	No	N/A	2ndLevel
1. Instrument calibrated per manufacturer's instructions and at SOP specified levels ?				
2. ICV/CCV analyzed at appropriate frequency and within control limits?				
3. ICB/CCB analyzed at appropriate frequency and within +/- RL or +/- CRDL (CLP)?				
4. CRA run (CLP only)?				
B. Sample Results				
1. Were samples with concentrations > the high calibration standard diluted and reanalyzed?				
2. All reported results bracketed by in control QC ?				
3. Sample analyses done within holding time?				
C. Preparation/Matrix QC				
1. LCS done per prep batch and within QC limits ?				
2. Method blank done per prep batch and < RL or CRDL (CLP) ?				
3. MS run at required frequency and within limits ?				
4. MSD or DU run at required frequency and RPD within SOP limits?				
D. Other				
1. Are all nonconformances documented appropriately ?				
2. Current IDL/MDL data on file?				
3. Calculations and Transcriptions checked for error ?				
4. All client/ project specific requirements met?				
5. Date of analysis verified as correct ?				

Analyst: _____ **Date:**_____
Comments:
_____
_____

2nd Level Reviewer : _____ **Date:**_____
_____
_____

APPENDIX C

MSA GUIDANCE

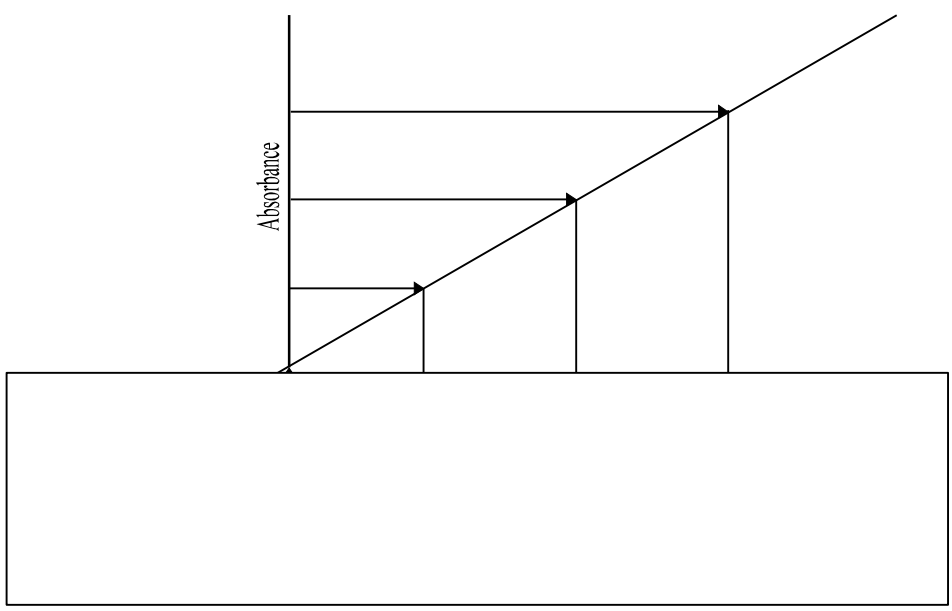
APPENDIX C. MSA GUIDANCE

Method of Standard Addition

Four equal volume aliquots of sample are measured and known amounts of standards are added to three aliquots. The fourth aliquot is the unknown and no standard is added to it. The concentration of standard added to the first aliquot should be 50% of the expected concentration. The concentration of standard added to the second aliquot should be 100% of the expected concentration and the concentration of standard added to the third aliquot should be 150% of the expected concentration. The volume of the unspiked and spiked aliquots should be the same (i.e., the volume of the spike added should be negligible in relation to the volume of sample).

To determine the concentration of analyte in the sample, the absorbance (or response) of each solution is determined and a linear regression performed. On the vertical axis the absorbance (or response) is plotted versus the concentrations of the standards on the horizontal axis using 0 as the concentration of the unspiked aliquot. An example plot is shown in Figure 1. When the resulting line is extrapolated back to zero absorbance, the point of interception of the horizontal axis is the concentration of the unknown. Calculate the correlation coefficient (r) and the x-intercept (where y=0) of the curve. The concentration in the digestate is equal to the negative x-intercept.

Figure 1



- For the method of standard additions to be correctly applied, the following limitations must be taken into consideration.
- The plot of the sample and standards must be linear over the concentration range of concern. For best results, the slope of the curve should be similar to that of a plot of the aqueous standard curve.
- The effect of the interference should not vary as the ratio of the standard added to the sample matrix changes.

APPENDIX D

TROUBLESHOOTING GUIDE

APPENDIX D. TROUBLESHOOTING GUIDE

Problem	**Possible Cause**
Poor or No Absorbance or Sensitivity Check failed	Incorrect wavelength Dirty windows Window loose Etched or dirty optics Wrong lamp Bad lamp Not enough or no sample introduced Empty sample cup Incorrectly made standards Gas leak EDL power supply set on “Continuous”
Erratic Readings	Source lamp not aligned properly Lamp not prewarmed Injection tip partially clogged Contaminated reagents Contaminated glassware Drying tube saturated Bad lamp Injection tip hitting outside of tube Injection tip coated or not set properly Leak in sample tubing Power fluctuations Air bubbles in tubing
EDL Won’t Light	Lamp cable not plugged in Lamp power set at 0 Lamp is dead Power supply fuse is blown Short in cord
Standards reading twice or half normal absorbance or concentration	Incorrect standard used Incorrect dilution performed Dirty cell
Background Correction Light Blinking	Background screen or attenuator faulty

APPENDIX E

CONTAMINATION CONTROL GUIDELINES

APPENDIX E. CONTAMINATION CONTROL GUIDELINES

The following procedures are strongly recommended to prevent contamination:

All work areas used to prepare standards and spikes should be cleaned before and after each use.

All glassware should be washed with detergent and tap water and rinsed with 1:1 nitric acid followed by deionized water.

Proper laboratory housekeeping is essential in the reduction of contamination in the metals laboratory. All work areas must be kept scrupulously clean.

Powdered or Latex Gloves must not be used in the metals laboratory since the powder contains silica and zinc, as well as other metallic analytes. Only vinyl or nitrile gloves should be used in the metals laboratory.

Glassware should be periodically checked for cracks and etches and discarded if found. Etched glassware can cause cross contamination of any metallic analytes.

Autosampler trays should be covered to reduce the possibility of contamination. Trace levels of elements being analyzed in the samples can be easily contaminated by dust particles in the laboratory.

The following are helpful hints in the identification of the source of contaminants:

Reagents or standards can contain contaminants or be contaminated with the improper use of a pipette.

Improper cleaning of glassware can cause contamination.

Separate glassware if an unusually high sample is analyzed and soak with sulfuric acid prior to routine cleaning.

APPENDIX F

PREVENTIVE MAINTENANCE

APPENDIX F. PREVENTIVE MAINTENANCE

A maintenance log is used to record when maintenance is performed on instruments. When an instrument problem occurs indicate the date, time and instrument number, then identify the problem and corrective action in the maintenance log.

The following procedures are required to ensure that that the instrument is fully operational.

Cold Vapor Atomic Absorption (Leeman PS 200) (1)

Daily	Semi-annually	Annually
Clean lens.	Check Hg lamp intensity.	Change Hg lamp.
Check aperture.		Check liquid/gas separator.
Check argon flow.		
Check tubing.		
Check drain.		
Replace drying tube.		

Cold Vapor Atomic Absorption (PE 5000) (1)

Daily	Monthly
Clean aspirator by flushing with DI water.	Clean cell in aqua regia.
Check tubing and replace if needed.	Clean aspirator in aqua regia.
Clean windows with methanol.	
Change silica gel in drying tube.	
Check argon gas supply.	
Adjust lamp.	

PITT-WC-0018

Cyanide-Semi-Automated, Pyridine-Barbituric Acid for Total (Method 335.4) and Amenable (SM 4500-6) Cyanide Analyses in Water and Soil (Method 9012A)

Controlled Copy
Copy No.: _____
Implementation Date:_____

OPERATION-SPECIFIC STANDARD OPERATING PROCEDURE

Title: Cyanide-Semi-Automated, Pyridine-Barbituric Acid for Total (Method 335.4)& Amenable(SM 4500-G) Cyanide Analyses in Water and Soil(Method 9012A)

(SUPERSEDES: PITT-WC-0018, Rev. 3.4, 7/01/00)

Prepared by: _____

Reviewed by: _____
Technical Specialist

Approved by: _____
Quality Assurance Manager

Approved by: _____
Environmental, Health and Safety Coordinator

Approved by: _____
Laboratory Director

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1. SCOPE AND APPLICATION

1.1 This method is applicable to the determination of Total and Amenable Cyanide in waters and solids. It is based on SW846 Method 9012A, EPA 335.4 and SM 4500-CN G.

2. SUMMARY OF METHOD

2.1 Cyanide, as HCN, is released by distilling/refluxing the sample with strong acid and is trapped in a sodium hydroxide solution.

2.2 The sodium hydroxide solution is analyzed colorimetrically on an autoanalyzer using the pyridine-barbituric acid method.

3. DEFINITIONS

3.1 LCS: The Laboratory Control Sample (LCS) is a spiked laboratory control sample used to monitor the accuracy of the analytical process independent of possible interference effects due to sample matrix. The LCS is processed through all method steps with the samples. The LCS must be prepared from a source independent of the calibration standard materials. Successful analyte recovery for the LCS provides assurance that the method is in control.

3.2 LCSD: The Laboratory Control Sample Duplicate (LCSD) is processed with the LCS when insufficient sample is not available to process a MS/MSD. The LCS/LCSD is used to demonstrate batch precision. An LCSD is only required for batch QC, when a MS/MSD is not present. The LCSD is prepared from the same materials as the LCS.

3.3 MB: A Method Blank (MB) is prepared with reagent grade water and all reagents used to process the samples. The MB is processed along with the samples through all procedures including distillation. It is used to monitor laboratory and/or reagent contamination.

3.4 CCV: A Continuing Calibration Verification (CCV) Standard assures that the method calibration is in control. A CCV is run at intervals of up to ten samples within a sequence. The CCV may be prepared from the same source material as the LCS standard, however, the CCV is not distilled.

3.5 MS: Matrix Spike (MS) is an aliquot of one sample in the QC batch that is spiked with a known amount of the target analyte. As a part of the QC batch, it accompanies the sample through all the steps of the analytical process.

3.6 MSD: Matrix Spike Duplicate (MSD) consists of a replicate portion of the sample which was designated as the MS. This portion is spiked and processed exactly as the MS.

3.7 MS/MSD results are used to determine the effects of the sample matrix on the precision and accuracy of the analytical process. Due to the potential variability of the matrix of each sample, the MS and the MSD results may not have immediate bearing on any sample except the one spiked.

3.8 QC Batch: QC batch is a set of 20 or fewer environmental samples plus associated laboratory QC samples that are similar in composition and that are processed within the same time period with the same reagents and standard lots. Laboratory QC samples such as LCS, matrix QC samples, and blanks are not included in the sample count for batching purposes.

3.9 Reagent Grade Water: Laboratory water which is produced by a Millipore DI system or equivalent. Reagent grade water must be free of the analyte of interest as demonstrated through the analysis of MBs.

3.10 Continuing Calibration Blank (CCB): A non-distilled reagent-water blank. CCBs will be run immediately following each instrument calibration and CCV. An instrument blank must be free of analyte down to the reporting limit. All reportable data must be bracketed by acceptable CCB samples.

4. INTERFERENCES

4.1 Nitrites and nitrates interfere, but are eliminated by the addition of sulfamic acid.

4.2 Chlorine interference can be removed by dropwise addition of sodium arsenite to the sample until there is no reaction to KI-starch paper. This is done upon notification from the sample custodian. The analyst will then document the removal of residual chlorine on the sample condition upon receipt form.

NOTE: For SM 4500-CN G, Amenable cyanide, half of the sample is chlorinated for one hour by addition of $Ca(OCl_2)$ solution while maintaining a pH of 11-12. Then chlorine is removed by addition of sodium arsenite.

4.3 Sulfide interference can be removed by adding an excess of bismuth nitrate to the waste before distillation. This is done for the 9012A (soil) method. For Method 335.4, sulfides are removed by the addition of cadmium carbonate until there is no reaction to lead acetate paper.

5. SAFETY

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

5.2 Eye protection that satisfies ANSI Z87.1 (as per the Chemical Hygiene Plan), laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

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

5.4 Exposure to chemicals must be maintained **as low as reasonably achievable**, therefore, unless they are known to be non-hazardous, all samples must be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

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

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

6. EQUIPMENT AND SUPPLIES

6.1 Cyanide Distillation Apparatus – Midi "Easy-Dist System"

6.2 Vacuum Pump

6.3 Graduated Cylinders: Various sizes

6.4 Volumetric Flasks: Various Sizes

6.5 Automated Pipette

6.6 Balance: Accurate to 0.1 mg

6.7 Autoanalyzer: See manufacturer for requirements

6.8 Potassium Iodide (KI) Indicator Paper

6.9 Lead Acetate Indicator Paper

6.10 pH paper

7. REAGENTS AND STANDARDS

7.1 Use reagent grade water (1 microohm) for all solutions.

7.2 Sodium Hydroxide (0.25 N): In a 1L volumetric flask, dissolve 10.0g NaOH in approximately 900mL reagent-grade water. Dilute to volume and invert three times. Store in a plastic bottle. As an alternative, a NaOH solution can be purchased.

7.3 Phosphate Buffer 1.0 M: In a 1L volumetric flask, dissolve 138gm KH_2PO_4 in approximately 800mL reagent-grade water. Dilute to volume and mix thoroughly.

7.3.1 Working Phosphate Buffer: In a 250mL Volumetric Flask, add 1.0mL of 30 % Brg 35 solution. Bring up to volume with phosphate buffer (7.3). Mix thoroughly.

7.4 Chloramine-T: Dissolve 2.0g of chloramine-T hydrate in 500mL reagent-grade water. ***Prepare fresh weekly.***

7.5 Pyridine - Barbituric Acid Reagent: In the fume hood, place 15g barbituric acid in a 1L beaker and add 100 mL of reagent grade water, rinsing down the sides of the beaker to wet the barbituric acid. Add 75 mL pyridine (C_5H_5N) with stirring and mix until the barbituric acid dissolves. Add 15 mL concentrated hydrochloric acid (12 M HCl) and mix. Transfer to a 1L volumetric flask, dilute to volume with reagent grade water, and mix thoroughly. (This solution is not degassed.)

7.6 Standards Preparation: Do not de-gas standards.

7.6.1 Stock Standard 1000 mg CN/L equivalent: In a 1L volumetric flask, dissolve 2.0g potassium hydroxide (KOH) in approximately 500 mL reagent grade water. Add 2.51g potassium cyanide (KCN). CAUTION: KCN IS HIGHLY TOXIC. AVOID INHALATION OF DUST OR CONTACT WITH THE SOLID OR SOLUTIONS. Dilute to volume and mix thoroughly. Standardize this solution weekly. Note: Prepare in Fume Hood. Alternatively the 1000mg/L cyanide stock standard may be purchased as a commercial reference standard product.

7.6.2 Working Stock Standard 10 ppm: Pipette 1mL of the Stock Standard (7.6.1) above, into a 100mL volumetric flask. Dilute to volume with reagent grade water.

7.7 Working Standards: Set of seven. A subset of the seven standards may be used, however the standard curve may not have fewer than five standards.

7.7.1 Standard Curve for Cyanide: 0.5, 0.4, 0.30, 0.2, 0.1, 0.05, and 0.01 mg/L. Using a calibrated automatic pipette, pipette 12.5, 10.0, 7.5, 5.0, 2.5, 1.25 and 0.25mL of the working stock standard (Section 7.6.2) into 250 mL volumetric flasks. When brought

to volume with .25 N NaOH, the standard solutions are 0.5, 0.4, 0.3, 0.2, 0.1, 0.05 and 0.01 mg/L, respectively.

7.7.2 Alternatively: prepare a 1.0ppm standard from the working standard (i.e. add 10mL of 7.6.2 10ppm standard to a volumetric and bring up to volume with .25 N NaOH. Mix thoroughly. Follow manufacturer's instructions for preparing standard calibration curve.

7.7.3 To verify the efficiency of the distillation procedure, 0.40 and 0.05mg/L standards will be distilled and checked against the curve. The recovery must be within ±10 percent.

7.7.4 Independent Stock Standard (1000 mg CN/L): Prepare and standardize as in 7.6.1 except use a lot number of standard different from the one used in 7.6.1.

7.7.4.1 LCS/MS/MSD Working Stock 10ppm: Prepare as in 7.6.2 using the1000ppm standard in 7.7.4.

7.8 Reagent for cyanides amenable to chlorination (for SW-846):

7.8.1 Calcium Hyprochlorite solution (0.35m), $Ca(OCl)_2$. Combine 5g of calcium hypochlorite and 100 mL of reagent grade water. Shake before using.

7.8.2 Sodium Hydroxide solution (0.25 N) NaOH. Dissolve 10g of NaOH in one liter of water. As an alternative, a NaOH solution can be purchased.

7.8.3 Sodium Arsenite (0.1N) $NaAsO_2$. Dissolve 3.2g $NaAsO_2$ in 250 mL water.

7.8.4 Potassium Iodide - starch test paper.

7.8.5 Powdered cadmium carbonate.

7.9 Reagents for total cyanides (for EPA Method 335.4):

7.9.1 Calcium hypochlorite solution: See Section 7.10.1.

7.9.2 Sodium Hydroxide solution: See Section 7.10.2.

7.9.3 Potassium Iodide - starch test paper.

7.9.4 Powdered cadmium carbonate.

7.10 Reagents for Distillation of Cyanide

7.10.1 NaOH, 0.25 N: 50g of NaOH dissolved in reagent grade water and diluted to 1 liter in a volumetric flask. As an alternative, a NaOH solution can be purchased.

7.10.2 Concentrated H_2SO_4

7.10.3 Magnesium Chloride Solution: 510g of $MgCl \bullet 6H_2O$ dissolved and diluted to 1 Liter with reagent grade water in a volumetric flask. As an alternative, a $MgCl \bullet 6H_2O$ solution can be purchased.

7.10.4 Bismuth Nitrate Solution: Dissolve 30.0g of $Bi(NO_3)_3 \bullet 5H_2O$ in 100 mL of reagent grade water. Continue to stir solution and add 250 mL of glacial acetic acid. Stir until dissolved. Dilute to 1 liter with reagent water.

7.10.5 Sulfamic Acid

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1 Solid samples are unpreserved. Water samples are preserved with NaOH to a pH >12. All samples are stored at 4°C in plastic or glass containers.

8.2 The holding time is 14 days from date of sampling

9. QUALITY CONTROL

9.1 A Laboratory Control Sample is processed on each day of analysis with each batch of 20 or fewer environmental samples. The LCS is prepared from a standard source independent of the material used for instrument calibration. The LCS recovery for waters must be ±15 percent of the true value. Amenable CN LCS and the LCS for soils must be within the manufacturers control limits. If the LCS fails criteria, the analyst will check calculations and instrument performance and reanalyze the LCS once. If the LCS is still outside control limits, all samples in the QC batch will be reprepared and reanalyzed. If this is not possible due to limited sample quantity, the laboratory project manager will be notified and an analytical narrative provided with the data. If reprepared and reanalysis will be outside of holding time, the client should be notified and approval from the client must be obtained before reanalysis.

9.2 Method Blanks are processed and run at a frequency of one per QC batch. The method blank is run within the analytical sequence, that is bracketed by acceptable calibration standards and instrument blanks (9.5). Method blanks must be free of analyte down to the reporting limit. The method blank is analyzed along with the samples associated with it for reporting purposes. all reportable data must have an acceptable method blank. All samples within a QC batch, which is associated with an unacceptable blank, will be re-prepped and reanalyzed. If this is not possible due to limited sample quantity, the laboratory project manager will be

notified and an analytical narrative provided with the data. If repreparation and reanalysis is outside of the holding time, the client should be notified and approval from the client must be obtained before reanalysis.

9.3 Continuing Calibration Verifications will be run after every ten or fewer samples. Acceptance limits are ±10 percent of the true value of the standard. The CCV may be prepared from the same material as the LCS, however the CCV does not get distilled. All reported data must be bracketed by an acceptable calibration curve and a CCV, or by consecutive acceptable CCVs. Samples associated with an unacceptable CCV will be reanalyzed. If this is not possible due to limited sample quantity, the laboratory project manager will be notified and an analytical narrative provided with the data. If repreparation and reanalysis is outside of the holding time, the client should be notified and approval from the client must be obtained before reanalysis.

9.4 An MS/MSD pair is processed with each batch of 20 or fewer environmental samples. The MS/MSD recoveries should be within ±25 percent of the true value, and the RPD between the MS and MSD should be ±20 percent. If the MS and the MSD fails recovery criteria, the analyst will check calculations and instrument performance, in order to evaluate evidence of matrix interference. If the LCS is acceptable and the MS/MSD are comparable and outside of QC limits, then a matrix effect is indicated and narrated accordingly. If the sample selected for spiking requires dilution because the initial concentration of the sample is excessively high, then the MS/MSD should be run at the same dilution as the unspiked sample If the resulting spike is over range, this should be documented and narrated in the data report. The MS/MSD should never be run at a dilution greater than the associated sample as this alters the matrix of the sample and thereby makes it invalid.

9.5 A Continuing Calibration Blank (CCB), which is a nondistilled reagent water blank, will be run immediately following each instrument calibration and CCV. An instrument blank must be free of analyte down to the reporting limit. All reportable data must be bracketed by acceptable instrument blanks. Samples associated with the unacceptable blanks will be reanalyzed. If this is not possible due to limited sample quantity, the laboratory project manager will be notified and an analytical narrative provided with the data. If repreparation and reanalysis is outside of the holding time, the client should be notified and approval from the client must be obtained before reanalysis.

9.6 QC Batch is up to twenty samples and associated QC prepared and analyzed within the same time period by the same personnel. The QC batch includes a method blank and LCS/LCSD pair or Method Blank LCS/MS/MSD. It would also include and field QC such as field blanks, rinsate blanks, and/or field duplicates.

10. CALIBRATION AND STANDARDIZATION

10.1 A standard curve is analyzed daily on the auto analyzer for cyanide. The correlation coefficient must be greater than or equal to 0.995.

10.2 The cyanide stock solution, 1000 ppm, must be initially standardized, then restandardized weekly or as needed based upon recovery of the LCS.

10.3 Cyanide stock standardization: To a titrating flask, add 2.5 mL CN stock 1000 mg/L. Dilute with 100 mL of reagent grade water. Add five drops of rhodanine indicator to all four beakers. Titrate with AgNO3 to a salmon-colored end point. Include brand name of chemical and lot number in the standard logbook.

$$\frac{(A - B)\ 1000\ mg/L}{C} = \text{True Value of Stock}$$

A = Volume of $AgNO_3$ for titration of sample.
B = Volume of $AgNO_3$ for titration of blank.
C = CN - added to 100mL of reagent grade water = 2.5mL.

10.4 The recovery of the distillation apparatus should be verified by preparing and distilling two standards equivalent to a high level (0.40 mg/L) and a low-level standard (0.05 mg/L) from the calibration curve. These distilled standards should be within 10% of the equivalent calibration standards. If not, corrective actions should be taken to improve recoveries before proceeding with sample preparation and analysis.

11. PROCEDURE

11.1 <u>Amenable Cyanide (Chlorinated Aliquot):</u>

11.1.1 Place up to 50mL (waters) or 1 g (solids) into a 100mL beaker. Add 50mL of reagent water to non-waters. Place the beaker on a stir plate and begin mixing. Drop by drop, add calcium hypochlorite, while maintaining a pH of 11-12 by addition of NaOH, until an excess of chlorine is reached. Test for chlorine excess using KI paper. A distinct blue color on the test paper indicates a sufficient chlorine level. If necessary, add additional calcium hyprochlorite and/or NaOH solution. Allow the sample to chlorinate for one hour. Analyze an unchlorinated aliquot of sample (50mL or 1g) following the total cyanide method.

11.1.2 After one hour add 1mL portions of 0.1N sodium arsenate until KI-starch paper shows no residual chlorine. Add 5mL of excess sodium arsenate to ensure the presence of excess reducing agent.

NOTE: After the sample is chlorinated to decompose the cyanides, both the chlorinated and the untreated samples are subjected to distillation (Section 11.3). The difference between the CN concentrations found in the two samples is expressed as cyanide amenable to chlorination.

11.1.2.1 Some unidentified organic chemicals may oxidize or form breakdown products during chlorination, giving higher results for cyanide after chlorination than before chlorination.

11.1.2.2 If problems occur and redistillation and reanalysis is not possible due to limited sample quantity, the laboratory project manager will be notified and an analytical narrative provided with the data. If repreparation and reanalysis will be outside of the holding time, the client should be notified and approval obtained before reanalysis.

11.2 Total Cyanide:

11.2.1 Water LCS is prepared by taking 0.8mL of the LCS/MS/MSD working stock (7.7.4.1) to 50mL reagent grade water. The theoretical value is 0.16 mg/L.

11.2.2 Soil LCS is purchased from independent vendor.

11.2.3 Matrix spike and matrix spike duplicate for waters: add 0.5mL of the working stock standard (7.6.2) to 50mL of sample. The theoretical value is 0.10 mg/L.

11.2.4 Soil matrix spike and matrix spike duplicate: Add 0.5mL of the working stock standard (7.6.2) to 1g of sample. The theoretical value is 5mg/kg.

11.2.5 Sample Preparation Procedure: For solid samples, (9012A) proceed to section 11.2.8. For water samples (335.4) proceed to section 11.2.6.

11.2.6 For water samples (335.4), LCS, MS/MSD, and blanks pour 50mL of sample into a distillation flask. Check for the presence of sulfides with lead acetate paper. If sulfides are present, treat 25mL more of the stabilized sample (pH≥12) with powdered cadmium carbonate until there is no reaction to the lead acetate paper. Filter the solution through a dry filter paper into a dry beaker. From the filtrate, measure the sample to be used for analysis.

11.2.7 Assemble the cyanide distillation apparatus. Turn on the vacuum source and adjust the flow such that an even stream of air bubbles is in the scrubber tube. Through the inlet tube, add approximately 0.2g of sulfamic acid, and mix for three minutes prior to the addition of the 2.5mLs of concentrated sulfuric acid. Rinse the inlet tube with reagent water. Add 2.0mL magnesium chloride solution and rinse the inlet tube with reagent grade water. Proceed to section 11.2.9.

11.2.8 For solids, weigh g of sample and transfer it to a distillation flask and add 50mL of reagent grade water. Add 50 mL of 0.25 N NaOH solution to the absorber tube and assemble the scrubber. Assemble the cyanide distillation apparatus. Turn on the vacuum source and adjust the flow such that an even stream of air bubbles is in the scrubber tube. Through the inlet tube, add approximately 0.2g of sulfamic acid, 5.0mL of bismuth nitrate solution and mix for three minutes prior to the addition of the 2.5mLs of concentrated sulfuric acid. Rinse the inlet tube with reagent water. Add 2.0mL magnesium chloride solution and rinse the inlet tube with reagent grade water.

11.2.9 Turn on the cooling water and the heat source. Heat the sample to boiling. The sample is distilled/refluxed under acidic conditions for one and one-half hours. Be sure to adjust the airflow as necessary. After the heating period, turn off the heat and allow to cool for fifteen minutes. Keep the vacuum on.

11.2.10 Disconnect the scrubber and drain the sodium hydroxide solution into a 125mL volumetric flask. Dilute to volume with reagent water rinsings from the absorber tube. Be sure to properly label the flask.

11.3 Calibration volumes of standards, blank, LCS, samples, and MS/MSDs are introduced into the septum by the sampler. The sample is delivered to the analytical cartridge by a peristaltic pump. It is then combined with reagents in a continuously moving stream. As the sample moves through the cartridge it passes through mixing coils and heating/distillation both and/or a dializer as specified by test conditions. A color is produced by the specific analyte in the sample. The intensity of the color is determined by the amount of analyte present. This colored stream then flows to the photometer where the color intensity is measured and converted to an electronic signal.

11.3.1 Consult the autoanalyzer operations manual for any instrument problems and routine maintenance.

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

12. DATA ANALYSIS AND CALCULATIONS

12.1 Total Cyanide sample concentrations are computed by comparing sample peak heights with the standard curve using the following equation. Conversion of results to µg/L is accomplished, where necessary, by multiplication of results in mg/L by 1000.

$$C = A \times DF$$

Where

C = Sample concentration in mg/L
A = Concentration from calibration curve in mg/L
DF = Dilution factor

12.2 **Calculations for Amenable Cyanide Samples:**

Amenable Cyanide, mg/L or mg/Kg =
Total Cyanide (mg/L or Mg/Kg) - Chlorinated Cyanide (mg/L or mg/Kg)

12.3 Percent Recovery (%R) Calculation:

$$\%R = \frac{\text{observed value}}{\text{true value}} \times 100\%$$

12.4 The matrix spike and analytical spike percent recovery calculation:

MS Percent Recovery:

$$\text{MS \% Recovery} = \left(\frac{\text{Observed Conc. of MS} - \text{Conc. of Smp}}{\text{True Spike Conc.}} \right) \times 100\ \%$$

12.4.1 When sample concentration is less than the instrument detection limit, use 0 for sample results only for purposes of calculating percent recovery.

12.4.2 The units for reporting spike sample results will be identical to those used for reporting sample results (µg/L for aqueous and mg/Kg dry weight basis for solid).

12.5 Duplicate Sample Relative Percent Difference calculation:

$$RPD = \frac{|X_1 - X_2|}{\left(\frac{X_1 + X_2}{2}\right)} \times 100\ \%$$

Where:

X1 = Original Result
X2 = Duplicate Result

13. POLLUTION PREVENTION

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

14. WASTE MANAGEMENT

14.1 Waste generated in the procedure will be segregated, and disposed according to the facility hazardous waste procedures. The Environmental Health and Safety Coordinator should be contracted if additional information is required.

15. REFERENCES

15.1 SW846, Test Methods for Evaluating Solid Waste, Third Edition; Total and Amenable Cyanide, Automated UV; Method 9012 A, Revision 1, December 1996.

15.2 EPA 600/4-79-020, Methods for Chemical Analysis of Water and Wastes, March 1983; Cyanide, Total; Method 335.4.

15.3 Standard Methods for the Examination of Water and Waste Water 18th Edition, 1992; Cyanides Amenable to Chlorination after distillation. SM 4500-CN G.

15.4 Miscellaneous (Tables, Appendices, Etc.)

15.5 All sample preparation and analysis information will be documented. Raw data will be forwarded for reporting and for inclusion in the project files.

CORP-IP-0004

Toxicity Characteristic Leaching Procedure and Synthetic Precipitation Leaching Procedure

STL STANDARD OPERATING PROCEDURE

TITLE: TOXICITY CHARACTERISTIC LEACHING PROCEDURE AND SYNTHETIC PRECIPITATION LEACHING PROCEDURE

(SUPERSEDES: NONE)

Prepared by: _____
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1. SCOPE AND APPLICATION

1.1. This SOP describes the application of the Toxicity Characteristic Leaching Procedure (TCLP), SW846 Method 1311. The Toxicity Characteristic (TC) of a waste material is established by determining the levels of 8 metals and 31 organic chemicals in the aqueous leachate of a waste. The TC is one of four criteria in 40 CFR Part 261 to determine whether a solid waste is classified as a hazardous waste. The other three are corrosivity, reactivity and ignitability. The TC Rule utilizes the TCLP method to generate the leachate under controlled conditions which were designed to simulate leaching through a landfill. EPA's "worst case" waste disposal model assumes mismanaged wastes will be exposed to leaching by the acidic fluids generated in municipal landfills. The EPA's model also assumes the acid/base characteristics of the waste will be dominated by the landfill fluids. The TCLP procedure directs the testing laboratory to use a more acidic leaching fluid if the sample is an alkaline waste, again in keeping with the model's assumption that the acid fluids will dominate leaching chemistry over time.

1.2. The specific list of TC analytes and regulatory limits may be found in Appendix A.

Note: The list in Appendix A does not include the December 1994 EPA rule for Universal Treatment Standards for Land Disposal Restrictions. Those requirements include 216 specific metallic and organic compounds and, in some cases, lower detection limit requirements (see 40 CFR 268.40). TCLP leachates are part of the new Universal Treatment Standards, but the conventional analytical methods will not necessarily meet the new regulatory limits. Consult with the client and with STL Technical Specialists before establishing the instrumental methods for these regulations.

1.3. This SOP also describes the application of the Synthetic Precipitation Leaching Procedure (SPLP) which was designed to simulate the leaching that would occur if a waste was disposed in a landfill and exposed only to percolating rain water. The procedure is based on SW846 Method 1312. The list of analytes for SPLP may extend beyond the toxicity characteristic compounds shown in Appendix A. With the exception of the use of a modified extraction fluid, the SPLP and TCLP protocols are essentially equivalent. Where slight differences may exist between the SPLP and TCLP they are distinguished within this SOP.

1.4. The procedure is applicable to liquid, solid, and multiphase wastes.

1.5. The results obtained are highly dependent on the pH of the extracting solution, the length of time that the sample is exposed to the extracting solution, the temperature

during extraction, and the particle size/surface area of the sample. These parameters must be carefully controlled.

1.6. The reporting limits are based on the individual samples as well as the individual analysis techniques. However, the sample is determined to be hazardous if it contains any analyte at levels greater than or equal to the regulatory limits.

1.7. If a total analysis of the waste demonstrates that individual analytes are not present in the waste, or that they are present but at such low concentrations that the appropriate regulatory levels could not possibly be exceeded, the procedure need not be run. If the total analysis results indicate that TCLP is not required, the decision to cease TCLP analysis should be remanded to the client.

1.8. If an analysis of any one of the liquid fractions of the procedure leachate indicates that a regulated compound is present at such a high concentration that, even after accounting for dilution from the other fractions of the leachate, the concentration would be equal to or above the regulatory level for that compound, then the waste is hazardous and it may not be necessary to analyze the remaining fractions of the leachate. However, the remaining analyses should not be terminated without the approval of the client.

1.9. Volatile organic analysis of the leachate obtained using a bottle extraction, normally used for extractable organics and metals, can be used to demonstrate that a waste is hazardous, but only the ZHE option can be used to demonstrate that the concentration of volatile organic compounds is below regulatory limits.

2. SUMMARY OF METHOD

2.1. For liquid wastes that contain less than 0.5% dry solid material, the waste, after filtration through 0.6 to 0.8 µm glass fiber filter, is defined as the TCLP leachate.

2.2. For wastes containing greater than or equal to 0.5% solids, the liquid, if any, is separated from the solids and stored for later analysis. The particle size of the remaining solid phase is reduced, if necessary. The solid phase is extracted with an amount of extraction fluid equal to 20 times the weight of the solid phase. For TCLP, the extraction fluid employed for extraction of non-volatile analytes is a function of the alkalinity of the solid phase of the waste. For SPLP, the extraction fluid employed is a function of the region of the country where the sample site is located if the sample is a soil. If the sample is a waste or wastewater the extraction fluid employed is a pH 4.2 solution. Two leachates may be generated: a) one for analysis of non-volatile constituents (semi-volatile organics, pesticides, herbicides and metals and/or b) one from a Zero Headspace Extractor (ZHE) for analysis of volatile organic constituents.

Following extraction, the liquid leachate is separated from the solid phase by filtration through a 0.6 to 0.8 µm fiber filter.

2.3. If compatible (i.e., multiple phases will not form on combination), the initial liquid phase of the waste is added to the liquid leachate and these are prepared and analyzed together. If incompatible, the liquids are analyzed separately and the results are mathematically combined to yield a volume-weighted average concentration.

3. DEFINITIONS

3.1. "Leachate" is used to refer to the TCLP solution generated from this procedure.

3.2. "Percent Wet Solids" is that fraction of a waste sample (as a percentage of the total sample) from which no liquid may be forced out by an applied pressure.

4. INTERFERENCES

4.1. Oily wastes may present unusual filtration and drying problems. As recommended by EPA (see Figure 3), oily wastes will be assumed to be 100% liquid and analysis for total concentrations of contaminants will be performed. This applies specifically to samples containing viscous non-aqueous liquids that would be difficult to filter.

4.2. Wastes containing free organic liquids (i.e., those with separable non-aqueous liquid phases) will be assumed to be 100% liquid and totals analysis will be performed to determine if the oil exceeds TCLP limits.

4.3. Solvents, reagents, glassware and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks as described in the Section 9.0 and the individual determinative SOPs.

4.4. Glassware and equipment contamination may result in analyte degradation. Soap residue on glassware and equipment may contribute to this. All glassware and equipment should be rinsed very carefully to avoid this problem.

4.5. Phthalates may be eliminated by proper glassware cleanup and by avoiding plastics. Only glass, Teflon or Type 316 stainless steel tumblers may be used for leachates to be analyzed for organics. Plastic tumblers may be used for leachates to be analyzed for the metals.

4.6. Overexposure of the sample to the environment will result in the loss of volatile components.

4.7. Potential interferences that may be encountered during analysis are discussed in the individual analytical methods.

5. SAFETY

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

5.2. Eye protection that satisfies ANSI Z87.1 (as per the Chemical Hygiene Plan), laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

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

5.3.1. Chemicals that have been classified as **carcinogens**, or **potential carcinogens**, under OSHA include:

Methylene chloride

5.3.2. Chemicals known to be **flammable** are:

Methanol

5.3.3. The following materials are known to be **corrosive**:

Hydrochloric acid, nitric acid, sulfuric acid, acetic acid, sodium hydroxide

The following materials are known to be **oxidizing agents**:

Nitric Acid.

5.4. Gas pressurized equipment is employed in this procedure. Be sure all valves and gauges are operating properly and that none of the equipment, especially tubing, is over-pressurized. CAUTION: Do not open equipment that has been pressurized until it has returned to ambient pressure.

5.5. A rotary agitation apparatus is used in this procedure. Certain samples may break the glass jars used in the procedure. For these samples, extra caution, including plastic or polyethylene overwraps of the glass jar, may be necessary.

5.6. Secure tumbler and extraction apparatus before starting rotary agitation apparatus.

5.7. During sample rotation, pressure may build up inside the bottle. Periodic venting of the bottle will relieve pressure.

5.8. Exposure to chemicals must be maintained as low as reasonably achievable, therefore, unless they are known to be non-hazardous, all samples must be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

5.9. The preparation of standards and reagents and glassware cleaning procedures that involve solvents such as methylene chloride will be conducted in a fume hood with the sash closed as far as the operation will permit.

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

5.11. Due to the potential for ignition and/or flammability, do not attempt to dry non-aqueous liquid samples in an oven.

6. EQUIPMENT AND SUPPLIES

6.1. Extraction vessels

6.1.1. For volatile analytes - zero-headspace extraction (ZHE) vessel, gas-pressure actuated, Millipore YT3009OHW or equivalent (see Figure 2).

6.1.2. For metals - either borosilicate glass jars (1/2 - 1 gallons, with Teflon lid inserts) or 1 L HDPE (Nalgene or equivalent) bottles may be used.

6.1.3. For non-volatile organics - only borosilicate glass may be used.

6.2. Vacuum filtration apparatus, capable of 0 - 50 psi and stainless steel pressure filtration apparatus (142 mm diameter), capable of 0 - 50 psi.

6.3. Borosilicate glass fiber filters, 0.6 - 0.8 µm (Whatman GF/F 14.2 cm, 0.7 µm or equivalent). When analyzing for metals, wash the filters with 1 N nitric acid and de-

ionized water prior to use. Glass fiber filters are fragile and should be handled with care.

6.4. Rotary agitation apparatus, multiple-vessel, Associated Design and Manufacturing Company 3740-6 or equivalent (see Figure 1). The apparatus must be capable of rotating the extraction vessel in an end-over-end fashion at 30 ± 2 rpm.

6.5. ZHE Extract Collection Devices are used to collect the initial liquid phase and the final extract of the waste from the ZHE device, either of the following may be used:

6.5.1. Gas-tight syringes, 100 mL capacity, Hamilton 0158330 or equivalent, or

6.5.2. Tedlar bags

6.6. Top loading balance, capable of 0 - 4000 ± 0.01g (all measurements are to be within ± 0.1 grams).

6.7. pH meter and probe capable of reading to the nearest 0.01 unit, and with automatic temperature compensation.

6.8. pH probes.

6.9. Magnetic stirrer/hotplate and stirring bars.

6.10. VOA vials, 20 mL, with caps and septa.

6.11. Glass jars, 1/2 - 1 gallon, with Teflon lid-inserts.

6.12. Nalgene plastic bottles, 1 liter.

6.13. Miscellaneous laboratory glassware and equipment.

7. REAGENTS AND STANDARDS

7.1. Reagent water for non-volatile constituents must be produced by a Millipore DI system or equivalent. For volatile constituents, water must be passed through an activated carbon filter bed (Milli-Q or tap water passed through activated carbon). Reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks.

7.2. Hydrochloric acid, 1 N: Carefully add 83 mL concentrated reagent grade HCl to 800 mL reagent water, cool and dilute to 1 liter with reagent water. Cap and shake to mix well.

7.3. Nitric acid, 1 N: Carefully add 64 mL concentrated reagent grade HNO_3 to 800 mL of reagent water, cool and dilute to 1 liter with reagent water. Cap and shake to mix well.

7.4. Sodium hydroxide, 1 N: Carefully add 40 g reagent grade NaOH pellets to 800 mL reagent water, stir until the pellets are completely dissolved, cool and dilute to 1 liter with reagent water.

CAUTION: Heat is generated during this process.

7.5. Acetic acid, glacial: concentrated, reagent grade liquid (HOAc).

7.6. pH calibration solutions: buffered to a pH of 4, 7, and 10. Commercially available. Fresh buffer solution must be used each day of analysis.

7.7. TCLP Leaching Fluids

7.7.1. General Comments

7.7.1.1. The pH of both solutions listed below should be monitored daily and the pH probes are to be calibrated prior to use.

7.7.1.2. The leaching fluids MUST be prepared correctly. If the desired pH range is not achieved and maintained, the TCLP may yield erroneous results due to improper leaching. If the pH is not within the specifications, the fluid must be discarded and fresh extraction fluid prepared.

7.7.1.3. Additional volumes of extraction fluids listed above may be prepared by multiplying the amounts of acetic acid and NaOH by the number of liters of extraction fluid required.

7.7.2. TCLP Fluid #1: Carefully add 5.7 mL glacial acetic acid and 64.3 mL of 1 N NaOH to 500 mL reagent water in a 1 liter volumetric flask. Dilute to a final volume of 1 L with reagent water, cap and shake to mix well. When correctly prepared, the pH of this solution is 4.93 ± 0.05.

7.7.3. TCLP Fluid #2: Carefully add 5.7 mL glacial acetic acid to 500 mL reagent water in a 1 liter volumetric flask. Dilute to a final volume of 1 L with reagent water, cap and shake to mix well. When correctly prepared, the pH of this solution is 2.88 ± 0.05.

7.8. Nitric acid, 50% solution: Slowly and carefully add 500 mL concentrated HNO_3 to 500 mL reagent water. Cap and shake to mix well.

7.9. Sulfuric acid / nitric acid (60/40 weight percent mixture) H_2SO_4/HNO_3. Cautiously mix 60 g of concentrated sulfuric acid with 40 g of concentrated nitric acid.

7.10. SPLP Leaching fluids

7.10.1. SPLP solutions are unbuffered and exact pH may not be attained. The pH of TCLP and SPLP fluids should be checked prior to use. If not within specifications, the fluid should be discarded and fresh fluid prepared.

7.10.2. SPLP fluid #1: Add 60/40 weight percent mixture of sulfuric and nitric acids to reagent water until the pH is 4.20 ± 0.05 This fluid is used for soils from a site that is east of the Mississippi River and for wastes and wastewaters.

7.10.3. SPLP fluid #2: Add 60/40 weight percent mixture of sulfuric and nitric acids to reagent water until the pH is 5.00 ± 0.05. This fluid is used for soils from a site that is west of the Mississippi River.

7.10.4. SPLP fluid #3: This fluid is reagent water and is used for leaching of volatiles. Additionally, any cyanide-containing waste or soil is leached with fluid #3 because leaching of cyanide containing samples under acidic conditions may result in the formation of hydrogen cyanide gas.

7.11. Methanol and methylene chloride - used to aid in cleaning oil contaminated equipment.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Samples being analyzed for non-volatile organic compounds should be collected and stored in glass containers with Teflon lid liners. Chemical preservatives shall NOT be added UNTIL AFTER leachate generation.

8.2. Samples being analyzed for metals only can be collected in either glass or polyethylene containers.

8.3. When the waste is to be evaluated for volatile analytes, care should be taken to minimize the loss of volatiles. Samples shall be collected and stored in a manner

intended to prevent the loss of volatile analytes (e.g., samples should be collected in Teflon lined septum capped vials with minimal headspace and stored at 4 ± 2 ^{o}C). Samples should be opened only immediately prior to extraction.

8.4. Samples should be refrigerated to 4 ± 2 ^{o}C unless refrigeration results in irreversible physical changes to the waste. If precipitation occurs, the entire sample (including precipitate) should be extracted.

8.5. The minimum TCLP sample collection size is determined by the physical state or states of the waste and the analytes of concern. The amount of waste required varies with the percent solids. The lower the percent solids, the more waste will be required for preliminary and final testing. For aqueous samples containing between 0.5 and 10% solids, several kilograms of sample are required to complete the analyses. The general minimal requirements when the samples are 100% solids include: 1 - 32 oz jar for semi-volatile organic analysis and metals, and 1 - 4 oz jar for volatile organic analysis. Low density sample materials, such as rags or vegetation, will require larger volumes of sample. For liquid samples (less than 50% solids), minimum requirements are 2 - 32 oz jars for semi-volatile organic analysis and metals, and 2 - 8 oz jars for volatile organic analysis. If volatile organic analysis is the only requested parameter, 2 separate jars are required. If matrix spike or duplicate control samples are requested, additional sample volume is required. If sufficient sample volumes were not received, analyses cannot be started and the client should be notified as soon as possible.

8.6. TCLP leachates should be prepared for analysis and analyzed as soon as possible following extraction. Leachates or portions of leachates for metallic analyte determinations must be acidified with nitric acid to a pH less than 2, unless precipitation occurs. If precipitation occurs upon addition of nitric acid to a small aliquot of the leachate, then the remaining portion of the leachate shall not be acidified and the leachate shall be analyzed as soon as possible. All other leachates should be stored under refrigeration (4 ± 2 °C) until analyzed. ZHE leachates must be stored in VOA vials filled to eliminate all headspace.

8.7. Samples are subject to appropriate treatment within the following time periods:

Table 1 - Holding Times (days)

Parameter	Collection to TCLP Leach	TCLP Leach to Preparation	Preparation to Analysis	Total Elapsed Time
Volatiles:	14	N/A	14	28
Semi-volatiles:	14	7	40	61
Mercury:	28	N/A	28	56
Other Metals:	180	N/A	180	360

NOTE: The initial holding time is measured from date of collection to date extraction started, and subsequent holding times are measured from the date extraction starts**.** If sample holding times are exceeded, the values obtained will be considered minimal concentrations. Exceeding holding times is not acceptable in establishing that a waste does not exceed the regulatory level. Exceeding the holding time will not invalidate characterization if the waste exceeds the regulatory limit.

9. QUALITY CONTROL

9.1. Quality Control Batch (QC Batch) - QA-003 defines a QC Batch as a set of up to 20 field samples of similar matrix that behave similarly and are processed using the same procedures, reagents and standards within the same time period. The same lot of reagents must be used within a batch. A minimum of one TCLP extraction blank (Method Blank), one Laboratory Control Sample (LCS), one Matrix Spike (MS), and one Matrix Spike Duplicate (MSD) will be prepared with each TCLP leachate batch.

9.2. Batching Samples - Groups of samples with visibly different bulk matrices (e.g., petroleum sludge and soil samples) must be batched separately for QC testing purposes.

9.3. TCLP Extraction Blanks - A minimum of one blank (using the same extraction fluid as used for the samples) must be prepared and analyzed for every batch of samples extracted in a particular vessel type. The blanks are generated in the same way as the samples (i.e., blanks will be tumbled and filtered with the samples). Extraction vessels will be uniquely numbered. Each time a new batch is set up the blank should be rotated sequentially to the next vessel to ensure all vessels are periodically checked. Consult the STL QC Program and the individual analysis SOPs for blank acceptance criteria.

9.4. 9.4. Laboratory Control Sample (LCS) - A LCS is required with each batch of 20 or fewer samples. The LCS shall be generated after a batch of TCLP leachates have been generated (i.e., at the time of the preparative digestion or extraction) by spiking an

□

aliquot of the appropriate extraction fluid used for that batch. Consult the individual analysis SOPs for additional LCS guidance (i.e., spike amounts, spike levels, recovery criteria, etc.).

9.5. Matrix Spike (MS/MSD) - Matrix spikes are used to monitor the performance of the analytical methods on the matrix and to assess the presence of interferences. A MS/MSD pair are required with each batch of 20 or fewer samples.

9.5.1. Matrix spikes are to be added after filtration of the TCLP leachate. Spikes are not to be added prior to the TCLP leaching. For metals, matrix spikes are to be added before preservation with nitric acid.

9.5.2. The use of internal calibration or alternate methods may be needed when the recovery of the matrix spike is below the expected performance (see Section 9.6.2).

9.5.3. Consult the individual analysis SOPs for additional guidance on spike compounds and levels.

9.6. Corrective Actions

9.6.1. Consult the STL QC Program and individual analysis SOPs for corrective action for blanks and LCS

9.6.2. Method of Standard Additions (MSA) shall be used for metals if all of the following conditions are met:

- Recovery of the analyte in matrix spike is not at least 50%,
- the concentration of the analyte does not exceed the regulatory level, and
- the concentration of the analyte measured in the sample is within 20% of the appropriate regulatory level.

If the matrix spike recovery is 5% or less due to dilution or matrix interference, contact the project manager and client for guidance. The client should also be contacted prior to initiation of any MSA steps. Refer to the individual analysis SOPs for details on how to perform MSA analysis.

10. CALIBRATION AND STANDARDIZATION

10.1. Refer to appropriate analysis SOPs.

11. PROCEDURE

11.1. GENERAL COMMENTS

11.1.1. One-time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented on a Nonconformance Memo kept in the project file and described in the final report. The variation must be approved by a project manager, Technical Specialist and QA Manager. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

11.2. PRELIMINARY SAMPLE EVALUATIONS (Refer to Flow Chart #1, Appendix D)

11.2.1. Preliminary TCLP evaluations (percent solids, particle size, selection of extraction fluid, and fluid/leachate compatibility) are required to be done using a minimum of a 100 gram aliquot of waste. This aliquot may also undergo the actual TCLP or SPLP extraction for Non-volatiles ONLY IF it has NOT been oven dried. If the solid portion is oven dried, a separate aliquot must be used for the actual leaching procedure.

11.2.2. Consult the holding times for the appropriate tests (Section 8.7) and prioritize extractions such that holding times are not exceeded.

11.2.3. Determine the total volume of TCLP leachate (solid phase leachate + liquid filtrate) that needs to be generated for analysis according to the following:

Table 2. Minimum Required Leachate Volume

Analysis	Required Volume (mL)
Volatiles	3 x 20
Semi-volatiles	400
Pesticides	200
Herbicides	200
Metals	300

11.2.3.1. SPLP - similar volumes are required for volatiles and metals. If semivolatiles, pesticides or herbicides are required, a full 1 L volume must be prepared for each test requested.

11.2.3.2. For TCLP and SPLP samples used for matrix spike and matrix spike duplicate analysis, three times the listed volumes are required.

11.2.4. **Sample Description** (enter data on Worksheet 1)

11.2.4.1. Record the number of phases observed in the sample. It is common that when more than one container of multi-phasic materials is received from the field, each container will show different amounts of each phase.

11.2.4.1.1. If the sample has multiple phases and is received in more than 1 bottle then the contents of each bottle should be combined in a single larger container prior to processing the sample further. If this is not possible, then the alternate procedure described in the following section should be used.

11.2.4.1.2. Properly record the relative amounts of each phase by measuring the depth of the layers in each container after the contents have been allowed to settle. Determine the combined volume of each phase for all containers. Then mark the phase composition on a single container, mix thoroughly to obtain a representative subsample, and accurately measure the phase composition according to the following procedure. The two sets of values (combined volumes per phase and phase composition for one container) are used to determine the correct volume/mass adjustments on the final result. This procedure is not appropriate if testing will be done for volatile organic compounds.

11.2.4.2. Solid - record the visible presence of a solid material heavier than water. If the sample contains more than one solid phase (e.g., wood and sediment mixed with water), attach additional documentation to Worksheet 1, line A1.

11.2.4.3. Liquid - record the number of liquid phases observed in the sample according to apparent density. It may be impossible to distinguish apparent density if only one liquid phase is observed and there is no indication on the COC form. If this is the case, record it as aqueous material and let the subsequent analytical record show if the liquid is organic.

11.2.5. **Percent Solid Phase** (enter data on Worksheet No. 1)

11.2.5.1. Percent Solids and ZHE Extractions - The ZHE filtration apparatus cannot accurately determine percent solids less than 5%. If an extraction is to be performed solely for volatile organic compounds and the percent solids concentration is apparently greater than 5%, proceed to Section 11.4 (Procedure: ZHE Extraction Procedure, Volatile Constituents). Otherwise, continue with the steps in this section. The aliquot of sample used here cannot be used again for the ZHE extraction.

11.2.5.2. Determine Type of Filtration Apparatus Needed

11.2.5.2.1. If the waste will obviously yield no free liquid when subjected to pressure filtration (i.e., it is 100% solid), then proceed to Section 11.2.6 (Particle-size Reduction).

11.2.5.2.2. If the sample is mostly a non-viscous liquid (water or non-viscous organic liquid) of low solids content (<10%) or a highly granular, liquid containing waste vacuum filtration may be used.

11.2.5.2.3. If the sample is viscous (sludge or has high solids content), use pressure filtration.

11.2.5.3. Weight of filter - Measure and record this value before loading the filter into the filter holder (Worksheet 1, line B1).

11.2.5.4. Weight of subsample and filtrate for percent solids measurement

11.2.5.4.1. Assemble the filtration apparatus (use blunt forceps to handle the 0.6 to 0.8 µm filter membrane).

11.2.5.4.2. Homogenize the waste, transfer a minimum of a 100 g subsample to the weighing vessel. Measure and record the gross weight (Worksheet 1, line B2a).

11.2.5.4.3. Measure and record the tare weight of the filtration vessel (Worksheet 1, line B3b).

11.2.5.4.4. Transfer the sample to the filtration device attempting to spread the waste sample evenly over the surface of the filter. Measure and record the tare weight of the empty weighing vessel and any residual sample (Worksheet 1, line B2b).

11.2.5.4.5. Calculate and record the net weight of sample used for testing (Worksheet 1, line B2c).

11.2.5.5. Filtration for percent solids

11.2.5.5.1. Slowly apply gentle pressure or vacuum of 10 psi to the filtration apparatus. Allow the sample to filter until no SIGNIFICANT additional liquid has passed through the filter during a 2 minute period.

11.2.5.5.2. Repeat previous step by increasing the pressure in 10 psi increments until a maximum of 50 psi is reached. Stop the filtration when no additional filtrate is generated within a 2 minute period.

Note: Some samples will contain liquid material that does not filter (e.g., oil). Do not attempt to filter the sample again by exchanging filters. Viscous oils or any wastes which does not pass through the filter is classified as a solid.

11.2.5.5.3. Remove the filtrate collection vessel, weigh and record the gross weight (Worksheet 1, line B3a).

11.2.5.5.4. Calculate and record the net weight of filtrate (Worksheet 1, line B3c). This result will be used in the percent solids calculation.

11.2.5.5.5. Pour the filtrate into a graduated cylinder. Measure and record the volume of the aqueous phase (Worksheet 1, line B7). Measure and record the volume of any organic phase (Worksheet 1, line B8). If more than one organic phase is observed, enter "see below" and provide a description at the bottom of Worksheet 1. These results will be used in the final sample calculations (Worksheets 5 & 6).

11.2.5.5.6. Retain the filtrate for use in Section 11.2.8 (Determination of Filtrate/Extraction Fluid Compatibility), and for possible recombination with the filtrate obtained in Section 11.3.

11.2.5.6. Percent of Wet Solids

11.2.5.6.1. Calculate the total weight of wet solids using Equation 0 on Worksheet 1 and record the result on line B4.

11.2.5.6.2. Calculate the weight percent of wet solids using Equation 1 on Worksheet 1 and record the result on line B5.

11.2.5.6.3. If the percent wet solids result is ≥ 0.5% and < 5.0%, and it is noticed that a small amount of the aqueous filtrate is entrained in the wetting of the filter, proceed to Section 11.2.5.7 to complete the percent solids measurement on a dry-weight basis.

Note: If obviously oily (non-aqueous) material is entrained on the filter, do not dry the filter; proceed to Section 11.2.6 (Particle-Size Reduction).

11.2.5.6.4. If the percent wet solids result is greater than 5.0%, proceed to Section 11.2.6 (Particle-Size Reduction) and mark "≥0.5%" on Worksheet 1, line B6c.

11.2.5.6.5. If the percent wet solids result is less than 0.5%, discard the solid phase. No leaching will be necessary; the filtrate is equivalent to the final leachate.

11.2.5.7. Weight percent of dry solids (skip this step for oily samples).

Note: These steps are required only if it is noticed that a small amount of the filtrate is entrained in wetting of the filter and the percent wet solids content is ≥ 0.5% and < 5.0 %.

11.2.5.7.1. Remove the filter with the wet solids from the filtration apparatus.

11.2.5.7.2. Dry the filter and solid phase at 100 ± 20 ° C.

11.2.5.7.3. Remove the filter from the oven and allow to cool in a desiccator.

11.2.5.7.4. Weigh and record the gross dry weight (Worksheet 1, line B6a).

11.2.5.7.5. Repeat the drying step. Weigh and record the second gross dry weight (Worksheet 1, line B6b). If the two weightings do not agree within 1%, perform additional drying and weighing until successive weighings agree within 1%.

11.2.5.7.6. Calculate the weight percent of dry solids using Equation 2 on Worksheet 1 and record the result on line B6c.

11.2.5.7.7. If the dry solids result is ≥ 0.5% and the sample will be extracted for non-volatile constituents, proceed to Section 11.2.6 (Particle Size Reduction) using a fresh wet portion of waste.

11.2.5.7.8. If the percent solids result is less than 0.5%, discard the solid phase. No leaching will be necessary; the filtrate is the TCLP leachate. Proceed to Section 11.2.8 (Determination of Filtrate/Leachate Compatibility) to determine whether or not the material is a non-aqueous, immiscible liquid.

11.2.6. **Particle-size Reduction for Fluid Selection** (enter data on Worksheet 2)

11.2.6.1. The subsample used for fluid selection must consist of particles less than 1 mm in diameter (versus the less than 1 cm requirement

for the material used for the actual extraction). The method requires a smaller particle size to partially compensate for the shorter duration of contact time with the leachate solution as compared to the full extraction. Inappropriate use of coarser materials could result in the selection of the wrong fluid type.

11.2.6.2. Surface area exclusion - size reduction is not required if the sample surface area is greater than or equal to 3.1 cm^2 per gram. Enter "No" on Worksheet 2, line C1.

11.2.6.3. If the sample contains particles greater than 1 mm in diameter, crush, cut, or grind the solids to the required size. Enter "Yes" on Worksheet 2, line C1.

11.2.6.4. Consult your supervisor or manager when dealing with unusual sample matrices (e.g., wood, cloth, metal, brick).

11.2.7. **Determination of Appropriate Extraction Fluid** (Worksheet 2)

11.2.7.1. If the solid content is greater than or equal to 0.5%, and if the sample is being analyzed for metals or nonvolatile organic compounds, the type of leaching solution must be determined.

11.2.7.2. Follow times, temperature, and particle size specified in this section as closely as possible. If reaction time between the acid solution and solid waste is too short or too long, the procedure may produce false pH readings.

11.2.7.3. For SPLP, refer to Section 7.10 for fluid selection. Matrix type must be specified by the client. Check special instructions or see the project manager, then put a check mark by the fluid type selected (Worksheet 2, D).

11.2.7.4. The TCLP leaching fluid for all volatiles is Fluid #1.

11.2.7.5. For TCLP leach fluid determination for non-volatile analytes, continue with the following steps.

11.2.7.6. Calibrate the pH meter with fresh buffer solution in accordance with the pH SOP.

11.2.7.7. Weigh out a 5.0 ± 0.1 g subsample (less than 1 mm particle size) of the solid phase into a 250-mL beaker, and enter a "✔" on

Worksheet 2, line C2. If 5.0 grams not used, enter the actual weight on line C2.

11.2.7.8. Add 96.5 ± 1.0 mL of reagent water, cover with a watchglass, and stir for 5 minutes on a stirrer, and enter a "✔" on Worksheet 2, line C3. If a different volume used, enter the actual volume on line C3.

11.2.7.9. Measure and record the sample pH (Worksheet 2, line C4).

Note: To avoid damaging the pH probe when organic liquid is present, use narrow range pH indicator paper.

11.2.7.10. If the pH is less than or equal to 5.0, use Fluid #1 and proceed to Section 11.2.8 (Fluid Compatibility).

11.2.7.11. If the fluid pH is greater than 5.0, add 3.5 mL 1 N HCl, cover with a watchglass. Slurry the sample briefly then heat at 50 ^{o}C for 10 minutes. Enter a "✔" on Worksheet 2, line C5 and C6).

Note: The heating cycle is a critical step. If the solid waste does not remain in contact with the acidic solution under specified time and temperature conditions, an erroneous pH may be measured.

11.2.7.12. Cool to room temperature.

11.2.7.13. Measure and record the pH immediately after the sample has reached room temperature (Worksheet 2, line C7).

11.2.7.13.1. If the pH is less than or equal to 5.0, use Fluid #1. Enter a "✔" on Worksheet 2, line D1.

11.2.7.13.2. If the pH is greater than 5.0, use Fluid #2. Enter a "✔" on Worksheet 2, line D2.

11.2.8. **Determination of Filtrate/Extraction Fluid Compatibility** (skip this step for SPLP extractions)

11.2.8.1. Place 5 mL of the appropriate leaching fluid (determined in the previous step) into a 20-25 mL vial.

Note: Use fluid type # 1 if simply testing the filtrate for a sample with less than 0.5% solids.

11.2.8.2. Add 5 mL of the initial filtrate, cap and shake.

11.2.8.3. If the phases are miscible, the initial filtrate and solid phase leachate will be physically recombined upon completion of the leachate generation. Enter a "✔" on Worksheet 2, line D3 for TCLP, or on line D1 for SPLP.

11.2.8.4. If the phases are NOT miscible, enter "No" on Worksheet 2, line D3. The initial filtrate and the solid phase leachate will be prepared and analyzed separately and the results mathematically combined (see Section 12.1.4).

11.2.9. For samples requiring analysis for semi-volatile organics, pesticides, herbicides or metals proceed to Section 11.3.

11.2.10. For samples requiring analysis for volatile organics (ZHE), proceed to Section 11.4.

11.3. **BOTTLE EXTRACTION PROCEDURE: NON-VOLATILE CONSTITUENTS: SEMI-VOLATILES, PESTICIDES, HERBICIDES, METALS** (Refer to Flow Chart #2, Appendix D)

11.3.1. All masses should be recorded to the nearest 0.1 g.

11.3.2. Determine the minimum amount of solid phase necessary to provide sufficient leachate. The amount of leachate required is given in section 11.2.3. The minimum amount of solid phase in grams is the volume of leachate required divided by 20.

1.3.3. The aliquot used in the Preliminary Evaluation MAY be used for this procedure ONLY if it was not oven dried AND sufficient volume of leachate would be generated. If the sample is 100% solid or if the preliminary aliquot was not oven dried proceed directly to Section 11.3.7 (Particle Size Reduction). If the Preliminary Evaluation aliquot was oven dried then, using a fresh aliquot of sample, continue as described in Sections 11.3.3 through 11.3.6.

1.3.4. Examine the sample and determine the type of filtration to employ per Section 11.2.5.2.

1.3.5. Repeat the steps outlined in Sections 11.2.5.3 through 11.2.5.5.3. Use a weight of sample that will generate sufficient solid phase (See section 11.3.2). The minimum sample weight (before filtration) is 100 g.

1.3.6. Determine and record the volume (mass) of the initial filtrate. Cover with aluminum foil and retain for use as defined in Section 11.3.18.

1.3.7. Determine and record the "solid" phase mass by subtracting the mass of the liquid filtrate from the mass of the subsample.

1.3.8. Evaluate the solid portion of the waste for particle size. If it contains particles greater than 1 cm in size, prepare the solid portion of the waste for leaching by crushing, cutting, or grinding such that all particles are less than 1 cm in size (i.e., capable of passing through a 9.5 mm, 0.375 inch, standard sieve). Size reduction is not required if the sample surface area is greater than or equal to 3.1 cm^2 per gram. If particle size reduction was required, record this on Worksheet 3, line E1.

1.3.8.1. Consult your supervisor or manager when dealing with unusual sample matrices (e.g., wood, cloth, metal, brick). Scissors or shears may be used to cut cloth, plastic or sheet metal. Saws may be used for wood or solid metal. Bricks, rocks, or other solids amenable to grinding should be subcontracted out for particle size reduction (Contact PA or PM). Note that size reduction to fine powder is not appropriate, and could invalidate results. If necessary, consult client for guidance.

1.3.9. Quantitatively transfer the solid sample from the filtering (11.3.6) or particle size reduction step (11.3.7) into an appropriate extractor bottle. (Plastic bottles can be used if metals only are to be analyzed, glass must be used for organics.) Include the filter. If filtering and/or particle size reduction were not necessary, weigh a minimum 100 g sample and transfer into the extractor bottle.

1.3.10. Determine the weight of extraction fluid to be added.

$$\text{Weight of extraction fluid} = \frac{20 \times (\%\text{solids}) \times (\text{weight of waste filtered})}{100}$$

1.3.11. **Slowly** add the appropriate mass of the appropriate leaching fluid (e.g., 20 g of sample would require 400 g of leaching fluid). Record the weight of the solid sample used for the extraction on Worksheet 3, line E2 and the amount of extraction fluid added on line F1.

1.3.12. Ensure any effervescence has stopped before capping the bottle tightly. Secure in a rotary agitator and rotate end-over-end at 28-32 rpm for 16-20 hours. The temperature of the room should be 23 ± 2°C. The room temperature and time should be checked at both the start and end of the extraction and recorded on Worksheet 3, lines G1 through G3.

NOTE: As agitation continues, pressure may build up within the bottle for some types of wastes. To relieve excessive pressure, the bottle may be removed and opened periodically in a properly vented hood to relieve any built-up pressure.

1.3.13. Remove the bottle and filter the sample using vacuum or pressure filtration by filtering through a new glass fiber filter as discussed in Sections 11.2.5.5.1 - 11.2.5.5.2. For final filtration of the TCLP leachate, the glass fiber filter may be changed, if necessary, to facilitate filtration. Filters must be acid washed if metals are to be determined (see Section 6.3). The entire sample need not be filtered; however, sufficient volume should be generated to support the required analyses. Record the date and time the filtration is completed on Worksheet 3, Line G4.

1.3.14. If the waste contained no initial filtrate, this solution from 11.3.12 is defined as the TCLP leachate.

1.3.15. If the waste did yield an initial filtrate, consult the worksheet for initial filtrate/leachate compatibility. If they are compatible, they are to be combined in the correct proportions (see Section 12.1.4) and mixed well. This combined solution is defined as the TCLP leachate.

1.3.16. If the individual phases are NOT compatible, they are to be prepared and analyzed separately and the results combined mathematically. See Section 12.1.5.

1.3.17. Measure and record the pH of the TCLP leachate on Worksheet 3, Line 5. (Do not attempt to measure the pH of oily samples as the probe may be rendered inoperable.)

1.3.18. Prepare subsamples for metals for MS/MSD quality control testing using the appropriate TCLP spiking solution (do not spike for organics). Refer to the appropriate determinative SOPs for further guidance on the spike components, levels and action criteria.

1.3.19. Immediately preserve the leachate as follows:

Metals	pH < 2 w/50% HNO_3 for non-oils (do not acidify oils)
All others	Refrigerate to 4 ± 2 ^oC

Note: Refer to Section 8.6 if precipitation occurs upon preservation.

1.3.20. Label each sample with the appropriate information and submit to the appropriate analytical groups for prep and analysis with copies of the TCLP preparation worksheets.

1.4. ZHE EXTRACTION PROCEDURE: VOLATILE CONSTITUENTS (Refer to Flow Chart #3, Appendix D)

1.4.1. Use the ZHE device to obtain a TCLP leachate for analysis of volatile compounds only. Leachate resulting from the use of the ZHE shall NOT be used to evaluate the mobility of non-volatile analytes (e.g., metals, pesticides, etc...).

1.4.2. Due to some shortcomings of the method, losses of volatile compounds may occur. Extra care should be observed during the ZHE procedure to ensure that such losses are minimized. Charge the ZHE with sample only once and do not open the device until the final extract has been collected. Do not allow the waste, the initial liquid phase or the extract to be exposed to the atmosphere any longer than necessary.

1.4.3. If the TCLP extraction is for volatile components only, refer to Section 11.2.5.1 before proceeding.

1.4.4. All masses should be recorded to the nearest 0.1 g.

1.4.5. Assemble the ZHE apparatus. Test for leakage by closing all valves except the gas inlet/outlet valve and pressurizing to 50 psi. Allow to stand for 15 minutes and check the pressure on the built-in gauge to make sure it is not leaking. If the pressure is NOT 50 psi, consult your supervisor.

1.4.6. Adjust the ZHE piston in the ZHE body to the appropriate height (slightly moisten the O-rings with leaching fluid if necessary).

1.4.7. Consult the worksheet and examine the sample. If the sample appears to be different from the preliminary information found on the worksheet, consult your supervisor.

1.4.8. If the preliminary evaluations indicated the need for particle size reduction, homogenize the waste, weigh out a sufficient size subsample and prepare for

leaching by crushing, cutting, or grinding such that all particles are less than 1 cm in size as measured with a ruler (Do NOT sieve the sample). Size reduction is not required if the sample surface area is greater than or equal to 3.1 cm^2 per gram If particle size reduction was required record this on Worksheet 4, Line H1.

Note: To minimize loss of volatiles, samples for volatiles that require particle size reduction should be kept in sample storage (at 4 ºC) until immediately before size reduction. Aggressive reduction which would generate heat should be avoided and exposure of the waste to the atmosphere should be avoided to the extent possible. Size reduction to a fine powder is not appropriate. Also see Section 11.3.11.

1.4.8.1. Consult your supervisor or manager when dealing with unusual sample matrices (e.g., wood, cloth, metal, brick). Scissors or shears may be used to cut cloth, plastic or sheet metal. Saws may be used for wood or solid metal. Bricks, rocks, or other solids amenable to grinding should be subcontracted out for particle size reduction (Contact PA or PM).

1.4.9. Place the ZHE apparatus on the balance and tare the balance.

1.4.10. Determine the appropriate size subsample to weigh using the percent solids information from Section 11.2.5 and record the weight used on Worksheet 4, Line H2.

1.4.10.1. For wastes that are 100% solids, a 25 g sample is used.

1.4.10.2. For wastes containing < 0.5% solids the liquid portion of the waste, after filtration, is defined as the TCLP leachate. Filter enough of the sample to support all of the volatile analyses required.

1.4.10.3. For wastes containing ≥ 0.5% and < 5.0% solids, a 500 g subsample of waste is recommended.

1.4.10.4. If the sample has ≥ 5.0% solids, the appropriate sample size should be determined using the equation in Section 12.1.2.

Note: For wastes containing greater than 0.5% wet or dry solids (Section 11.2.5), the “solids” value from the ZHE filtration process may be used to determine the volume of fluid to load into the ZHE. This approach is recommended since the solids value from Section 11.2.5 may differ from the

filtration solids due to sample variability or differences in the filtration apparatus.

1.4.11. Homogenize and transfer an appropriate size subsample of the waste into the ZHE and record the mass on Worksheet 4, Line I1.

1.4.12. Carefully place the glass fiber filter between the support screens and secure to the ZHE. Tighten all the fittings.

1.4.13. Place the ZHE in a vertical position; open both the gas AND liquid inlet/outlet valves. Attach a gas line to the gas inlet/outlet valve.

1.4.14. If the waste is 100% solid, slowly increase the pressure to a maximum of 50 psi to force out as much headspace as possible and proceed to Section 11.4.18.

1.4.15. If the waste is < 100% solids, carefully apply gentle pressure of 10 psi (or more, if necessary) to force all headspace slowly out of the ZHE. At the FIRST appearance of liquid from the liquid inlet/outlet valve, quickly close the valve and discontinue gas pressure.

1.4.16. Assemble a syringe and place the plunger in all the way. Adjust the tension on the plunger to provide slight drag. Attach the pre-weighed syringe or Tedlar bag to the liquid inlet/outlet valve and open the valve. Record the tare weight of the collection device on Worksheet 4, Line 3b.

1.4.17. Carefully apply gas pressure of no more than 10 psi to force out the liquid phase. Allow the sample to filter until no SIGNIFICANT additional filtrate has passed in a 2 minute period.

Note: If the capacity of the syringe is reached, close the liquid inlet/outlet valve, discontinue gas pressure, remove the syringe and return to Section 11.4.15.

1.4.18. Repeat previous step increasing the pressure in 10 PSI increments until 50 psi is reached and no significant liquid has passed in a 2 minute period. Remove the collection device and record the total weight of the collection device with filtrate on Worksheet 4, Line 3a. Close the valve and discontinue gas pressure. Transfer the filtrate to VOA vials and label appropriately. Calculate the weight of filtrate collected and record on Worksheet 4, Line I3c.

Notes: If the original waste contained less than 0.5% solids (Section 11.2.5), this filtrate is defined as the TCLP leachate and you may

proceed to Section 11.4.28. Otherwise, save the vials by storing at 4 C under minimal headspace conditions, for recombination as in Section 11.4.27.

The material remaining in the ZHE is defined to be the "solid" phase. Calculate the weight of the solid phase using Equation 4.

1.4.19. Based on the information from Sections 11.2.5 and 11.4.11 and using the formula in 12.1.3, determine the weight of fluid to load into the ZHE on the "solid" phase. The ZHE device has approximately a 500-mL capacity. Based on the need to add an amount of extraction fluid equal to 20 times the mass of the "solid" phase, the ZHE can therefore accommodate a maximum of 25 grams of "solid".

Note: The TCLP ZHE prep uses only TCLP fluid #1; the SPLP ZHE prep uses only SPLP fluid #1.

1.4.20. Load the fluid transfer reservoir with an excess of Fluid #1 and preflush the transfer line to eliminate air pockets. Be sure the required volume remains.

1.4.21. Attach the transfer line to the liquid inlet/outlet valve and open the valve. Carefully pump the required volume into the ZHE and close the valve. Disconnect the transfer line.

1.4.22. Check the ZHE to make sure all the valves are closed and manually rotate the ZHE (end-over-end) 2 or 3 times. Reposition the ZHE in the vertical position.

1.4.23. Pressurize the ZHE to 5-10 psi. Allow to stand for 10 minutes, and then recheck the pressure. If the ZHE appears to be leaking, follow the corrective action protocols recommended by the manufacturer and repeat the analysis.

1.4.24. Slowly open the liquid inlet/outlet valve to bleed out any headspace that may have been introduced during the introduction of the Fluid. Upon the first sign of liquid from the valve, close the valve.

1.4.25. Repressurize the ZHE to 5-10 psi and place in the rotary agitator. Rotate at 28-32 rpm for 16-20 hours. Room temperature should be 23 ± 2 °C. The room temperature and time should be checked at both the start and end of the extraction and recorded on Worksheet 4, lines J1, J3 and J4.

1.4.26. Confirm that the pressure of 5-10 psi was maintained throughout the leaching. If it was NOT maintained, return to Section 11.4.1 and repeat the leachate with a new aliquot of sample.

1.4.27. Attach a syringe or Tedlar bag and open the liquid inlet/outlet valve to collect the aqueous leachate and proceed as outlined in 11.4.19 - 11.4.20. Record the volume/mass of the leachate and any oil phase on Worksheet 4, Lines J7 and J7a. Record the date and time the filtration is completed on Worksheet 4, Line J6.

Notes: If the waste contained an initial liquid phase, the liquid may be filtered directly into the same collection device holding the initial liquid phase of the waste.

A separate filtrate collection container must be used if combination would create multiple phases or there is not enough volume left within the filtrate collection container.

1.4.28. If the waste contained an initial filtrate (Section 11.4.18) that is miscible with the solid phase leachate (as determined in Section 11.2.8), the solid phase leachate and the initial filtrate are directly recombined in the correct proportions (see Section 12.1.4). If the individual phases are NOT compatible, they are to be collected, prepped and analyzed separately.

Note: Chill the filtrate and receiving vessels before recombining.

1.4.29. Following collection, store the TCLP leachate in 3 20-mL VOA vials with minimal headspace at 4 ± 2 ^{o}C and prepare for analysis as soon as possible using the appropriate organic extraction procedure (see Section 16.3).

1.4.30. If the individual phases are analyzed separately, combine the results mathematically by using the recombination calculation in Section 12.1.5.

DATA ANALYSIS AND CALCULATIONS

12.1. Calculations

12.1.1. Calculation of Percent Wet Solids:

$$Percent\ \ Wet\ Solids = 100\left(\frac{Mass,"solid"\ phase}{Mass, initial\ subsample}\right)$$

12.1.2. Calculation of weight of waste to charge to ZHE:

$$Weight\ of\ \ waste\ to\ charge\ to\ ZHE = 100\left(\frac{25}{\%wet\ solids}\right)$$

12.1.3. Calculation of weight of extraction fluid to use:

$$Weight\ of\ Extraction\ fluid = \frac{20\ x\ \%\ wet\ solids\ x\ weight\ of\ waste\ to\ be\ extracted}{100}$$

12.1.4. Calculation of volume of initial filtrate phase to recombine with solid phase leachate:

$$\text{Volume of filtrate for recombination} = \left(\frac{Weight\ of\ solids\ leached}{Total\ weight\ of\ solids}\right)\left(\frac{Leachate\ recovered}{Fluid\ added}\right)\left(Volume\ of\ initial\ aqueous\ filtrate\right)$$

12.1.5. Mathematical recombination of analytical results:

$$Final\ Analyte\ Concentration = \frac{(V_1 \times C_1) + (V_2 \times C_2)}{V_1 + V_2}$$

V_1 = total volume of the initial filtrate phase (L).
C_1 = analyte concentration in initial filtrate phase (mg/L).
V_2 = volume of the theoretical solid phase leachate (L).
C_2 = analyte concentration in solid phase leachate (mg/L).,

12.2. REPORTING REQUIREMENTS

12.2.1. Follow these reporting conventions for multi-phase samples:

12.2.1.1. If both phases have positive results, use the values from each phase to calculate the recombined result. Use the reporting limit for each phase to calculate the recombined reporting limit.

12.2.1.2. If both phases are “ND,” not detected, the recombined result is “ND,” and the reporting limit is calculated from the reporting limit for each phase.

12.2.1.3. If one phase is “ND” and the other phase has a positive result, use the reporting limit for the “ND” phase and the positive value for the other phase to calculate the combined result. The combined reporting limit is based on the reporting limit for both phases. If the combined result is less than the combined reporting limit, then

supply a footnote to indicate that "a positive result was detected below the calculated detection limit."

12.2.2. Units - regardless of the nature of the sample, all TCLP and SPLP results are reported in units of mg/L.

12.2.3. For limits and significant figures, consult the appropriate analytical methods (Section 16.3).

12.2.4. Anomalies - all anomalies observed during the leach procedure must be noted on the worksheet or an anomaly form. Some examples of such anomalies are:

12.2.4.1. Sample was monolithic - subsample was obtained by crushing, cutting, grinding, sawing, etc.

12.2.4.2. Insufficient sample - less than the required 100 g minimum was available.

12.2.4.3. Multiple phases - "X" phases were present.

12.2.4.4. Sample was oil - single phase.

12.2.4.5. Sample contained liquid which did not filter under test conditions.

12.3. REVIEW REQUIREMENTS

12.3.1. Review all applicable holding times. If a holding time was exceeded, confirm that a holding time violation form was properly documented and routed.

12.3.2. If Total analysis results are available, those results may be compared with the TCLP analysis results according to the following:

$$Total \geq 20 \times TCLP$$

NOTE: Assumes the sample is 100% Solids.

12.3.3. Total constituent analysis results can be used to demonstrate the TCLP protocol is unnecessary. In performing a TCLP analysis, there is a 20:1 dilution of the original sample with the leaching solution. Thus, if the "total constituent" result is less than 20 times the TC level, it is impossible for the leachate to "fail" and the TCLP does not need to be performed. For example, the TC level for lead is 5.0 mg/L (ppm). Therefore, if a sample of lead-

contaminated soil contains less than 100 ppm total lead, a TCLP test need not be run for lead.

METHOD PERFORMANCE

13.1. Refer to individual analysis SOPs.

13.2. Training Qualification:

The group/team leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience.

POLLUTION PREVENTION

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

WASTE MANAGEMENT

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

REFERENCES

16.1. EPA Method 1311 toxicity characteristic leaching procedure (TCLP). SW-846, 3rd Edition, Updated September 1994.

16.2. Method 1312, Synthetic Precipitation Leaching Procedure, Revision 0, November 1992, SW-846 Proposed Update II.

16.3. Related Documents

16.3.1. Toxicity Characteristic: Corrections to Final Rule. Method 1311, Federal Register, Vol. 55, No. 126, Friday, June 29, 1990.

16.3.2. Toxicity Characteristic: Final Rule. Method 1311, Federal Register, Vol. 55, No. 61, Thursday, March 29, 1990.

16.3.3. Technical Background Document and Response To Comments, Method 1311, Toxicity Characteristic Leaching Procedure, USEPA/OSW, April, 1989.

16.3.4. QA-003, STL QC Program

16.3.5. CORP-IP-0003: Acid Digestion of Aqueous Samples by SW846 and MCAWW 200 Series Methods.

16.3.6. CORP-MT-0001: Inductively Coupled Plasma-Atomic Emission Spectroscopy, Spectrometric Method for Trace Element Analysis, Method 6010A and Method 200.7.

16.3.7. CORP-MT-0003: Graphite Furnace Atomic Absorption Spectroscopy, SW846 Method 7000A and MCAWW 200 Series Methods.

16.3.8. CORP-MT-0005: Preparation and Analysis of Mercury in Aqueous Samples by Cold Vapor Atomic Absorption, SW-846 7470A and MCAWW 245.1.

16.3.9. CORP-IP-0003: Acid Digestion of Aqueous Samples by SW846 and MCAWW 200 Series Methods.

16.3.10. CORP-MS-0002: Determination of Volatile Organics by GC/MS based on Methods 8240B and 8260A.

16.3.11. CORP-MS-0001 : GC/MS Analysis Based on Method 8270B, SW846.

16.3.12. CORP-GC-0001: Gas Chromatographic Analysis Based on Methods 8000A, 8010B, 8020A, 8080A and 8150B, SW846.

16.3.13. CORP-OP-0001: Extraction and Cleanup of Organic Compounds from Waters and Soils, Based on SW846 3500 Series, 3600 Series, 8150 and 600 Series Methods.

17. MISCELLANEOUS

17.1. Modifications/Interpretations from Reference Methods

17.1.1. Section 8: Preliminary Evaluations. Section 7.1 of the source method states that the sample aliquot used for the preliminary evaluation "...may not actually undergo TCLP extraction." Section 7.1.5 of the source method indicates that the portion used for the preliminary evaluation may be used for either the ZHE or non-volatile extraction if the sample was 100% solid. Section 7.1.5 further indicates that if the sample was subjected to filtration (i.e., < 100% solid) that this aliquot may be used for the non-volatile extraction procedure only as long as sufficient sample is available (minimum 100 g). Samples which have been subjected to the oven drying step may not

be used for TCLP extraction because solid phase degradation may result upon heating.

17.1.2. Section 11.2.5.6.3: Percent Solids Determination. Section 7.1.2 of the source method indicates that "if the percent wet solids is ≥ 0.5% and it is noticed that a small amount of the filtrate is entrained in wetting of the filter" that the filter should be oven dried to determine percent dry solids ". Drying of oil or organic matrices can both be hazardous and inappropriate. Additionally, it may be impossible to achieve a constant weight when performing this step. Due to safety concerns, if obviously oily or heavy organic matrices are entrained on the filter, the filter is not oven dried.

17.1.3. Section 11.2.8: Preliminary Determination of Filtrate/Extraction Fluid Compatibility. Section 7.2.13 of the source method provides no guidance as to how to make this determination. As a result, the procedure herein was developed and incorporated into the Preliminary Determinations section.

17.1.4. Section 9.2: TCLP Extraction Blanks. Section 8.1 of the source method states that a minimum of one blank for every 20 extractions "...that have been conducted in an extraction vessel." STL has interpreted this to mean one blank per twenty samples leached per TYPE of leaching vessel (i.e., Bottle or ZHE) per leach fluid used.

17.1.5. Section 11.2.7.9: Determination of Appropriate Extraction Fluid. Method 1311 does not address the appropriate approach to take if the pH equals 5.0. This SOP requires that Fluid #1 must be used if the pH is less than or equal to 5.0.

17.1.6. Section 9.4: QA/QC - Matrix Spikes. Section 8.2 of the source method states "A matrix spike shall be performed for each waste type..." and "A minimum of one matrix spike must be analyzed for each analytical batch." Further, Section 8.2.3 of the source method also states "The purpose of the matrix spike is to monitor the performance of the analytical methods used, and to determine whether matrix interferences exist." The standard STL QAPP is designed to address the performance monitoring of analytical methodology through the LCS program. A minimum of one MS and MSD will be prepared for each TCLP leachate batch. The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Due to the potential variability of the matrix of each sample, the MS/MSD results have immediate bearing only on the specific sample spiked and not all samples in the batch.

17.1.7. Section 8.2.2 of the source method states that "In most cases, matrix spikes should be added at a concentration equivalent to the corresponding regulatory

level." The method also states "If the analyte concentration is less than one half the regulatory level, the spike concentration may be as low as one half of the analyte concentration but may not be less than five times the method detection limit". For several analytes, spiking at the regulatory level is inappropriate to the range of analysis afforded by the determinative methods. Due to the wide range in these levels, STL spikes at the levels specified in the determinative SOPs.

17.2. Modifications from Previous SOP

None

17.3. Facility Specific SOPs

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

17.4. Documentation and Record Management

The following documentation comprises a complete TCLP preparation raw data package:

- Completed worksheets (Appendix C)
- Non-conformance summary (if applicable).
- Anomaly documentation (if applicable).

1.

APPENDIX A

TABLES

Table 3 - Toxicity Characteristic Analytes and Regulatory Levels (Final Rule)

Contaminant	mg/L
Arsenic	5.0
Barium	100.0
Benzene	0.5
Cadmium	1.0
Carbon tetrachloride	0.5
Chlordane	0.03
Chlorobenzene	100.0
Chloroform	6.0
Chromium	5.0
o-Cresols	200.0
m-Cresols	200.0
p-Cresols	200.0
Total Cresols (used if isomers not resolved)	200.0
2,4-D	10.0
1,4-Dichlorobenzene	7.5
1,2-Dichloroethane	0.5
2,4-Dinitrotoluene	0.13
1,1-Dichloroethylene	0.7
Endrin	0.02
Heptachlor (& epoxide)	0.008
Hexachlorobenzene	0.13
Hexachlorobutadiene	0.5
Hexachloroethane	3.0
Lead	5.0
Lindane	0.4
Mercury	0.2
Methoxychlor	10.0
Methyl ethyl ketone	200.0
Nitrobenzene	2.0
Pentachlorophenol	100.0
Pyridine	5.0
Selenium	1.0
Silver	5.0
Tetrachloroethylene	0.7
Toxaphene	0.5
Trichloroethylene	0.5
2,4,5-Trichlorophenol	400.0
2,4,6-Trichlorophenol	2.0
2,4,5-TP (Silvex)	1.0
Vinyl chloride	0.2

APPENDIX B

FIGURES

Figure 1 & 2 - Rotary Agitation Apparatus and Zero Headspace Extraction Vessel (ZHE)

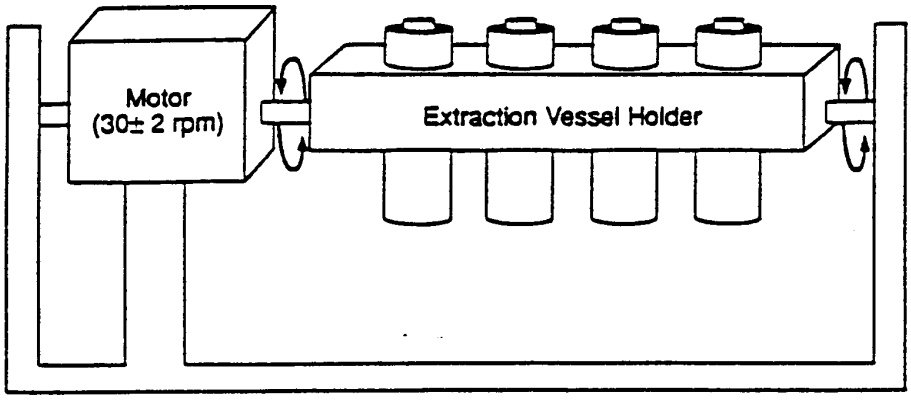


Figure 1. Rotary Agitation Apparatus

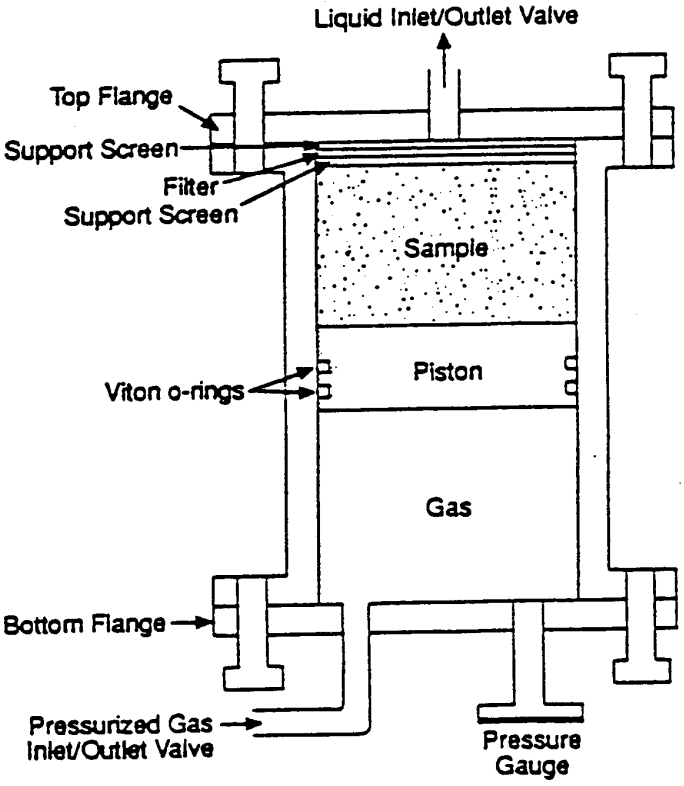


Figure 3 - US Environmental Protection Agency Memorandum #35, Page 1

Figure 3 - US Environmental Protection Agency Memorandum #35, Page 10

Oily Waste Analysis

One of the most frequently asked questions on the MICE Service concerns the application of the TCLP, Method 1311, to oily wastes. Many callers request technical guidance on the extraction of oily wastes due to the difficulty in the filtration on these types of waste. In many cases, an oily waste does not filter completely due to premature clogging of the glass fiber filter. This can result in the retention of standing liquid on the glass fiber filter. Material that do not pass through the glass fiber filter at the conclusion of the filtration step is defined by the method as the solid phase of the waste. The solid phase is then subjected to the leaching procedure of the TCLP. For oily wastes, clogging of the glass fiber filter can result in an overestimation of the amount of solid material available for leaching.

To solve this problem, the Agency recommends a conservative approach, one that probably will overestimate the amount of leaching. Rather than performing the TCLP extraction on the unfiltered portion of the oily waste, assume the waste is 100% liquid (e.g., will pass through the glass fiber filter) and perform a totals analysis on the oily waste to determine if the oil exceeds the appropriate regulatory level.

Filterable waste oil generated during the TCLP must be analyzed for a variety of organic and inorganic analytes. The OSW recognizes the difficulty in achieving acceptable performance for the analysis of waste oil using methods currently provided in SW-846. As a result, the Agency will provide several new methods for the preparation and analysis of oil samples to the Organic Methods Workgroup in July. In addition, a microwave assisted digestion procedure should improve the analysis of metals and will be proposed as part of the Second Update of the Third Edition of SW-846. Brief descriptions of these techniques are provided below, for additional information on the organic procedures contact Barry Lesnik at (202) 260-7459. For additional information on microwave digestion contact Ollie Fordham (202) 260-4778.

The use of purge-and-trap (Method 5030) for volatiles in oil generally results in severe contamination of analytical instrumentation. Traps, transfer lines and chromatography columns may become contaminated with oil. This leads to elevated baselines, hydrocarbon background in subsequent analyses, and cross-contamination. Headspace (Method 3810) is currently allowed only as a screening procedure in SW-846. The Agency is evaluating the use of headspace in conjunction with isotope dilution mass spectrometry for the quantitative analysis of volatiles in oil. Headspace reduces interference problems encountered with purge-and-trap. However, headspace quantitation can be questionable because the distribution of analytes is not

APPENDIX C

WORKSHEETS

TCLP/SPLP Worksheet 1 - Sample Description

Laboratory Sample No.					
Field Sample No.					
A. Sample Description					
Number of phases					
1.					
2.					
a. lighter than					
b. water					
c. heavier than water					
B. Percent Solid Phase					
1. weight of filter (g)					
2. weight of subsample					
a. gross weight (g)					
b. tare weight (g)					
c. net weight (g)					
3. weight of filtrate					
a. gross weight (g)					
b. tare weight (g)					
c. net weight (g)					
4. total weight wet solids[0]					
5. weight percent wet solids[1] (%)					
6. weight percent dry solids[2] (%)					
a. gross dry weight (g)					
b. final gross dry weight[2] (g)					
c. percent dry solids (%)					
7. volume of initial aqueous filtrate (mL)					
8. volume of initial organic filtrate (mL)					

[0] Total Weight of wet solids $= \left(2c - 3c\right)$

[1] Weight percent wet solids $= 100\left(\frac{Total\ weight\ wet\ solids,\ B4}{Weight\ of\ subsample,\ B2c}\right)$

[2] Weight percent dry solids $= 100\left(\frac{\left(Gross\ dry\ weight,\ B6b\right) - \left(weight\ of\ filter,\ B1\right)}{Weight\ of\ subsample,\ B2c}\right)$

Comments: _____

_____

Analyst: _____ Date: _____

TCLP/SPLP Worksheet 2 - Selection of Extraction Fluid

TCLP

Laboratory Sample No.					
Field Sample No.					
C. Extraction Fluid Determination—does not apply to determination of volatile organic components.					
1. particle size reduction? yes/no (<1 mm)					
2. sample weight, ✓ if 5.0 ± 0.1 g					
3. volume of water, ✓ if 96.5 ± 1.0 mL					
4. initial pH (after 5 min. mixing time)					
5. if pH >5.0, ✓ if 3.5 mL 1N HCL					
6. ✓ if heated and held at 50^0C for ten minutes					
7. secondary pH (at room temperature)					
D. Selection of Extraction Fluid					
1. ✓ if pH from § C (4) or § C (7) is <5.0, use extraction fluid No. 1.					
2. ✓ if pH from § C (7) IS >5.0, use extraction fluid No. 2					
3. ✓ if filtrate and fluid are miscible					

SPLP

Laboratory Sample No.					
Field Sample No.					
D. Selection of Extraction Fluid (✓ one)					
Fluid 1: Soils—East of the Mississippi River; Wastes; or Wastewaters.					
Fluid 2: Soils—West of Mississippi River					
Fluid 3: If VOCs or Cyanide containing wastes.					
1. ✓ if filtrate and fluid are miscible					

Comments: _____
_____

Analyst: _____ Date: _____

TCLP/SPLP Worksheet 3 - Extraction for Metals, Semi-Volatile Organic Components and Pesticides/Herbicides

Laboratory Sample No.					
Field Sample No.					
E. Determination of Samples Size for Leach Testing—the method requires a minimum 100 gram sample size for extraction					
1. particle size reduction? yes/no (<9.5 mm)					
2. weight of wet solids after filtration (g)					
F. Determination of Amount of Extraction Fluid—the selection of the correct extraction fluid is found in Section D., Worksheet No. 2					
1. Fluid weight = 20 x solids weight (g)					
G. Record of Extraction Test—the extraction period is specified as 18 ± 2					
1. room temperature initial (^oC) final (^oC)					
2. vessel number					
3. extraction start time					
4. extraction stop time					
5. date and time filtration complete					
6. pH of leachate					
7. volume of leachate (for multiphase samples only) (mL)					
8. volume of initial aqueous filtrate for recombination[3] (mL)					
9. combined initial aqueous + leachate (mL)					

[3] Volume of filtrate used for recombination $= \left(\frac{Weight\ of\ solids\ leached,\ E2}{Total\ weight\ of\ solids,\ B4}\right)\left(\frac{Leachate\ recovered,\ G6}{Fluid\ added,\ F1}\right)\left(Volume\ of\ initial\ aqueous\ filtrate,\ B7\right)$

Comments: _____

_____

Analyst: _____ Date: _____

TCLP/SPLP Worksheet 4 - Zero Headspace Extraction (ZHE)

Laboratory Sample No.					
Field Sample No.					
H. Determination of Sample Size for Leach Testing—maximum 25 grams					
1. particle size reduction? yes/no (<9.5 mm)					
2. weight of wet solid (g)					
I. Determination of Amount of Extraction Fluid No. 1					
1. weight of material added to ZHE (g)					
2. volume of filtrate in syringe (mL)					
3. weight of filtrate in syringe					
a. gross weight (g)					
b. tare weight (g)					
c. net weight (g)					
4. wet solids in ZHE[4] (g)					
5. weight of fluid to add[5] (g)					
J. Record of ZHE Extraction Text—the extraction period is as 18 ± 2 hours.					
1. room temperature initial (°C) final (°C)					
2. ZHE vessel number					
3. extraction start date & time					
4. extraction stop date & time					
5. ✓ if still under positive pressure					
6. filtration completed date & time					
7. volume of filtrate recovered after leaching (mL)					
a. volume of oil recovered after leaching (mL)					
8. volume of initial aqueous filtrate for recombination[6] (mL)					
9. combined initial aqueous + leachate (mL)					

[4] Solids remaining in ZHE $= (Material\ added, I1) - (Weight\ of\ filtrate\ in\ syringe, I3)$

[5] Weight of fluid to add $= 20(Wet\ solids\ in\ ZHE, I4)$

[6] Volume of filtrate used for recombination $= \left(\frac{Weight\ of\ solids\ leached, I4}{Total\ weight\ of\ solids, B4}\right)\left(\frac{Leachate\ recovered, J7}{Fluid\ added, I5}\right)(Volume\ initial\ aqueous\ filtrate, B7)$

Comments: _____

_____

Analyst: _____ Date: _____

TCLP/SPLP Worksheet 5 - Organic Results

TCLP/SPLP ZHE Worksheet No. 5
Organic Results

Sample Number: _____

Organics Preparation		Volume	Units
Combined initial Aqueous/Leachate from § J9	V_A		mL
Oil phase Volume for Calculations[7]	V_O		mL

Analyte		Oil Phase			Combined Initial Aqueous/Leachate			Final Results	
Compound	Std. Reporting Limit (mg/L)	Dilution Factor	Result C_O	Reporting Limit	Dilution Factor	Results C_A	Reporting Limit	Result C_{Final}	Reporting Limit

$$C_{Final} = \frac{(C_A \times V_A) + (C_O \times V_O)}{V_A + V_O}$$

[7] Volume of oil phase for calculation = $\left(\frac{Wet\ solids\ leached,\ I4}{Total\ solid,\ B4}\right)\left(\frac{Leachate\ recovered,\ J7}{Fluid\ added,\ I5}\right)(Initial\ volume\ of\ oil,\ B8) + (Oil\ recovered\ from\ leaching,\ J7a)$

Comments: _____
_____

Analyst: _____ Date: _____

TCLP/SPLP Worksheet 6 - Metals Results

Metals Results

Sample Number : _____

Metals Preparation		Volume	Units
Combined Initial Aqueous/Leachate from §G8	VA		mL
Oil phase volume for calculations[8]	VO		mL

Analyte		Oil Phase			Combined Initial Aqueous/Leachate			Final Results	
Element	Std. Reporting Limit (mg/L)	Dilution Factor	Result C_O	Reporting Limit	Dilution Factor	Results C_A	Reporting Limit	Result C_{Final}	Reporting Limit
Arsenic	0.5								
Barium	10								
Cadmium	0.1								
Chromium	0.5								
Lead	0.5								
Mercury	0.0002								
Selenium	0.25								
Silver	0.5								

$$C_{Final} = \frac{(C_A \times V_A) + (C_O \times V_O)}{V_A + V_O}$$

[8] $$\text{Volume of oil phase for calculation} = \left(\frac{Wet\ solids\ leached,\ E2}{Total\ solid,\ B4}\right)\left(\frac{Leachate\ recovered,\ G7}{Fluid\ added,\ F1}\right)(Initial\ volume\ of\ oil,\ B8) + (Oil\ recovered\ from\ leaching,\ G6a)$$

Notes: If sample contains no solids, volume of oil phase (V_0) is the volume of the initial organic filtrate

In cases where analytes are detected in only one phase, a footnote indicating a result reported below the reporting limit should be included.

Comments: _____

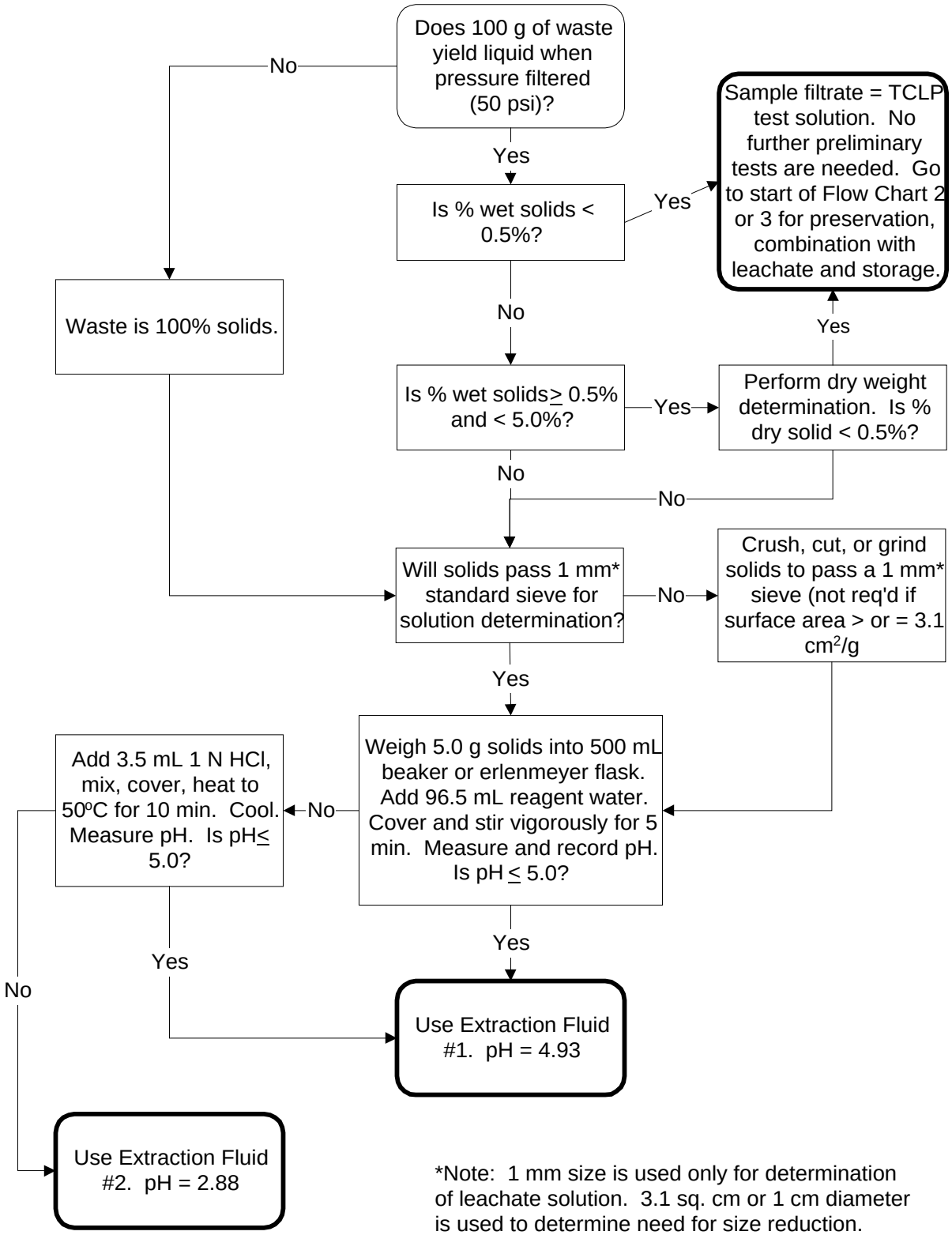
_____

Analyst: _____ Date: _____

APPENDIX D

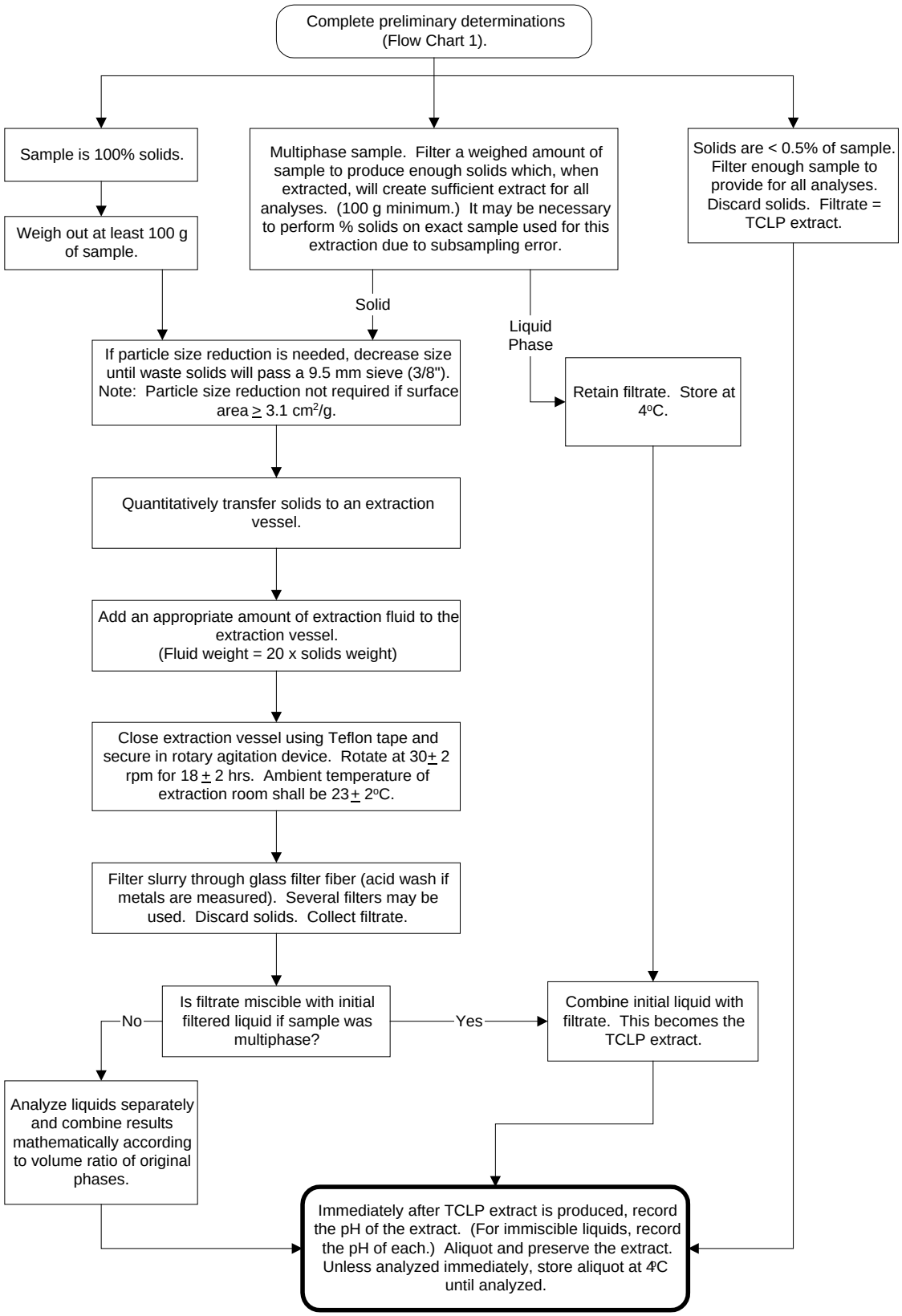
FLOW CHARTS

Flow Chart 1. Preliminary Sample Evaluation (Section 11.2)

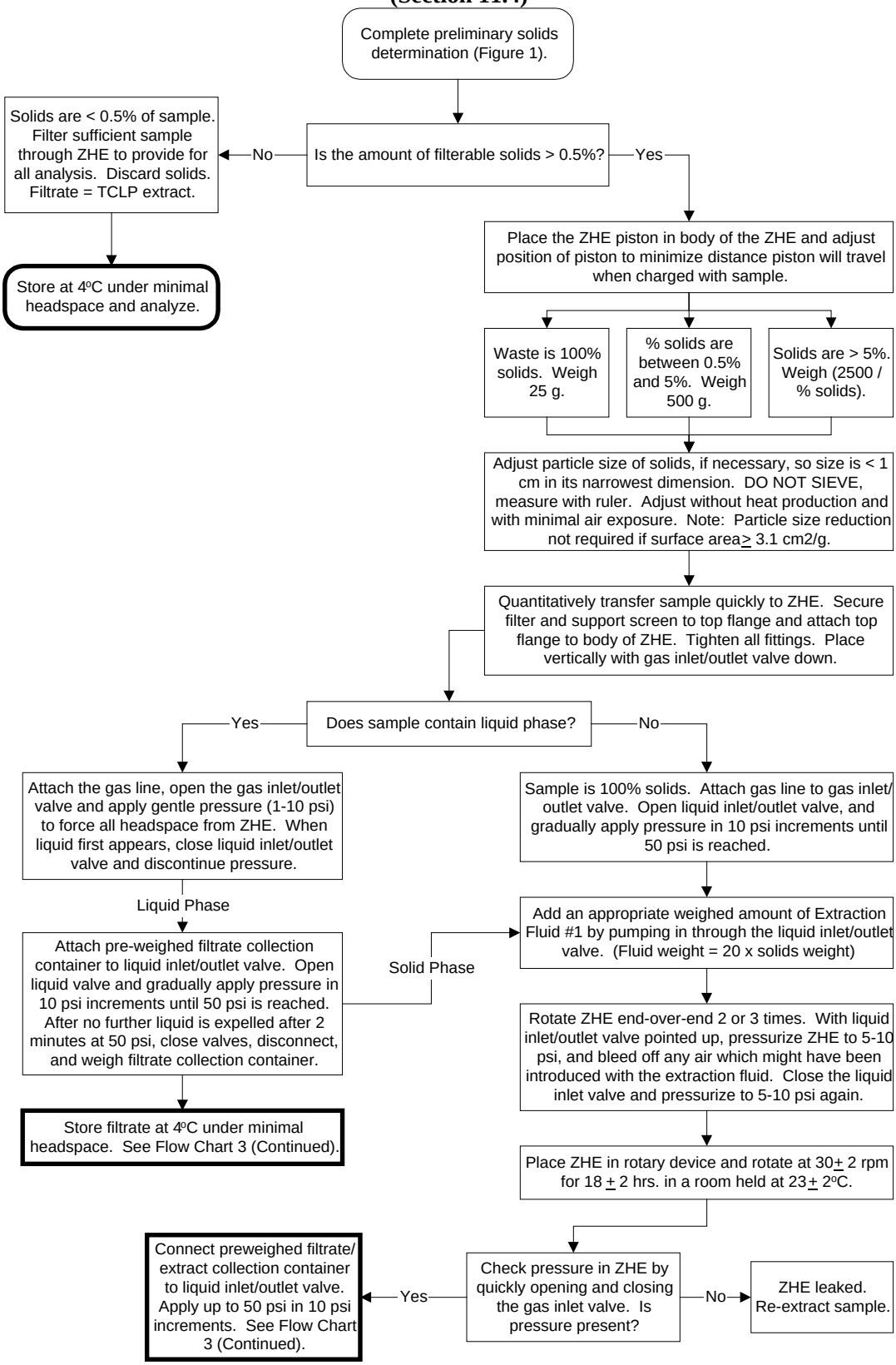


*Note: 1 mm size is used only for determination of leachate solution. 3.1 sq. cm or 1 cm diameter is used to determine need for size reduction.

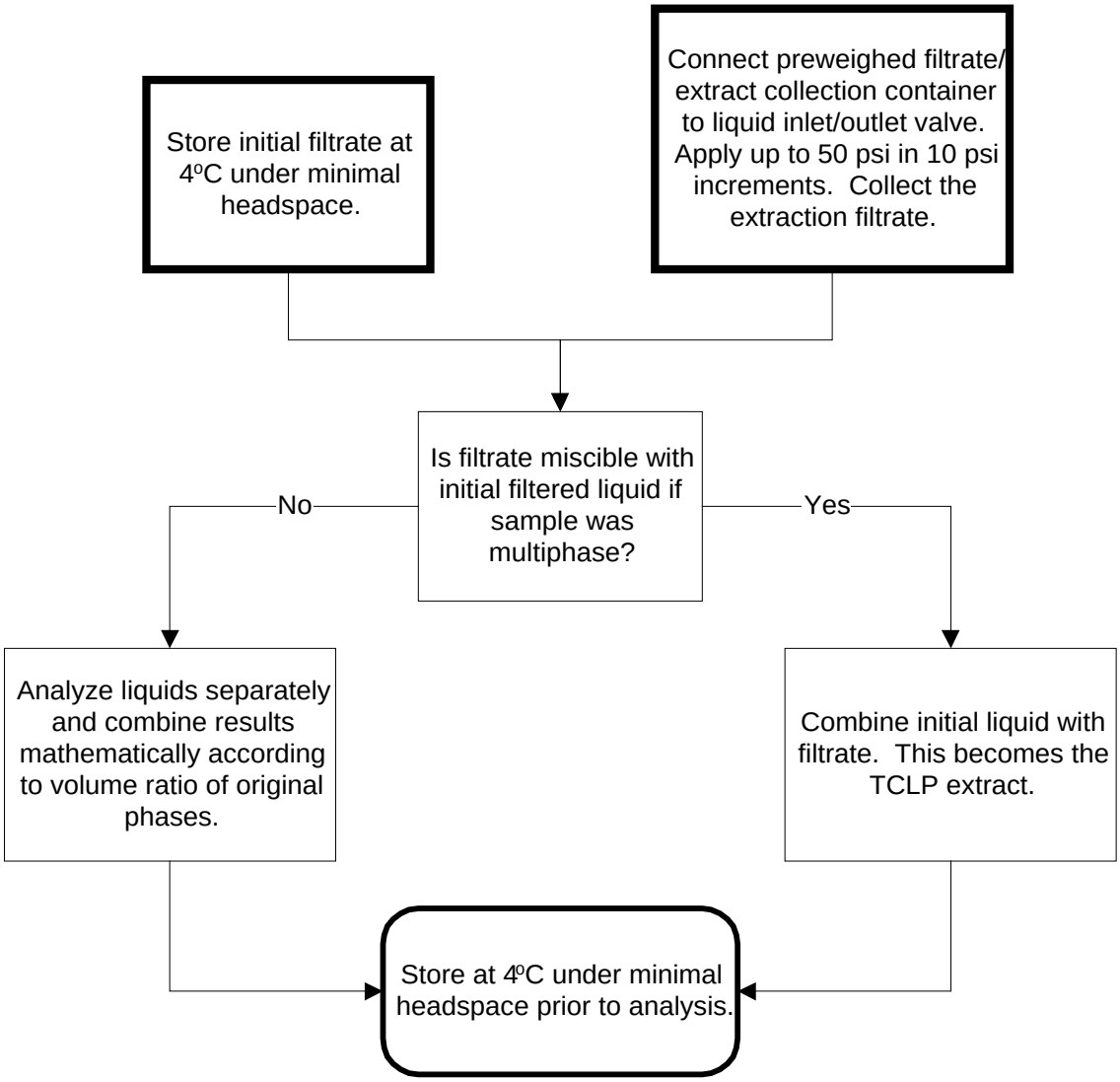
Flow Chart 2. Bottle Extraction, Non-Volatile Constituents (Section 11.3)



Flow Chart 3. ZHE Extraction, Volatile Constituents (Section 11.4)



Flow Chart 3. ZHE Extraction (Continued)



NC-WC-0017

Total Organic Carbon (TOC) and Total Inorganic Carbon (TIC)
SW 846 Method 9060 and EPA Method 415.1

LABORATORY-SPECIFIC

QUANTERRA® STANDARD OPERATING PROCEDURE

TITLE: TOTAL ORGANIC CARBON (TOC) AND TOTAL INORGANIC CARBON (TIC)

(SUPERSEDES: REVISION 1, DATED 11/20/96)

Intranet Controlled

Prepared by: _____
Date

Reviewed by: _____
Technology Specialist Date

Approved by: _____
Quality Assurance Manager Date

Approved by: _____
Environmental Health and Safety Coordinator Date

Approved by: _____
Laboratory Director Date

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1. SCOPE AND APPLICATION

1.1. This method is applicable to the determination of Total Organic Carbon (TOC) or Total Inorganic Carbon (TIC) in waters and similar matrices. It is based on SW846 Method 9060 and EPA Method 415.1. The working linear range is instrument dependent at 1 mg/L to 50 mg/L with a reporting limit of 1 mg/L.

1.2. This document accurately reflects current laboratory standard operating procedures (SOP) as of the date above. All facility SOPs are maintained and updated as necessary.

1.3. QuantIMS method codes are I8 (415.1 TIC), AY (9060 TIC), DA (415.1 – TOC) FM (9060 – TOC).

2. SUMMARY OF METHOD

2.1. Organic carbon is converted to carbon dioxide (CO_2) using chemical oxidation. The CO_2 is then measured by an infrared detector.

3. DEFINITIONS

3.1. Refer to the glossary in the Quality Assurance Management Plan (QAMP), current version.

4. INTERFERENCES

4.1. Contaminants in solvents, reagents, glassware, and other processing apparatus that lead to discrete artifacts may cause Method interferences. All of these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. Specific selection of reagents may be required to avoid introduction of contaminants.

4.2. Carbonate and bicarbonate interfere but are eliminated by the acidification and purging step of the instrument.

5. SAFETY

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

5.2. Eye protection that satisfies ANSI Z87.1 (per the Chemical Hygiene Plan), Laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and

reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

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

5.3.1. The following materials are known to be **corrosive:** Phosphoric **Acid, Sulfuric Acid**.

5.4. Exposure to chemicals must be maintained **as low as reasonably achievable,** therefore, unless they are known to be non-hazardous, all samples must be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

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

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

6. EQUIPMENT AND SUPPLIES

6.1. O•I Corporation Model 1010 TOC Analyzer with 1051 vial multisampler and Printer

6.2. Nitrogen Gas and Regulator

6.3. Volumetric flasks: Various sizes

6.4. Volumetric pipettes: Various sizes

6.5. Vials: 40 mL glass

6.6. Graduated cylinders: Various sizes

6.7. pH Strips

6.8. Whatman filter #4

6.9. Top loading balance: capable of accurately weighing ± 0.01 g

7. REAGENTS AND STANDARDS

7.1. Reagents

7.1.1. Sodium Persulfate: Reagent Grade

7.1.2. Sodium Persulfate Solution: Add 200 g sodium persulfate ($Na_2S_2O_8$) to a 1 liter volumetric flask and dilute to volume with reagent water.

7.1.3. Phosphoric Acid, concentrated: Reagent Grade

7.1.4. Phosphoric Acid Solution: Carefully add 59 mL concentrated phosphoric acid (H_2PO_4) to 900 mL of reagent water in a 1 liter volumetric flask. Dilute to volume with reagent water.

7.1.5. Sulfuric Acid, concentrated: Reagent Grade

7.2. Standards

7.2.1. All standards should be prepared in volumetric flasks, using volumetric pipettes, and diluted to volume with reagent water.

7.2.2. TOC Stock Standard

7.2.2.1. Primary and secondary sources are needed.

7.2.2.2. TOC 1000 mg/L

7.2.2.2.1. Dilute 1.06 g KHP (potassium acid phthalate) to volume in a 500 mL volumetric flask.

7.2.2.3. Prepare every six months.

7.2.3. TOC Calibration Standards

7.2.3.1. Prepare the following standards from the primary stock standard described in Section 7.2.2.2.1.

Concentration (mg/L)	Volume (mL)	Stock Concentration (mg/L)	Final Volume (mL)
50	5	1000	100
25	2.5	1000	100
10	1	1000	100
1	0.1	1000	100

7.2.4. TOC Verification Standard (LCS, MS/MSD and CCV)

7.2.4.1. Prepare the following standard from the secondary stock standard described in Section 7.2.2.2.1.

Concentration (mg/L)	Volume (mL)	Stock Concentration (mg/L)	Final Volume (mL)
25	12.5	1000	500

7.2.4.2. Prepare when setting up run.

7.2.5. TIC Stock Standard 1000 mg/L

7.2.5.1. Add 3.5 g Na_2HCO_3 (sodium bicarbonate) and 4.418 g Na_2CO_3 (sodium carbonate) to a 1000 mL flask. Dilute to volume with reagent water.

7.2.5.2. Prepare every 3 months.

7.2.6. TIC Calibration Standard

7.2.6.1. Prepare in the same manner as the TOC calibration standard (Section 7.2.3.1), using the TIC stock standard described in Section 7.2.5.1.

7.2.6.2. Prepare weekly.

7.2.7. TIC Verification Standard (LCS, MS/MSD and CCV)

7.2.7.1. Prepare in the same manner as the TOC verification standard (Section 7.2.4.1), using the TIC stock standard described in Section 7.2.5.1.

7.2.7.2. Prepare daily.

8. SAMPLE PRESERVATION AND STORAGE

8.1. Samples are preserved to a pH < 2 with sulfuric acid (H_2SO_4) or hydrochloric acid (HCl) and stored in plastic or glass containers at 4°C ± 2° C.

8.2. The holding time is twenty-eight days from sampling to analysis.

9. QUALITY CONTROL

9.1. Batch Definition

9.1.1. A batch is a group of no greater than 20 samples, excluding QC samples (LCS, MS, MSD, and Method Blanks), which are processed similarly with respect to the procedure. All samples within the batch must be treated with the same lots of reagents and the same processes. All samples within the batch must be treated with the same processes.

9.2. Method Blank (MB)

9.2.1. One method blank (MB) must be processed with each preparation batch. The method blank consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. The method blank should not contain any analyte of interest at or above the reporting limit.

9.2.2. A method blank consisting of 40 mL of reagent water and all reagents added to the samples must be prepared and analyzed with each batch of samples. The method blank is used to identify any background interference or contamination of the analytical system, which may lead to the reporting of elevated concentration levels or false positive data.

9.2.3. Corrective Action for Blanks

9.2.3.1. If the analyte level in the method blank exceeds the reporting limit for the analytes of interest in the sample, all associated samples are reprepared and reanalyzed. If this is not possible due to limited sample quantity or other considerations, the corresponding sample data **must be taken in consultation with the client and must be addressed in the project narrative.**

9.2.3.2. If there is no analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. **Such action must be taken in consultation with the client and must be addressed in the project narrative.**

9.3. Laboratory Control Sample

9.3.1. Laboratory Control Samples are well characterized; laboratory generated samples used to monitor the laboratory's day to day performance of routine analytical methods. The LCS is used to monitor the accuracy of the analytical process, independent of matrix effects. Ongoing monitoring of the LCS results provides evidence that the laboratory is performing the method within accepted QC guidelines for accuracy and precision.

9.3.2. A 25 mg/L LCS (TOC or TIC) must be analyzed with each batch of samples.

9.3.3. Corrective Action for LCS

9.3.3.1. If any analyte is outside established control limits the system is out of control and corrective action must occur.

9.3.3.1.1. The only exception to the requirement established in section 9.3.3.1 occurs if the LCS recovery is biased high and the associated sample(s) are ND (non detect). Under this condition, the batch is acceptable.

9.3.3.2. Corrective action will be repreparation and reanalysis of the batch unless the client agrees that other corrective action is acceptable.

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

9.4.1. One MS/MSD pair must be processed for each batch. A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added. A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked identically as the MS) prepared and analyzed along with the sample and matrix spike. Some client specific data quality objectives (DQO's) may require the use of sample duplicates in place of or in addition to MS/MSD's. The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Due to the potential variability of the matrix of each sample, these results may have immediate bearing only on the specific sample spiked. Samples identified as field blanks cannot be used for MS/MSD analysis.

9.4.2. An MS/MSD consisting of 20 mL of sample and 20 mL of the 25 mg/L standard will be analyzed with each analytical batch of samples.

9.4.3. Corrective action for MS/MSDs

9.4.3.1. If the analyte recovery or RPD falls outside the acceptance range, the recovery of that analyte must be in control for the LCS. If the LCS recovery is within limits, then the laboratory operation is in control and the results may be accepted. If the recovery of the LCS is outside limits, corrective action must be taken. Corrective action will include repreparation and reanalysis of the batch.

9.4.3.2. If the native analyte concentration in the MS/MSD exceeds 4x the spike level for that analyte, the recovery data is reported as DIL (diluted out).

9.4.3.3. If an MS/MSD is not possible due to limited sample volume then a laboratory control sample duplicate (LCSD) should be analyzed. The RPD of the LCS and LCSD must be compared to the matrix spike RPD limits.

9.5. QC Acceptance Criteria

9.5.1. Control limits are established by the laboratory as described in NC-QA-0018.

10. CALIBRATION AND BLANKING

10.1. Recommended Initial Setup

Contant Settings		
STD Mass	=	6.76 ug C
Sample Vol	=	2.0 mL
Acid Vol	=	4 x 100 uL
Oxidant Vol	=	10 x 100 uL

10.1.1. Adjust the nitrogen to 30 psi using the flow valve on the tank. The gauge should always be set at 30 psi when the instrument is not in use.

10.1.1.1. If the main valve reads < 200 psi, the tank should be changed. **Do not** allow the tank to go empty.

10.1.2. Remove the reagent bottles and fill with appropriate reagents (phosphoric acid solution and sodium persulfate). Do not fill bottles completely full; leave a small amount of air space. Loosely reconnect caps (and tubing), and replace the bottles into the instrument.

10.1.3. Blank and calibrate the instrument when CCVs and/or CCBs fail to meet acceptance criteria or when other problems are encountered.

10.1.3.1. Choose “sequences” from the “databases” menu option, open up the calibration template.

10.1.3.2. Confirm all information. If blanking is required, it is best if done at this step. Enter the desired number of blanks (no less than five) in the “reagent blanks before” field.

10.1.3.3. Analyze an ICV/ICB

10.1.3.4. Save the file using the current date as the filename.

10.1.3.5. Update data file information:

10.1.3.5.1. Choose the setup menu option, go into win TOC output, change the log fill name and prefix counter.

10.1.3.6. When analysis is complete, print the run from "/utilities/view run log"

10.1.3.7. Evaluate the data. The correlation coefficient of the original curve must be ≥0.995 or recalibration is required.

10.2. Continuing Calibration

10.2.1. The run is checked at the beginning, after every ten samples, and at the end of the run of the same species (TOC or TIC) using a midrange CCV made from a secondary source (Section 7.2.4 or 7.2.7) to verify continued linearity. A CCV cannot vary from the original curve by more than ± 10%, or recalibration is required.

10.2.2. System cleanliness is checked every ten samples and at the end of the run using a Continuing Calibration Blank (CCB). A CCB cannot contain the analyte of interest above the reporting limit, or recalibration is required.

10.3. Analytical Documentation

10.3.1. Record all analytical information in the analytical logbook/logsheet, including the analytical data from standards, blanks, LCSs, MS/MSDs, and any corrective actions or modifications to the method.

10.3.2. All standards are logged into a department standard logbook. All standards are assigned a unique number for identification. The supervisor or designee reviews logbooks.

10.3.3. Documentation, such as all associated instrument printouts (final runs, screens, reruns, QC samples, etc.) and daily calibration data corresponding to all final runs, is available for each data file.

10.3.4. Sample results and associated QC are entered into the Laboratory Information Management System (LIMS) after final technical review.

11. PROCEDURE

11.1. Sample Preparation Procedure

11.1.1. Check the pH of the sample. If the pH > 2, add concentrated H_2SO_4 drop by drop to the sample (in the TOC vial) until the pH is < 2.

11.1.2. If excess particulate matter exists, filter an aliquot of sample through a Whatman #4 filter into a TOC vial.

11.2. Preparation Documentation

11.2.1. Record any sample preparation on the analytical logsheet.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Sample Analysis Procedure

12.1.1. Type a run protocol sequence into the computer using the run template, if desired. Update the data file information in the setup/winTOC output.

12.1.1.1. For method 9060, quadruplicate analysis is required. If quadruplicate reporting is requested each of four results are reported. Replicate analysis should be taken from separate vials, if available. If only one reportable result is requested per sample, the four results should be taken from one vial, and the average of the four results are reported.

12.1.1.2. For method 415.1 only one analysis is required. The single analysis result is reported directly from the instrument printout.

12.1.2. All samples and standards should be poured into 40 mL vials. Samples received in vials can be run in those containers, provided there is not an excess of solids.

12.1.3. Be sure the samples are loaded on the sampler, the first one positioned under the needle.

12.1.4. Click on the “Start” button.

12.1.5. Samples that fall outside the linear range (> 100 mg/L) of the instrument must be diluted and reanalyzed.

12.1.5.1. Samples following a high sample should be re-analyzed if carryover is a concern.

12.1.6. Print the run from “utilities/view run log.”

12.1.7. When analysis is complete, properly dispose of or put away samples and standards.

12.2. Calculations

12.2.1. ***Total Organic Carbon, mg/L = Average Instrument Value x Dilution***

Where:

TOC, mg/L = average of the 4 instrument values x dilution, calculated (without dilution) by the instrument.*

12.2.2. ***LCS % Recovery =***

$$\frac{\textit{Average of 4 instrument values*}}{25} \times 100$$

12.2.3. ***MS/MSD % recovery***

$$\frac{\dfrac{(\textit{Avg of 4 instrument values* MS or MSD}) - (\textit{Avg sample instrument value*} \div 2)}{12.5}}{100} \times$$

**One of the values may be judged erroneous and disregarded if three of the four are consistent. If no consistency can be found in the four values, the sample must be rerun.*

13. METHOD PERFORMANCE

13.1. Each laboratory must have initial demonstration of performance data on file and corresponding method detection limit files.

13.2. Training Qualifications:

13.2.1. The group/team leader has the responsibility to ensure that an associate who has been properly trained in its use and has the required experience performs this procedure.

14. POLLUTION PREVENTION

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

15. WASTE MANAGEMENT

15.1. Acid waste must be collected in clearly labeled acid water containers.

15.2. Solid materials (gloves, soiled paper products) are placed in the solid debris container. Do not put liquids in the solid waste container.

15.3. Refer to the Laboratory Sample and Waste Disposal plan.

15.4. Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices of Quanterra. They must have training on the hazardous waste disposal practices upon initial assignment to these tasks, followed by annual refresher training.

16. REFERENCES

16.1. References

16.1.1. SW846, Test Methods for Evaluating Solid Waste, Third Edition, Total Organic Carbon, Method 9060

16.1.2. EPA 600, Methods for Chemical Analysis of Water and Wastes, Organic Carbon, Method 415.1

16.1.3. Quanterra® Quality Assurance Management Plan (QAMP), current version.

16.2. Associated SOP

16.2.1. Statistical Evaluation of Data and Development of Control Charts, NC-QA-0018.

17. MISCELLANEOUS (TABLES, APPENDICES, ETC...)

17.1. Reporting limits

17.1.1. The lower reporting limit is 1 mg/L.

17.1.2. If samples require dilution or smaller volumes than specified in this method, the RL will be elevated.

17.2. Troubleshooting guide

17.2.1. See the manufacturer's instructions for an instrument troubleshooting guide and maintenance requirements.

17.3. Deviations from the Method

17.3.1. A blender is not used to homogenize samples.

PITT-WC-0058

Total Organic Carbon Analyses for Solid Matrices by Walkley Black

Controlled Copy
Copy No.: _____
Implementation Date:_____

OPERATION-SPECIFIC STANDARD OPERATING PROCEDURE

Title: Total Organic Carbon Analysis for Solid Matrices by Walkley Black

(SUPERSEDES: Enseco/Wadsworth Alert SOP No. LM-WALP-1071, Rev. 0, 12/13/93)

Prepared by: _____

Reviewed by: _____
Technical Specialist

Approved by: _____
Quality Assurance Manager

Approved by: _____
Environmental, Health and Safety Coordinator

Approved by: _____
Laboratory Director

Proprietary Information Statement:

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1. SCOPE AND APPLICATION

1.1 This Method is applicable to the determination of Total Organic Carbon (TOC) in soil and sediment samples. It is based on Standard Methods of Chemical Analysis.

2. SUMMARY OF METHOD

2.1 An aliquot of a solid sample is heated with excess potassium dichromate and concentrated sulfuric acid. After digestion and filtering, the solution is titrated with ferrous sulfate to determine the amount of dichromate reduced during digestion.

2.2 The reporting limit is 50 mg/Kg.

3. DEFINITIONS

3.1 LCS: Laboratory Control Sample processed through all method steps with the sample. The LCS is used to monitor the accuracy of the analytical process independent of possible interference effect due to sample matrix.

3.2 LCSD: Laboratory Control Sample Duplicate processed with the LCS when sufficient sample is not available to process a sample duplicate. A LCSD is used to demonstrate batch precision when the client has not supplied sufficient sample to prepare a duplicate sample analysis. A LCSD is required for a batch if a sample duplicate is not analyzed.

3.3 MB : Method Blank is prepared with the same reagent grade water that is used to dilute the sample. The method blank is used to monitor laboratory contamination.

3.4 SD: Sample Duplicate is a replicate aliquot of an environmental sample taken from the same sample container, when possible, and processed with the first aliquot of the sample. The sample and sample duplicate results are compared to determine the effect of the sample matrix on the precision of the analytical process.

3.5 QC Batch: The QC batch is a set of 20 or fewer environmental samples plus associated laboratory QC samples that are similar in composition and that are processed within the same time period and with the same reagents and standard lots. Laboratory QC samples such as LCS, matrix QC samples, method QC samples, and blanks are not included in the sample count for QC batching purposes.

3.6 Reagent Grade Water: Laboratory water produced by a Millipore DI system or equivalent. Reagent grade water must be free of the analyte of interest.

4. INTERFERENCES

4.1 If present, ferrous iron will be oxidized to ferric iron and therefore, consume dichromate and would bias the results high. Significant amounts of chloride could also consume dichromate and bias results high. Higher oxides of manganese can compete with dichromate for oxidizable substances and could bias results low.

5. SAFETY

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

5.2 Eye protection that satisfies ANSI Z87.1 (as per the Chemical Hygiene Plan), laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have become contaminated will be removed and discarded, other gloves will be cleaned immediately.

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

5.3.1 The following material is known to be corrosive: Sulfuric Acid (H_2SO_4)

5.4 Exposure to chemicals must be maintained **as low as reasonably achievable**, therefore, unless they are known to be non-hazardous, all samples must be opened, transferred, and prepared in a fume hood or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

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

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

6. EQUIPMENT AND SUPPLIES

6.1 Buret: 50 Class A

6.2 Analytical Balance: Capable of weighing to 0.0001g.

6.3 Hot Plate: Used in a hood.

6.4 Beakers: Various sizes (glass).

6.5 Graduated Cylinders: Various sizes, Class A

6.6 Volumetric Pipettes: Various sizes, Class A

6.7 Erlenmeyer Flasks: Various sizes

7. REAGENTS AND STANDARDS

7.1 Sulfuric Acid, concentrated

7.2 Ferroin Indicator, purchased at .025 M.

7.3 Potassium Dichromate Solution, 1N: Dissolve 49.04g of potassium dichromate (dried overnight at 105°C) in reagent water and diluted to 1L. Replace after six months.

7.4 Ferrous Sulfate Solution, 0.5N: Weigh 140g of FeSO4 7H2O into a 1L volumetric flask and dissolve with reagent water. Carefully add 15 mL of concentrated sulfuric acid and cool. Dilute to volume with reagent water.

7.5 Laboratory Control Sample (LCS), Potassium Hydrogen Phthalate, Weigh 0.05 gm for a 2.5 gm sample. Effective concentration = 47.05 ppm. Use this material for MS/MSD as needed.

7.6 Note: all standards materials should be measured in volumetric glassware and calibrated pipettes.

8. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 Container type: Glass.

8.2 Preservation: Cool, 4°C (± 2°C).

8.3 The holding time is 28 days from sampling to analysis.

9. QUALITY CONTROL

9.1 The laboratory control sample (LCS) is analyzed prior to the analysis of environmental samples and after every 20 or fewer environmental samples. The LCS recovery must be ±25 percent of the true value. If the LCS fails criteria, the analyst will check calculations and instrument performance and reanalyze the LCS once. If the LCS is still outside control limits, all samples in the QC batch will be reprepared and reanalyzed. If this is not possible due to limited sample quantity, the laboratory project manager will be notified and an analytical narrative provided with the data. If repreparation and reanalysis will be outside of holding time, the client should be notified and approval from the client must be obtained before reanalysis.

9.1.1 A laboratory control sample duplicate or LCSD is used to demonstrate batch precision when the client has not supplied sufficient sample to prepare a duplicate sample analysis. In this case the LCSD must be recovered within ±25 percent of the known value and an acceptable RPD of ≤20 percent with the LCS.

9.1.2 For programs that require a QC reference sample for every ten samples (i.e. such as for NYS samples), an LCS will be analyzed prior to the analysis of environmental samples and after every 10 or fewer environmental samples.

9.2 The Method Blank (MB) is processed with each batch of 20 or fewer environmental samples to assure the cleanliness of the reagents and apparatus. The blank must be less than the reporting limit or all samples associated with the unacceptable blank will be reanalyzed. If this is not possible due to limited sample quantity, the laboratory project manager will be notified and an analytical narrative provided with the data. If repreparation and reanalysis is outside of the holding time the client should be notified and approval from the client must be obtained before reanalysis.

9.3 A Sample Duplicate (SD) is analyzed with every set of twenty or fewer samples. Acceptance criteria is calculated as relative percent difference (RPD) between the original and duplicate sample analysis and the acceptable range is ≤20 percent. If the RPD is outside of criteria, the analyst will check calculations and instrument performance, reanalyze the samples once, evaluate results, and, if necessary, narrate it when reporting the data. The duplicate samples are not counted as part of the 20 or fewer environmental samples in the QC batch.

9.4 Control Charts are to be generated using in house data.

10. CALIBRATION AND STANDARDIZATION

10.1 The ferrous sulfate titrant is standardized as follows:

10.1.1 Place 10 mL of 1.00N potassium dichromate solution into a 250 mL Erlenmeyer flask and add reagent grade water to obtain a volume of about 100 mL.

10.1.2 Add 30 mL of concentrated sulfuric acid and cool.

10.1.3 Add 2 mL of ferroin indicator.

10.1.4 Titrate with ferrous sulfate solution to a reddish-brown endpoint.

10.1.5 Calculate the normality using the equation in Section 12.4.

11. PROCEDURE

11.1 Mix the sample thoroughly in a glass jar with a wooden tongue depressor before selecting a portion for analysis. Discard any foreign objects such as sticks, leaves, and rocks.

11.2 Weigh a maximum aliquot of soil of 2.50g to the nearest 0.01g. Record the weight on the analytical logsheet.

11.3 Place in a 500 mL Erlenmeyer flask and add 25 mL of 1N potassium dichromate and carefully add 20 mL of concentrated sulfuric acid. The sulfuric acid should be added to the sample while it is under a fume hood. Every effort should be made to limit fuming of the sample by adding the acid slowly letting it run down the side of the flask into the sample while gently swirling sample in the flask.

11.4 Continue to swirl for one minute.

11.5 Heat the sample on a preheated hot plate for two minutes, remove, and let stand for 30 minutes.

11.6 Add 200 mL of reagent grade water.

12. DATA ANALYSIS AND CALCULATIONS

12.1 Add ferroin indicator.

12.2 Titrate to a reddish-brown endpoint with 0.5N ferrous sulfate solution.

12.3 Document the amount of titrant on the analytical benchsheet.

12.4 Ferrous sulfate titrant standardization is determined using the following equation:

$$N_{\text{Ferrous Sulfate}} = \frac{10\ \text{mL}(K_2Cr_2O_7)\ (1.0\ N\ K_5Cr_2O_7)}{mg\ FeSO_4}$$

Where:
N = Normality

12.5 The sample result is calculated using the following equation.

$$\text{Total Organic Carbon, mg/Kg} = \frac{[(25)(\text{N Potassium Dichromate}) - (\text{mL Ferrous Sulfate})(\text{N Ferrous Sulfate})]}{\text{Weight of Soil (g)}} \times 0.336 \times 10^4$$

Where:
N = Normality

13. METHOD PERFORMANCE

13.1 Not Applicable.

14. POLLUTION PREVENTION

14.1 Not Applicable

15. WASTE MANAGEMENT

15.1 Solid materials (soil, gloves, soiled paper products) are placed in the solid debris container. Do not put liquids in the solid waste container.

15.2 All aqueous sample preparations can be rinsed down the drain with copious amounts of water.

15.3 Refer to the laboratory-specific waste disposal plan.

16. REFERENCES

16.1 Standard Methods of Chemical Analysis , 5th Edition, Scott, W.W., 1939

17. MISCELLANEOUS (TABLES, APPENDICES, ETC.)

17.1 All sample preparation and analysis information will be documented on laboratory bench sheets, computer printouts, standard logbooks, etc. All the documents associated with an analysis will be forwarded for reporting and for inclusion in the project files.

Acid Volatile Sulfide (AVS) and
Selected Simultaneous Extractable Metals in Sediment

Acid Volatile Sulfide (AVS) and Selected Simultaneous Extractable Metals in Sediment

Approvals and Signatures

QA Officer: Martha E. Boy Date: 11/14/95

Metals Manager: Kristine L. Aedi Date: 11/14/95

Wet Chemistry Manager: [illegible] Date: 11/14/95

1.0 Scope and Application

1.1 This method describes procedures for the determination of acid volatile sulfide (AVS) and for selected metals that are solubilized during the acidification step (simultaneously extracted metal, SEM).

1.2 This method uses the same conditions for release of both sulfide and metal from the sediment and thus provides a useful means of assessing the amount of metal associated with sulfide.

1.3 Note that Iron and Manganese are typically not included in the SEM metals compound list.

2.0 Summary of Method

2.1 The AVS in the sample is first converted to hydrogen sulfide by acidification with hydrochloric acid at room temperature. The hydrogen sulfide is then purged from the sample and trapped in aqueous solution. The amount of sulfide that has been trapped is then determined.

2.2 The SEM are selected metals liberated from the sediment during the acidification. These are determined by ICP analysis after filtration of the sample.

3.0 Sample Handling and Preservation

3.1 Soil samples are not preserved, but are maintained at 4° C until analysis.

3.2 Samples should be collected in wide mouth jars with a minimum of air space above the sediment.

3.3 Holding time for AVS is 14 days from sample collection. The SEM filtrate must be analyzed within 14 days.

4.0 Apparatus and Reagents

4.1 Iodine Solution (0.025 N):

Dissolve 25 gram KI in 700 ml DIH_2O. Add 3.2 gram I_2 and allow to dissolve. Bring to 1 liter with DIH_2O.

4.1.1 Standardize as follows: Dissolve approximately 2 gram KI in 150 ml DIH_2O. Add exactly 20 ml Iodine solution and mix. Bring to 200 ml with DIH_2O.

4.1.2 Titrate with 0.025 N Thiosulfate (using starch indicator, endpoint = blue to clear)

$$\text{Normality} = \frac{\text{ml Titrant x N Titrant}}{\text{mls iodine solution}}$$

4.2 Sulfide Standard

Preparation of Sulfide Stock:

a. small crystal (approximately 0.5 g) $Na_2S.9H_2O$ in tri-corner beaker. Rinse 3 times with DIH_2O. Dry crystal thoroughly with kimwipes.

b. weigh crystal to 0.1 mg and dissolve in 500 ml DIH_2O.

$$Formula\ 1 \quad - Concentration\ stock\ \frac{mg}{L} = \frac{(crystal\ wgt)\ (0.1335^{*})\ (1000\frac{mg}{g})}{0.51}$$

(*0.1335→ $Na_2S.9H_2O$ = 13.35 % S)

The stock should be approximately 100-150 mg/l.

4.3 Preparation of LCS Sulfide Stock

- Use source labelled for LCS.
- small crystal (approximately 0.5 g) $Na_2S.9H_2O$ in tri-corner beaker. Rinse 3 times with DIH_2O. Dry crystal thoroughly with kimwipes.
- weigh crystal to 0.1 mg and dissolve in 500 ml DIH2O.
- The stock should be approximately 100-150 mg/l- Use 5 mL of this stock for the LCS analysis.
- See Formula 1 for Calculation of this Stock Standard Concentration

$$Formula\ 1 \quad - Concentration\ stock\ \frac{mg}{L} = \frac{(crystal\ wgt)\ (0.1335^{*})\ (1000\frac{mg}{g})}{0.51}$$

(*0.1335→ $Na_2S.9H_2O$ = 13.35 % S)

4.4 <u>Thiosulfate Titrant (0.025 N)</u>

See D.O. SOP for preparation.

4.5 ICP instruments currently in use:

- Thermo Jarrell-Ash Trace (Trace) simultaneous inductively coupled plasma emission spectrometer. System includes 150 position autosampler and computer control. (3/94)

- Thermo Jarrell-Ash Enviro II (ICP3) simultaneous and sequential inductively coupled plasma emission spectrometer. System includes 150 position autosampler and computer control. (1/92)

4.6 Class A volumetric flasks

4.7 Class A volumetric pipets

4.8 ASTM Type 1 water

4.9 All blanks and standards are in a 5% HCl, 2% HNO_3 matrix.

4.10 Argon

4.11 Stock Standard Solutions (for Calibration use) purchased from SPEX

4.12 Calibration Check Standards (for Initial and Continuing Calibration) purchased from Inorganic Ventures

4.13 Interference Check Solutions made from standards purchased from SPEX or Inorganic Ventures

5.0 Procedure for AVS

5.1 Round bottom flasks must be rinsed with 25% Nitric Acid and DI water prior to each use.

5.2 Pipette 50 mls 1.0 M NaOH into the impingers (2 for each station).

5.3 Pour 50 ml 50% HCl into the funnel unit (be sure stopcock is closed).

5.4 Place 10 grams of soil sample into a double necked round bottom flask containing a one inch stir-bar and 100 mL DIH_2O. Use 10 grams beach sand for a prep blank

and 5 mL LCS stock for the LCS.

5.5 Assemble apparatus and adjust flow rate of nitrogen gas through system to 20 ml/min. Allow system to purge with nitrogen for approximately 10 minutes. Check that all connections are tight and all impingers are bubbling.

5.6 Slowly open the funnel stopcock and allow the 50% HCl to mix with the sample. Watch for possible reactions such as a rapid burst of bubbles, foaming, or bumping. Be prepared to stop or slow the addition of HCl until any reaction has subsided. It should take about two minutes to complete the HCl transfer.

5.7 Set timer for 60 minutes. During this time, frequently check flasks for adequate stirring and impingers for consistent nitrogen flow.

5.8 Following the 60 minute reaction time, turn off nitrogen gas, and disassemble the apparatus. Check that the pH of the sample is <2.

5.9 Transfer the scrubber solution to a 100 ml volumetric flask. Using a pipette bulb, blow out any solution contained in the fritted bubbler. Rinse this tube and all internal surfaces of the impinger with DIH_2O, bring to volume and invert 10 times to mix.

5.10 Repeat for each impinger. Take care to label each volumetric flask with sample designation and whether it is form the "front" or "back" position.

Hydrogen Sulfide Titration:

5.11 Transfer the scrubber solution (5.9) into a 250 ml erlynmeyer flask. Add 1 ml 50% HCl and 5 ml 0.025 N Iodine solution. Should all the iodine be reduced by the sulfide present, add a second 5 ml aliquot of Iodine. If necessary continue to add Iodine in 5 ml increments until Iodine color remains. Record total volume of Iodine added. Rinse sides of flask with DIH_2O and bring volume to approximately 200 ml.

5.12 Titrate with 0.025 N Thiosulfate to a straw color. Add a squirt of starch solution and titrate from blue to clear endpoint. Record initial and final volumes of titrant.

6.0 Sample Preparation for SEM Metals

6.1 After the generation of sulfide has been completed, filter the sediment suspension remaining through a 0.45 micron membrane filter. The filtering apparatus is acid and nanopure water rinsed prior to use.

6.2 Transfer the filtrate to a 250 mL volumetric flask. Rinse the filtering flask with distilled water, adding the rinses to the volumetric flask. Dilute to volume with nanopure water. The volumetric flasks should be acid leached then rinsed with nanopure water prior to use.

7.0 Calibration Preparation for SEM

7.1 All calibration standards are prepared from SPEX Plasma Standard stock solutions.

7.2 Intermediate standard solutions are made by quantitatively transferring aliquots of concentrated stock standards into a volumetric flask containing ASTM Type 1 water and an aliquot of HNO_3/HCl. When the appropriate metals standards have been added, the solution is brought to volume. The resulting intermediate standard solution is in a 5% HCl, 2% HNO_3 matrix.

7.3 Working standards are made by quantitatively diluting the intermediate standard to the needed concentrations.

7.4 Intermediate and working standards are stored at room temperature in storage bottles. These standards are kept until their expiration date.

8.0 Instrument Calibration for SEM

8.1 Each instrument is calibrated according to the manufacturer's recommendations . After the torch is ignited and the instrument's parameters are recorded (See the Maintenance Logs attached at the end of this SOP), the calibration standards are placed in an autosampler. A 5% HCl, 2% HNO_3 matrix solution is used for the calibration blank.

During calibration, multiple integrations (2 for the Trace ICP and 3 for ICP3) are performed per standard. There is a 120 second rinse between standards.

8.2 Initial calibration is performed once per batch.

9.0 Calculations

9.1 The final concentration of an element in the sample is reported in mg/Kg dry weight.

$$Formula\ 2\ -\frac{\mu Mole}{gram\,dry} = \frac{mg}{L_{sol}} * DF * \frac{L_{sol}}{g_{sample}} * \frac{100}{\%\,Solid} * \frac{1000\,ug}{1\,mg} * \frac{1\,\mu Mole}{x\ ug}$$

10.0 Quality Control

AVS Quality Control

10.1 A prep blank and Sulfide LCS will be prepared per set of 20 samples or per day whichever is more frequent.

10.2 A blank and a series of three (3) standards are titrated for each batch. Recovery for each must be 90-110%. The blank must be less than the detection limit.

10.3 A sulfide matrix spike should be analyzed per set of 20 samples or per day whichever is more frequent. The matrix spike should have a recovery of 75-125%. These control limits will be updated based on MDL studies and Control Chart data when it becomes available.

10.4 A replicate sample for sulfide is not required by the method but will be performed upon request of the client.

SEM Quality Control

10.5 Interelement Correction Factors

Interelement Correction Factors are determined annually for spectral interference due to Al, Ca, Fe, and Mg and are determined for both ICP instruments at all wavelengths used for each analyte reported by ICP. A 100 ppm stock solution of each interferent is analyzed and any result found above the negative or positive value of the instrument detection limit is recorded within the instrument. The

result in ppb is divided by the concentration of interferent in ppb to determine the IEC constant. This number is entered into IEC tables of the instrument. Correction factors for spectral interference due to analytes other than Al, Ca, Fe, and Mg may be determined in the same fashion and reported if they were applied.

10.6 Linear Range

The linear range verification check standard is analyzed and reported quarterly for each element analyzed by ICP. The analytically determined concentration of this standard shall be within 5% of the true value. This concentration is the upper limit of the ICP linear range and any result found above this limit, must be diluted and reanalyzed.

10.7 Dilute and reanalyze samples that are more concentrated than the linear calibration limit.

10.8 Analyze the method blank (prep) per sample batch to determine if contamination or any memory effects are occurring.

10.9 A replicate sample for sulfide is not required by the method but will be performed upon request of the client.

10.10 Verify calibration every 10 samples and at the end of the analytical run, using a calibration blank and a check standard. The results of the check standard are to agree within 10% of the expected value; if not, terminate the analysis, correct the problem, and reanalyze the previous ten samples.

The results of the calibration blank must be within the control limit of ± the reporting limit (CRDL), if not terminate the analysis, correct the problem, recalibrate, and reanalyze the previous 10 samples.

10.11 Verify the interelement and background correction factors at the beginning and end of an analytical run or twice during every 8-hour work shift, whichever is more frequent. Do this by analyzing the interference check sample. Results should be within +/- 20% of the true value. If not terminate the analysis, correct the problem, recalibrate, and reanalyze the samples.

10.12 A CRDL standard is analyzed at the beginning of each run to verify linearity near the CRDL. Although there are no contract specified control limits on this standard

at this time, the laboratory uses ± 25% as a warning there may be a problem.

10.13 A LRS (Linear Range Standard) is analyzed at the beginning of the run to verify the upper linear range. The highest calibration standard is analyzed for all analytes reported and the found concentration must be within 5% of the true value. If the measurements exceed ± 5%, the instrument is recalibrated for the effected analytes.

S3A

Test Method for Particle Size of Soils - Geotechnics

geotechnics

Standard Operating Procedures - SOP S3A
ASTM D422 MODIFIED
(Geotechnics Standard Test Method)

Title:	Test Method for Particle-size of Soils (Sieve and Hydrometer Analyses)
Reference Standard:	ASTM D-422-63 (Re-approved 1998) - Modified as highlighted herein
Material Applicability:	Soils
Target Property:	Particle size Distribution
Units:	Percent Finer
Test Equipment:	Drying Oven, Balance(0.01 gm), Specimen Containers and lids, #10 and #200 Washing Sieve, Sieve Nest including, 3", 2", 1½" , 1", 3/4", 3/8", #4, #10, #20, #40, #60, #140, and #200. Sieve Shaker, mixing apparatus, hydrometer bulb 152H, thermometers accurate to 0.5° C, dispersion cup, sedimentation cylinders, constant temperature source of deionized water, dispersing agent (40g/L solution of sodium hexametaphosphate)
Data Sheet:	DS-S3A, Wash Sieve Analysis; DS-S3AH, Hydrometer Analysis, DS-AP (New Method), DS-B (#10 Split).

Summary of the Procedure:

1. Per Geotechnics sample preparation procedure (SOP SA1) air-dry the as received material. Push and split the material through calibrated 3/4 inch screen.

2. Weigh the (+ 3/4 inch) material. The quantity should be as specified on Table 5.1.1 of the Reference Standard. Record as mass of coarse. Pass coarse material through 3", 2", 1 ½", 1" and 3/4" sieves, or those specified by the client.. Record the weight retained. Select a representative portion of the +3/4 inch material and obtain a moisture content as per SOP-S1 (ASTM D2216)..

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3. Select approximately 1000 g of (- 3/4 ") air-dried material. Oven dry the sample and determine a water content per SOP S1 (ASTM D2216). Wash material though #200 sieve. Discard (- #200) material.

3.1 An alternate method of –3/4 inch sample preparation, referred to as the "New Method" may be used. This involves determining the sample moisture content on a separate representative sample than the one to be tested for grain size. This enables testing time to be reduced by one day as the wet grain size sample can be washed over the #200 sieve immediately. Geotechnics prefers not to use this method unless directed to by the client

4. Oven dry the (+ #200) material overnight at 110 degrees C.

5. Place the material (+ #200) in a sieve nest that contains sieves 1/2", 3/8", #4, #10, #40, #60, #140, and #200. Put the whole assembly in the sieve shaker. Shake for 10 minutes. Record masses retained on each sieve. Do not overload sieves. Overload is determined by reference document REF-11 "Maximum Allowable Quantity of Material Retained on a Sieve", which is posted in the laboratory.

6. Record data on the Wash Sieve Analysis datasheet DCN: DS-3A (N: \Excel QA\Datasheets\Sievedat.xls)

7. Select approximately 300 g of air-dried (- 3/4 ") material. Pass through #10 sieve, collecting (- #10) material in pan. Verify that there is at least 120 grams of (- #10 material).

8. **This method does not require the determination of the hygroscopic moisture and correction factor.**

9. Mix 65-115 g of (- #10) material (depending on the kind of material) with 125 ml of prepared solution of dispersing agent in the 250 ml beaker. See Appendix A on how to prepare the solution.

10. Allow material to soak for at least 16 hours.

11. Transfer soil the solution into the dispersion cup. Fill 2/3 full with deionized water. Mix for 1 minute using the calibrated timer to monitor time.

12. After the soaking period, wash through #200 sieve ensuring that liquid and (- #200) are retained in pail. At least 20 grams of (- #200) material is required to perform the test. Use squeeze bottle of deionized water to remove all material from the beaker.

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13. Read and record the temperature of the deionized water tank. Ensure that it is 22 degrees C (+/- 3 degrees). If not, wait until temperature is within the acceptable range.

14. Pour into graduated cylinder. Add deionized water until the total volume is 1000 ml. Place rubber stopper on top. Turn cylinder upside and back at a rate of one 180 degree turn / second for a period of one minute.

15. Uncover the cylinder and place cylinder on table in preparation for hydrometer readings.

16. Take hydrometer readings at 2, 5, 15, 30, 60, 250, and 1440 minute intervals after allowing the hydrometer bulb to equilibrate in the cylinder for 20 to 25 seconds prior to reading. As soon as the reading is taken, carefully remove the hydrometer and place it with a spinning motion in a graduated cylinder of deionized water. It is important to remove the hydrometer immediately after each reading.

17. Place a calibrated thermometer in the cylinder and record the temperature immediately after the hydrometer readings.

18. Read the top of the meniscus during the hydrometer test.

19. Enter all the appropriate information on the Hydrometer Analysis data sheet DS-S3A (N: \Excel QA\Datasheets\Hyddat.xls).

20. After taking the last reading, pour the solution from the cylinder into a pan. Make sure that all the material is removed from the cylinder.

21. Put the pan in an oven at 110 degrees overnight until it is completely dry. Record the weight in order to determine the dry weight of the material used in the hydrometer test.

22. Transfer the data from the datasheets to the computer template CT-S3A (N: /Excel QA/Sievehyd.xls). Refer to SOP-S52 on how to transfer data from the data sheet to the spreadsheet. The Main.xls file prompts the data processor to choose a specific grain size analysis spreadsheet based on the presence or absence of +3/4" material, inclusion of Hydrometer analysis, and the type of classification required by the client.

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APPENDIX A

Preparation Procedure for the Dispersing Solution

1. Weigh 40 grams of Sodium Hexametaphosphate (dispersing agent) on an electronic balance.

2. Pour the dispersing agent into a 4 liter capacity beaker. Place the magnetic stirrer into the bottom of the beaker.

3. Add 1 liter of distilled water.

4. Place the beaker on an electromagnetic stirring machine.

5. Turn the machine on, and let it stir the solution until all of the dispersing agent is dissolved.

Pour the solution into a dark glass bottle, seal it and store it at room temperature. Recordthe date of preparation on a label and attach it to the bottle.

Appendix B

The choices of spreadsheets on the Main. xls file (see Sec. 17) are:

Sievehyd:	Sieve and hydrometer / USCS, USDA classification	(DCN: CT-S3A)
JSievehyd:	Sieve w/ +3/4" material, hydrometer / USCS,USDA	(DCN: CT-S3B)
Sivon:	Sieve only / USCS	(DCN: CT-S3C)
JSvon:	Sieve only including +3/4" material / USCS	(DCN: CT-S3D)
Saluda:	Removed from "Main" special use only	(DCN: CT-S3E)
SaludaJ:	Removed from "Main" special use only	(DCN: CT-S3F)
AASHTO:	Same as Sievehyd plus AASHTO classification	(DCN: CT-S3G)
AASHTOJ:	Same as JSievehyd plus AASHTO classification	(DCN: CT-S3H)
AASHTOSieveon:	Same as Sievon plus AASHTO classification	(DCN: CT-S3I)
AASHTOJSievon:	Same as JSievehyd plus AASHTO classifiction	(DCN: CT-S3H)
Grainhyd:	Same as Sievehyd but "New Method"(Pottstown)	(DCN: CT-S3K)
JGrainhyd:	Same as JSievehyd but "New Method"(Pottstown)	(DCN: CT-S3L)
Grainon:	Same as Sivon but "New Method"(Pottstown)	(DCN: CT-S3M)

PITT-WC-0026

PH electrometric
EPA Method 150.1, Method 9045C (soil) and SW846 9040B

LABORATORY-SPECIFIC

STL PITTSBURGH STANDARD OPERATING PROCEDURE

TITLE: PH ELECTROMETRIC EPA METHOD 150.1 METHOD 9045C (SOIL) AND SW-846 9040B

(SUPERSEDES: REVISION 1, 7/05/00)

Prepared by: _____
Date

Reviewed by: _____
Technology Specialist Date

Approved by: _____
Quality Assurance Manager Date

Approved by: _____
Environmental Health and Safety Coordinator Date

Approved by: _____
Laboratory Director Date

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1. SCOPE AND APPLICATION

1.1. This method is applicable to the determination of pH in waters, wastewaters, and solids. It is based on SW846 Methods 9040B and 9045C and EPA Method 150.1. The approximate working range is 1 - 14 pH units. Samples with a pH of < 1 are reported as < 1.

1.2. The associated method codes are PU (9040B), OZ (9045C), and AJ (150.1). The preparation codes are 88 and 1C.

1.3. This document accurately reflects current laboratory standard operating procedures (SOP) as of the date above. All facility SOPs are maintained and updated as necessary.

2. SUMMARY OF METHOD

2.1. The pH is determined electrometrically by using an electrode. The pH meter is calibrated with a series of known pH buffers.

3. DEFINITIONS

3.1. Refer to the glossary in the Quality Assurance Management Plan (QAMP), current version.

4. INTERFERENCES

4.1. Samples with very low or very high pH may give incorrect readings on the meter. For samples with a true pH of >10, the measured pH may be incorrectly low. This error can be minimized by using a low-sodium-error electrode.

5. SAFETY

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

5.2. Eye protection that satisfies ANSI Z87.1 (as per the Chemical Hygiene Plan), laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

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

5.4. Exposure to chemicals must be maintained **as low as reasonably achievable**, therefore, unless they are known to be non-hazardous, all samples must be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

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

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

6. EQUIPMENT AND SUPPLIES

6.1. pH meter with electrode(s) and temperature compensation

6.2. Beakers: various

6.3. Top loading balance: Capable of accurately weighing ±0.01 g

6.4. Stir plate and stir bars

6.5. Shaker or mechanical tumbler

7. REAGENTS AND STANDARDS

7.1. Standards

7.1.1. Target Calibration Standards

7.1.1.1. pH 4, 7, and pH 10 buffers, purchased

7.1.1.2.Fresh buffers are poured and used each working day.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Samples are not chemically preserved.

8.2. Samples are stored in plastic or glass containers at 4°C ± 2°C.

8.3. Samples should be analyzed as soon as possible after sampling, but not to exceed twenty-four hours.

9. QUALITY CONTROL

9.1. Batch Definition

9.1.1. A batch is a group of no greater than 20 samples excluding QC samples (LCS, method blank, and sample DUP) which are processed similarly, with respect to the procedure. All sample setups must be initiated within a 24 hour period from the initial preparation or extraction and without interruption of the process. All samples within the batch must be treated with the same lots of reagents and the same processes.

9.2. Duplicates

9.2.1. Sample duplicates are performed at a minimum frequency one per analytical batch and must meet laboratory-specific limits for precision.

10. CALIBRATION AND STANDARDIZATION

10.1. Initial Calibration

10.1.1. Refer to the manufacturer's manual for instrumental calibration.

10.1.2. The following procedure is applicable for use with the Accumet AR25 pH meter.

10.1.2.1. Rinse the electrodes with reagent water and place in the pH 4.0 buffer. Enter the value (4.0) of the standard into the pH meter using the touch screen. Allow the value to stabilize.

10.1.2.2. Rinse the electrodes and place in the pH 7.0 buffer. Enter the value (7.0) of the standard into the pH meter using the touch screen. Allow the value to stabilize.

10.1.2.3. Rinse the electrodes and place in the pH 10.0 buffer. Enter the value (10.0) of the standard into the pH meter using the touch screen. Allow value to stabilize.

10.1.3. The pH meter should be calibrated daily. The calibration is recorded on the analytical log sheet.

10.1.4. If the pH meter has been turned off, it must be calibrated prior to use.

10.2. Calibration Check / Continuing Calibration

10.2.1. A pH 7 buffer is analyzed before analysis and every ten samples to ensure the calibration remains linear.

10.2.2. The pH meter must be recalibrated if the buffer deviates by more than ± 0.05 s.u. If this range is exceeded, reanalyze all samples analyzed since the last pH buffer that met criteria.

11. PROCEDURE

11.1. One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and is approved by a Technical Specialist and QA Manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file.

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

11.3. Sample Preparation

11.3.1. Waters

11.3.1.1. No preparation necessary for waters and wastewaters.

11.3.2. Solids and Soils

11.3.2.1. Place 20 g (± 0.5 g) of sample in a beaker or other suitable container.

11.3.2.2. Add 20mL of reagent water and mix for five minutes.

11.3.2.3. Allow sample to stand for one hour to allow the solids to settle out.

11.4. Sample Analysis

11.4.1. Waters

11.4.1.1. Place the sample in a clean beaker using a sufficient volume to cover the sensing elements of the electrode(s). Allow the pH to stabilize (swirling or stirring may quicken stabilization). Record the pH on the analytical log sheet. Remove the electrodes from the sample. Rinse and gently dab off the electrodes between each measurement. Store the electrodes in pH 4 buffer when not in use.

11.4.2. Solids

11.4.2.1. Immerse the pH electrodes in the supernatant layer of the sample - be careful not to stir up solids. Allow pH to stabilize and record it on the analytical log sheet. Remove and rinse the electrodes between each measurement. Store electrodes in the pH 4 buffer.

NOTE: If the sample contains oil or other substances that will coat or damage the electrodes, the pH should be analyzed using pH Paper Method if client allows this change.

11.5. Analytical Documentation

11.5.1. Record all analytical information in the analytical logbook/log sheet, including the analytical data from standards and any corrective actions or modifications to the method.

11.5.2. All standards are logged into a department standard logbook. All standards are assigned a unique number for identification. Logbooks are reviewed by the supervisor or designee.

11.5.3. Documentation such as all associated instrument printouts (final runs, screens, reruns, QC samples, etc.) and daily calibration data corresponding to all final runs is available for each data file.

11.5.4. Sample results and associated QC are entered into the LIMs after final technical review.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Not Applicable

13. METHOD PERFORMANCE

13.1. Each laboratory must have initial demonstration of performance data on file and corresponding method detection limit files.

13.2. Training Qualifications:

13.2.1. The group/team leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience.

14. POLLUTION PREVENTION

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

15. WASTE MANAGEMENT

15.1. Solid materials (gloves, soiled paper products, etc.) are placed in the solid debris container. Do not put liquids in the solid waste container.

15.2. Refer to the Laboratory Sample and Waste Disposal plan.

15.3. Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices of STL. They must have training on the hazardous waste disposal practices upon initial assignment to these tasks, followed by an annual refresher training.

16. REFERENCES

16.1. References

16.1.1. SW846, Test Methods for Evaluating Solid Waste, 3rd Edition, pH Electrometric Measurement, Method 9040B

16.1.2. EPA 600, Methods for Chemical Analysis of Water and Wastes, pH (Electrometric), Method 150.1

16.1.3. SW846, Test Methods for Evaluating Solid Waste, 3rd Edition, Soil pH, method 9045C.

16.1.4. STL Pittsburgh Quality Assurance Management Plan (QAMP), current version.

16.1.5. QA-003, STL QA Program

17. MISCELLANEOUS (TABLES, APPENDICES, ETC...)

17.1. Reporting limits

17.1.1. Values of < 1 will be reported as less than 1. pH units are reported as s.u.

Navy IR CDQM

Navy Installation Restoration Chemical Data Quality Manual (IR CDQM)

Naval Facilities Engineering Command
Washington, DC 20374-5065

NFESC

Special Report

SP-2056-ENV

NAVY INSTALLATION RESTORATION CHEMICAL DATA QUALITY MANUAL (IR CDQM)

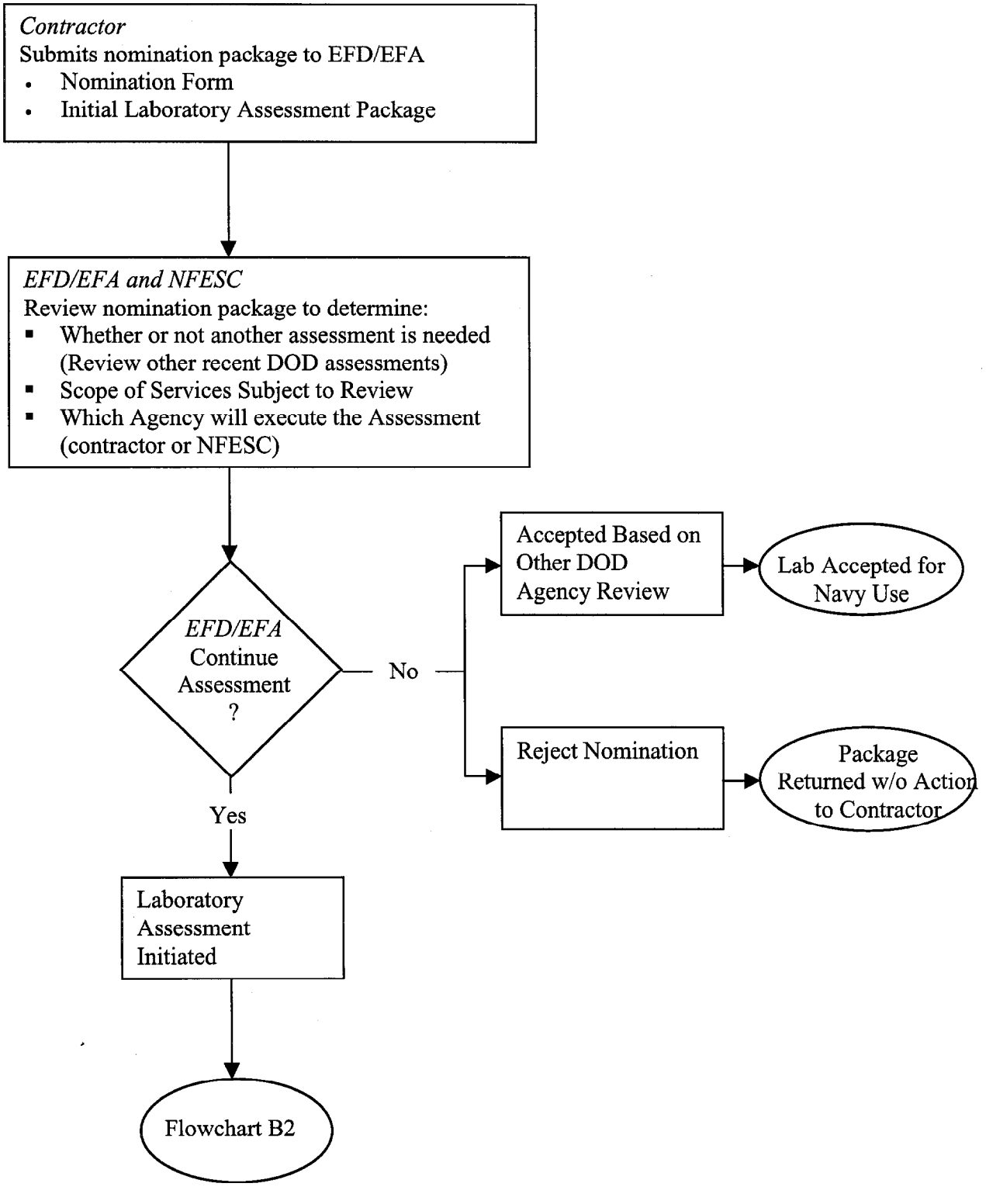
September 1999

Prepared by
Naval Facilities Engineering Service Center
1100 23rd Avenue
Port Hueneme, CA 93043-4370

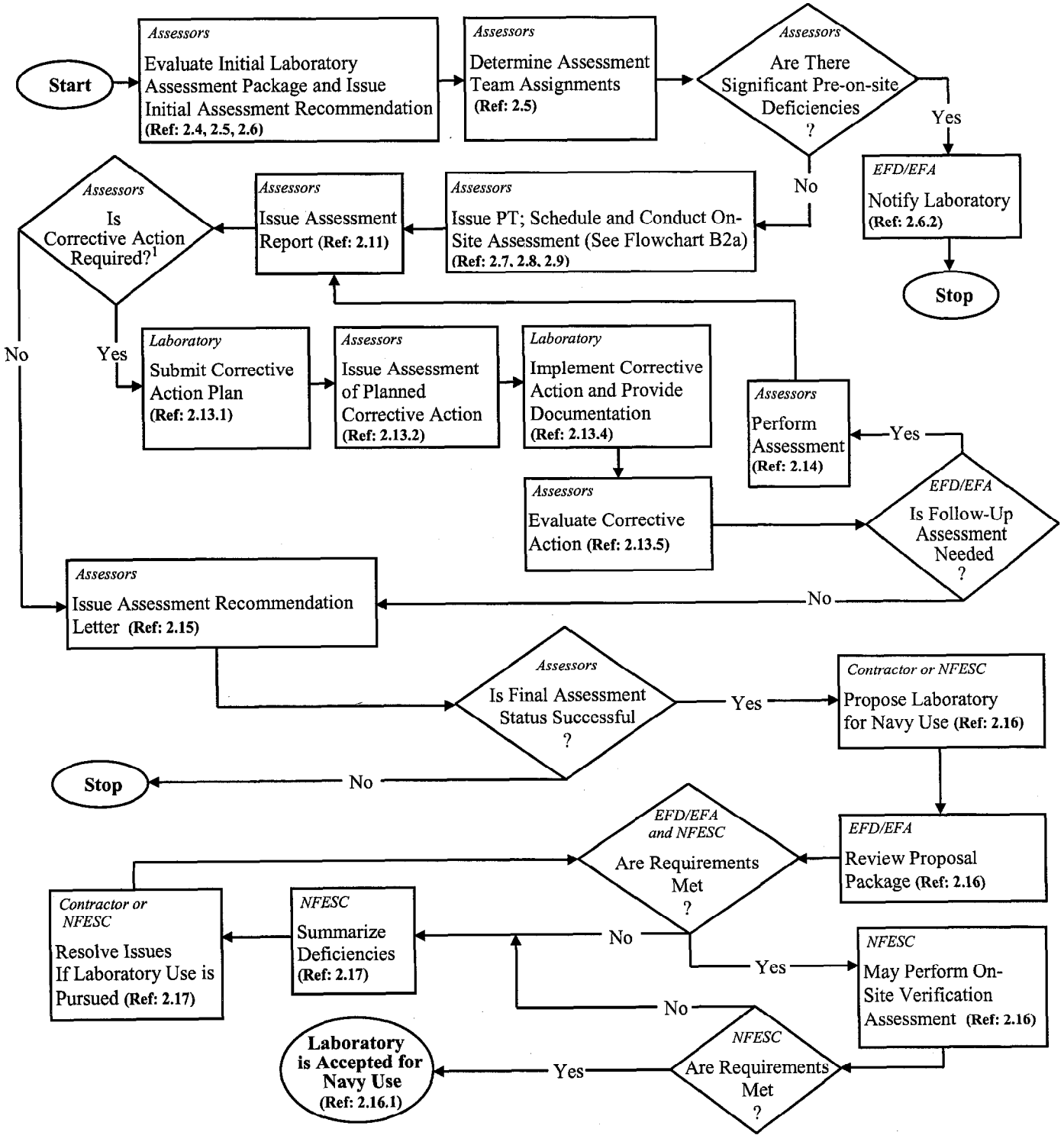
Approved for public release; distribution is unlimited

Printed on recycled paper

Flowchart B1:
Laboratory Assessment General Overview



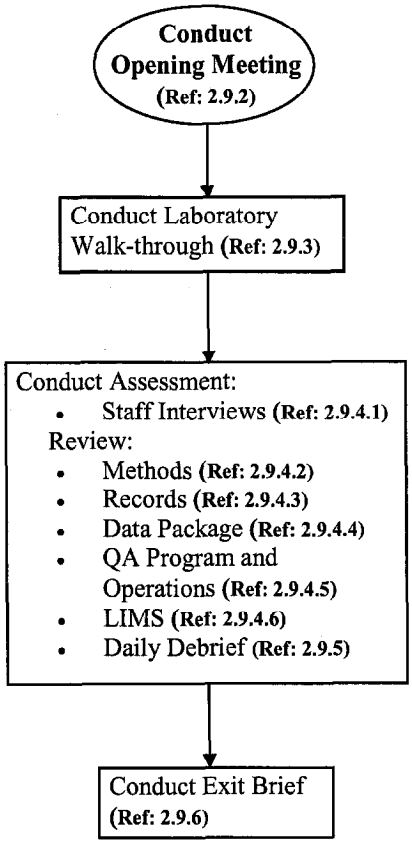
Flowchart B-2: Laboratory Assessment Procedure Flowchart



Note: The process may be terminated at anytime by the contractor, Navy, or the laboratory. (Ref 1.0)

[1] If the laboratory decides to appeal any deficiencies noted in the assessment report, they must do so within 14 calendar days. (Ref: 2.20)

Flowchart B2a:
Laboratory On-Site Assessment Procedure



Note 1: A daily debrief will be conducted at the conclusion of each day during the on-site assessment (Ref: 2.9.4.7).

Note 2: Each member of the assessment is responsible for keeping complete and accurate records of all assessment activities (Ref: 2.9.5).

Appendix B
Attachment 3
Enclosure 2
Laboratory Compliance Checklist

This checklist will be generated upon finalization of the Department of Defense Quality Systems Manual for Environmental Laboratories (Enclosure 1 to Appendix C)

Appendix B
Attachment 4
Assessor Evaluation Questionnaire

Please complete and return this form in the envelope provided. The feedback you provide will be used to evaluate and improve assessor performance. It will not affect the current assessment. Information provided on this questionnaire will not be communicated to the assessors until the laboratory completes the assessment process.

Assessor Name: _____
Laboratory Name: _____
Date of On-Site Assessment: _____
EFD/EFA Lab Will be Proposed to: _____

Please rank the assessor from 1 (low) to 5 (highest)

1. Ability to communicate orally	1	2	3	4	5
2. Ability to communicate in writing	1	2	3	4	5
3. Ability to act objectively and fairly	1	2	3	4	5
4. Ability to describe assessment results in a clear and impartial manner	1	2	3	4	5
5. Ability to adapt to different personalities during interviews	1	2	3	4	5
6. Professional characteristics	1	2	3	4	5
7. Knowledge of :					
a. Environmental laboratory methods	1	2	3	4	5
b. Quality assurance issues	1	2	3	4	5

Overall Rank: 1 2 3 4 5

Please provide comments: _____

If there is no self addressed envelope provided, please return this form to NFESC:

Commanding Officer
Naval Facilities Engineering Service Center, Code 413/ Pati Moreno
1100 23rd Avenue
Port Hueneme, CA 93043-4370

DOD QSM

Department of Defense Quality Systems Manual for Environmental Laboratories

DEPARTMENT OF DEFENSE QUALITY SYSTEMS MANUAL FOR ENVIRONMENTAL LABORATORIES

Prepared By

DoD Environmental Data Quality Workgroup
Department of Navy, Lead Service

Version 1
October 2000

5.0 QUALITY SYSTEM – ESTABLISHMENT, AUDITS, ESSENTIAL QUALITY CONTROLS, AND DATA VERIFICATION

5.1 Establishment

The laboratory shall establish and maintain a quality system based on the required elements contained in this Chapter and appropriate to the type, range, and volume of environmental testing activities it undertakes.

a) The elements of this Quality System shall be documented in the organization's quality manual.

b) The quality documentation shall be available for use by the laboratory personnel.

Quality System Documentation: This documentation includes the Quality Manual, standard operating procedure (SOP) documents, and other appropriate reference documents and texts. 5

c) The laboratory shall define and document its policies and objectives for, and its commitment to, accepted laboratory practices and quality of testing services.

d) The laboratory management shall ensure that these policies and objectives are documented in a Quality Manual and communicated to, understood, and implemented by all laboratory personnel concerned.

e) The Quality Manual shall be maintained current under the responsibility of the quality assurance officer.

5.2 Quality Manual

The Quality Manual and related quality documentation shall state the laboratory's policies and operational procedures established in order to meet the requirements of this Standard.

The Quality Manual shall list on the title page: a document title; the laboratory's full name and address; the name, address (if different from above), and telephone number of individual(s) responsible for the laboratory; the name of the quality assurance officer (however named); the identification of all major organizational units, which are to be covered by this quality manual; and the effective date of the version.

Quality Manual Updating: The following list reflects topic areas that shall be included in the Quality Manual. Additional details about each topic area are provided in the sections that follow. The Manual shall be reviewed at least annually for accuracy and adequacy, and updated as appropriate. All such reviews shall be documented and available for inspection. 6

The Quality Manual and related quality documentation shall also contain:

a) A quality policy statement, including objectives and commitments, by top management;

b) The organization and management structure of the laboratory, its place in any parent organization, and relevant organizational charts;

Corporations – Laboratory Relationships with Corporations: This includes the laboratory's relationship(s) to corporate affiliations and networks. 7

c) The relationship between management, technical operations, support services, and the quality system;

d) Procedures to ensure that all records required under this Chapter are retained, as well as procedures for control and maintenance of documentation through a document control system that ensures that all standard operating procedures, manuals, or documents clearly indicate the time period during which the procedure or document was in force;

Document Control – Distribution: Consistent with the definition of "Document Control" provided in NELAP Appendix B, this control system shall ensure that all analysts implementing the task(s) or procedure(s) described in that SOP shall be made individually aware that changes to an SOP have occurred. A copy of the updated SOP shall be available in close proximity to the work station (i.e., within the same work area).

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e) Job descriptions of key staff and reference to the job descriptions of other staff;

Personnel To Be Included in Quality Manual: At a minimum, the following managerial and supervisory staff (however named) shall be considered key staff, and their job descriptions shall be included in the Quality Manual and other related documents:

(1) Executive Staff (for example, Chief Executive Officer, Chief Operating Officer, laboratory director, technical director);
(2) Technical directors/supervisors (for example, section supervisors for organics and inorganics);
(3) Quality assurance systems directors/supervisors (for example, QA officer, quality auditors); and
(4) Support systems directors/supervisors (for example, information systems supervisor, purchasing director, and project managers).

In addition, the Quality Manual shall include job descriptions for key staff in each of these four areas, as appropriate to the laboratory.

If the size and organization of the laboratory precludes separate managers and/or supervisors in each of these key areas, the functions covered in the four areas shall be addressed in the job descriptions provided for the key staff.

The Quality Manual shall describe the relationship of the key staff listed above to other technical and support staff. Any changes in key personnel for the laboratory must be documented to all laboratory users.

Technical staff includes those individuals who conduct the work of the laboratory (for example, sample receipt and documentation staff, the chemists who run the analytical equipment). Support staff administers the business practices of the laboratory, as well as information management and contractual systems. Quality assurance staff oversees the implementation of the quality system, and reports to the quality assurance officer or his/her designee.

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f) Identification of the laboratory's approved signatories; at a minimum, the title page of the Quality Manual must have the signed and dated concurrence (with appropriate titles) of all responsible parties including the QA officer(s), technical director(s), and the agent who is in charge of all laboratory activities, such as the laboratory director or laboratory manager;

g) The laboratory's procedures for achieving traceability of measurements;

Traceability of Measurements: Standards addressing this issue are included in Section 9.0 (Measurement Traceability and Calibration), Section 10.5 (Documentation and Labeling of Standards and Reagents), and Section 12.0 (Records).

10

h) A list of all test methods under which the laboratory performs its accredited testing;

i) Mechanisms for ensuring that the laboratory reviews all new work to ensure that it has the appropriate facilities and resources before commencing such work;

j) Reference to the calibration and/or verification test procedures used;

k) Procedures for handling submitted samples;

l) Reference to the major equipment and reference measurement standards used, as well as the facilities and services used by the laboratory in conducting tests;

m) Reference to procedures for calibration, verification, and maintenance of equipment;

n) Reference to verification practices including interlaboratory comparisons, proficiency testing programs, use of reference materials, and internal quality control schemes;

o) Procedures to be followed for feedback and corrective action whenever testing discrepancies are detected or departures from documented policies and procedures occur;

p) The laboratory management arrangements for exceptionally permitting departures from documented policies and procedures or from standard specifications;

q) Procedures for dealing with complaints;

r) Procedures for protecting confidentiality (including national security concerns) and proprietary rights;

s) Procedures for audits and data review;

Audits – Quality Manual Specification: The Quality Manual shall also specify which records are considered necessary to conduct an adequate review. **11**

t) Processes/procedures for establishing that personnel are adequately experienced in the duties they are expected to carry out and are receiving any needed training;

u) Processes/procedures for educating and training personnel in their ethical and legal responsibilities, including the potential punishments and penalties for improper, unethical, or illegal actions;

Personnel Training – Ethical: Additional descriptions related to this requirement are included in Section 6.2. **12**

v) Reference to procedures for reporting analytical results; and

w) A Table of Contents and applicable lists of references, glossaries, and appendices.

5.3 Audits

Audits – Section Summary: The following subsections of 5.3 refer to internal assessment tools to be used by the laboratory. Section 5.3.1 discusses systems audits and technical audits, both of which shall be conducted annually to evaluate whether the quality system is being implemented at the operational level of the laboratory. Section 5.3.2 addresses higher-level managerial reviews, designed to evaluate whether the quality system itself is effective. These can be done in conjunction with each other or separately, at the discretion of the laboratory. This section also addresses requirements for a program to detect and prevent improper, unethical, or illegal actions. Section 5.3.3 addresses the review of all auditing activities. Section 5.3.4 addresses continuous quality control practices, which shall be conducted by the laboratory on an ongoing basis.

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5.3.1 Internal Audits

The laboratory shall arrange for annual internal audits to verify that its operations continue to comply with the requirements of the laboratory's quality system. It is the responsibility of the quality assurance officer to plan and organize audits as required by a predetermined schedule and requested by management. Such audits shall be carried out by trained and qualified personnel who are, whenever resources permit, independent of the activity to be audited. Personnel shall not audit their own activities except when it can be demonstrated that an effective audit will be carried out. Where the audit findings cast doubt on the correctness or validity of the laboratory's calibrations or test results, the laboratory shall take immediate corrective action and shall immediately notify, in writing, any client whose work may have been affected.

Audits – Internal: Internal audits shall include both technical audits and systems audits. They may be scheduled or unannounced. Technical audits verify compliance with method-specific requirements, as well as operations related to the test method (for example, sample preparation). (These operations include all actions related to data generation and the assurance of its quality.) Systems audits verify compliance with the laboratory's quality system, based on the NELAP Quality System, and documented in the laboratory's Quality Manual. Response to complaints, sample acceptance policies, and sample tracking methodologies are examples of procedures that would be reviewed as part of a systems audit. Data audits are considered a subset of technical audits.

An audit schedule shall be established such that all elements/areas of the laboratory are reviewed over the course of 1 year.

Personnel performing an internal audit shall complete the audit under the direction of the quality assurance officer, however named. To be considered "trained and qualified," the internal auditor shall be trained and qualified in conducting the type of audit under review.

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5.3.2 Managerial Review

The laboratory management shall conduct a review, at least annually, of its quality system and its testing and calibration activities to ensure its continuing suitability and effectiveness and to introduce any necessary changes or improvements in the quality system and laboratory operations. The review shall take account of reports from managerial and supervisory personnel, the outcome of recent internal audits, assessments by external bodies, the results of inter-laboratory comparisons or proficiency tests, any changes in the volume and type of work undertaken, feedback from clients, corrective actions, and other relevant factors. The laboratory shall have a procedure for review by management and maintain records of review findings and actions.

Audits – Managerial Review: This is a separate review from the internal audit discussed in Section 5.3.1 and shall be completed by laboratory managerial personnel. As noted in clarification box 13, however, internal audits and managerial reviews may be conducted in conjunction with each other. 15

5.3.3 Audit Review

All audit and review findings and any corrective actions that arise from them shall be documented. The laboratory management shall ensure that these actions are discharged within the agreed timeframe.

Audits – Timeframe of Audit Review: The timeframe for these actions shall be based on the magnitude of the problem and its impact on the defensibility and use of data. 16

5.3.4 Performance Audits

In addition to periodic audits, the laboratory shall ensure the quality of results provided to clients by implementing checks to monitor the quality of the laboratory's analytical activities. Examples of such checks are:

a) Internal quality control procedures using, whenever possible, statistical techniques (See Section 5.4 below);

b) Participation in proficiency testing or other interlaboratory comparisons (See NELAC Chapter 2.0);

c) Use of certified reference materials and/or in-house quality control using secondary reference materials, as specified in Section 5.4;

d) Replicate testings using the same or different test methods;

e) Re-testing of retained samples; and

f) Correlation of results for different parameters of a sample (e.g., total phosphorus should be greater than or equal to orthophosphate).

Audits – Laboratory Checks of Performance Audits: This section requires the laboratory to continuously evaluate the quality of generated data by systematically and routinely implementing control checks that go beyond those required by the test methods. The results of these checks (examples of which are listed above) shall be routinely reviewed after they are performed to monitor and evaluate the quality and usability of data generated by the laboratory. Although a supplemental review of these checks shall be included as part of the annual internal audits, the laboratory shall also ensure that the results of these checks are reviewed (and corrective action taken) on a regular and timely basis following the actual completion of the check to remedy the problem, avoid its recurrence, and improve the quality system overall. 17

5.3.5 Corrective Actions

a) In addition to providing acceptance criteria and specific protocols for corrective actions in the Method Standard Operating Procedures (Section 10.1.1), the laboratory shall implement general procedures to be followed to determine when departures from documented policies, procedures, and quality control have occurred. These procedures shall include, but are not limited to, the following:

   1) Identify the individual(s) responsible for assessing each QC data type;

2) Identify the individual(s) responsible for initiating and/or recommending corrective actions;

3) Define how the analyst should treat a data set if the associated QC measurements are unacceptable;

4) Specify how out-of-control situations and subsequent corrective actions are to be documented; and

5) Specify procedures for management (including the QA officer) to review corrective action reports.

Audits – Corrective Action: Managers, including the QA officer, are also responsible for acting upon corrective action report reviews. Furthermore, managers are ultimately accountable for the follow-through, verification, and evaluation of these corrective actions. Further explanatory clarifications of DoD expectations are provided as follows:

Nonconformance. The laboratory shall have an established, documented policy and procedures to identify and control work and test results that do not or may not meet expected or specified requirements, or are nonconforming or suspected to be nonconforming. Policy and procedures shall ensure that:

- Responsibilities and authorities for the managing of nonconforming work/results are designated.
- Actions to be taken following identification of a nonconformance are defined and implemented, and include, but are not limited to, evaluating the significance of a nonconformance; halting work and investigating the contributors to the nonconformance (for example, equipment, personnel, methods); withholding reports and certificates, as necessary; informing clients of nonconformance resulting from their samples and the need to recall results of nonconforming work already released to them; implementing corrective action, as needed, and evaluating the results. (See corrective action requirements below.)

Corrective Action. The laboratory shall have established, documented policy and procedures for actions to be taken to eliminate the causes of a nonconformance and to prevent recurrence. The corrective action process shall identify and implement corrective actions likely to eliminate the root cause of nonconformance(s). Laboratory policies and procedures shall ensure that:

- Responsibilities and authorities for instituting corrective action are designated.
- Possible causes of the nonconformance(s) are investigated.
- Root cause analysis is performed.
- Changes resulting from corrective action are recorded and retrievable.
- Corrective action(s) are monitored.
- Preventive action is taken to prevent recurrence.

Monitoring of Corrective Actions. After implementation of corrective action(s), the laboratory shall monitor their effects to determine if action(s) taken are effective in overcoming the nonconformance identified (i.e., the root cause has been eliminated and its recurrence prevented). Historical corrective action reports should be periodically reviewed to identify long-term trends or recurring problems.

Preventive Action. All operations shall be systematically and thoroughly reviewed at regular intervals to:

- Obtain input on the laboratory's operations;
- Determine what considerations need to be given to input (from reviews); and
- Determine how corrective action(s), if necessary, shall be carried out.

Reference: American Society for Quality Control. 1991. *Q2 – Quality Management and Quality System Elements for Laboratories – Guidelines.* 18

b) To the extent possible, samples shall be reported only if all quality control measures are acceptable. If a quality control measure is found to be out of control, and the data are to be reported, all samples associated with the failed quality control measure shall be reported with the appropriate data qualifier(s).

Data Qualifiers: Some of the standard data qualifiers, to be used by laboratories only, are listed below. Additional data qualifiers may be used by data validators when evaluating data usability (for example, an "R" flag for rejected data).

U – Undetected: The associated number is the reporting limit, adjusted by any dilution factor used in the analysis.
J – Estimated: The analyte was positively identified; the quantitation is an estimation (for example, matrix interference, below standard, outside the calibration range).
B – Blank contamination: Analyte detected above the reporting limit in an associated blank.
N – Nontarget analyte: Analyte is a tentatively identified compound (using mass spectroscopy).
Q – One or more quality control criteria (for example, LCS recovery, surrogate spike recovery, etc.) failed. Data usability should be carefully assessed by an individual experienced in data review who represents the data user or their agent. Assessment by DoD may result in rejection of data and potential contractual nonpayment based on unacceptable performance.

When other flags are required contractually, these shall be used.

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5.4 Essential Quality Control Procedures

These general quality control principles shall apply, where applicable, to all testing laboratories. The manner in which they are implemented is dependent on the types of tests performed by the laboratory (i.e., chemical, whole effluent toxicity, microbiological, radiological, air) and are further described in Appendix D. The standards for any given test type shall ensure that the applicable principles are addressed:

a) All laboratories shall have protocols in place to monitor the following quality controls:

Quality Control Actions: Quality control actions should be both batch-specific and time-based (i.e., those required to be conducted at specific time periods, such as for tunes and method detection limits [MDLs]). Batch-specific quality control actions include sample-specific quality control actions such as surrogate spikes.

20

1) Adequate positive and negative controls to monitor tests, such as blanks, spikes, reference toxicants;

2) Adequate tests to define the variability and/or repeatability of the laboratory results, such as replicates;

3) Measures to assure the accuracy of the test method, including sufficient calibration and/or continuing calibrations, use of certified reference materials, proficiency test samples, or other measures;

4) Measures to evaluate test method capability, such as detection limits and quantitation limits or range of applicability, such as linearity;

5) Selection of appropriate formulae to reduce raw data to final results, such as regression analysis, comparison to internal/external standard calculations, and statistical analyses;